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Survey of brominated flame retardants

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Survey of brominated flame retardants

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Preface

Background and objectives

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2011) includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic using computer models. For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on the LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, as well as information on environmental and health effects, alternatives to the substances, existing regulations, monitoring and exposure, and on-going activities under REACH, among others.

On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns certain brominated flame retardants. These substances were included in the first LOUS in 1998 and have remained on the list since that time.

The entry in LOUS for these substances is "Certain brominated flame retardants" with three examples from the group: Decabromodiphenyl ether (decaBDE), additive use of tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD).

The main reason for the inclusion in LOUS is that "*Certain brominated flame retardants are either persistent or can be degraded to persistent compounds, bioaccumulative or toxic.*"

The main objective of this study is, as mentioned, to provide background for the Danish EPA's consideration regarding the need for further risk management measures.

The process

The survey has been undertaken by COWI A/S (Denmark) in cooperation with NIPSECT (Denmark) and Building Research Establishment (U.K.) from March to October 2013. The work has been followed by an advisory group consisting of:

- Mikkel Aaman Sørensen, Danish EPA, Chemicals
- Dorte Bjerregaard Lerche, Danish EPA, Chemicals
- Katrine Smidt, Miljøstyrelsen, Soil and Waste
- Lulu Krüger, Danish Veterinary and Food Administration
- Hilde Balling, Danish Health and Medicines Authority
- Helle Fabiansen, The Danish Plastics Federation
- Lone Mikkelsen, The Ecological Council

- Jette Bjerre Hansen, Danish Competence Centre on Waste, DAKOFA
- Carsten Lassen, COWI A/S
- Allan Astrup Jensen, NIPSECT

Data collection

The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

The literature search included the following data sources:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention;
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHA's website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower);
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Data on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet);
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, and the European Food Safety Authority (EFSA);
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
 - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
 - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature;
 - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada;
 - PubMed and Toxnet databases for identification of relevant scientific literature.

Direct enquiries were also sent to Danish and European trade organisations and a few key market actors in Denmark.

Conclusion and summary

Over the period 2012-2015, all 40 substances and substance groups on the Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) will be subject to survey and review. On the basis of the results, the Danish EPA will assess the need for any further regulation: substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns brominated flame retardants (BFRs). The brominated flame retardants were included in the first list in LOUS in 1998 and have remained on the list since that time. The entry in LOUS for the brominated flame retardants is "certain brominated flame retardants" with three examples from the group: Decabromodiphenyl ether (decaBDE), additive use of tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD). It is not further specified which other brominated flame retardants are considered to be included. This survey addresses to some extent all brominated flame retardants, but focuses in some chapters on the three main brominated flame retardants: decaBDE, TBBPA and HBCDD, as well as two of the main brominated alternatives to decaBDE, decabromodiphenyl ethane (DBDPE) and ethylenebis(tetrabromophthalimide) (EBTEBPI). As a consequence, this summary contains sections for each of the focus substances as well as sections addressing all brominated flame retardants.

The substance group

Flame retardants are added to polymeric materials, both natural and synthetic, to enhance the flame-retardancy properties of the polymers. Fire safety regulations are to a large extent the driver for the use of flame retardants. Fire safety regulations in general do not include any specific requirements for the use of brominated flame retardants or other flame retardants. The regulations typically define some fire tests which the materials, articles or building components should pass, but it is up to the manufacturer or the builder to decide how the requirements are to be met.

Brominated flame retardants have in common that they contain bromine and are used to prevent the ignition of plastic materials and textiles. They all act by the same mechanism: through the release of hydrogen bromine during when the material is ignited which interrupts the further combustion process. Otherwise, the brominated flame retardants form a complex group of substances: aromatic, cycloaliphatic, aliphatic, polymeric and inorganic substances, all containing bromine. Some of the substances are used as additives, where the substances are not chemically bound in the polymer material, while others are used as reactive substances build into the polymer structure and not present as the original substance in the final polymer (except for trace amounts of un-reacted substances). This survey has identified 69 brominated flame retardants which have been pre-registered under REACH and/or are produced by the major international manufacturers of brominated flame retardants. Furthermore, 14 substances described in the literature, but not pre-registered or marketed by the major manufactures, are examined in the survey.

Production and use of brominated flame retardants

Global - The total global production of brominated flame retardants increased from 150,000 t/y in 1994 to approximately 360,000 t/y in 2011. The increase in production and consumption has primarily been in Asia. On a global scale, the brominated flame retardants account for approximately 20% of the consumption of flame retardants. Historically, the PBDEs and TBBPA (and its derivatives) have been the main brominated flame retardants, accounting for nearly 2/3 of the global

production in 1994. Globally, the majority of the brominated flame retardants are manufactured by four major manufacturers, and the substances are manufactured in the EU at one site only.

A detailed breakdown by substance and application area is not available. The major use area is electrical and electronic equipment, where the brominated flame retardants are also the dominating flame retardants. Other application areas include wiring and power distribution; textiles, carpets and furniture; building materials; means of transportation (vehicles, trains, airplanes, ships, etc.), and paints and fillers.

EU - In the EU, detailed data are available for three of the main brominated flame retardants: decaBDE, HBCDD and TBBPA, together accounting for approximately 40% of the total consumption. For other brominated flame retardants, data on the total production in and import to the EU are available in tonnage bands (e.g. 100-1,000 t/y) from the registration database from ECHAs website for brominated flame retardants for which the total import and production in 2013 was above 100 t/y. For polymeric brominated flame retardants no registration data are available. The consumption volumes are described further in the following sections.

Denmark - A comprehensive inventory of the use of brominated flame retardants in Denmark was carried out in 1999. Brominated flame retardants in imported articles and mixtures accounted for approximately 90% of the total content of brominated flame retardants in end-products placed on the market in Denmark in 1999. Of the total turnover of 330-660 tonnes of brominated flame retardants in end-products, more than 70% was in electrical and electronic equipment. This is likely still the situation. The brominated flame retardants in articles on the Danish market are more a reflection of the general use patterns in the EU and globally rather than of the use pattern in Danish industry. A full update of the 1999 inventory has been beyond the framework of this survey.

In Danish industry, the main application of brominated flame retardants in 1999 and 2012 was reactive brominated polyols used for production of flame-retarded polyurethane foams for building insulation.

Regulatory focus

The regulatory focus in the EU and Denmark has so far been on the two substance groups polybrominated diphenylethers (PBDEs) and polybrominated biphenyls (PBBs), while HBCDD has only very recently become subject to authorisation under REACH and listed under the Stockholm Convention on Persistent Organic Pollutants (POPs). The legislation is further described for each substance group below. One legal instrument at the EU level addresses the brominated flame retardants as a group: The WEEE Directive on waste electrical and electronic equipment (WEEE) requires selective treatment and proper disposal for materials and components of WEEE with brominated flame retardants. Furthermore, Nordic ecolabelling criteria for some product groups address all brominated flame retardants in common, while the Nordic and EU ecolabelling criteria for many products focus on specific brominated flame retardants or brominated flame retardants assigned specific risk-phrases.

PBDEs and PBBs

Regulatory framework - The PBDEs and PBBs have so far been considered the most problematic of the brominated flame retardants. Both groups are additive flame retardants. The Danish Action Plan for brominated flame retardants from 2001 had as one of its main aims an international restriction on the use of the PBDEs and PBBs. The use of hexaBB, tetraBDE, pentaBDE, hexaBDE and heptaBDE (refers to particular substances within the groups) is today strictly restricted by the Stockholm Convention, and are addressed by the POPs Regulation (Regulation (EC) No 850/2004) and the RoHS Directive in the EU which are the main implementing instruments for the provisions of the convention in the EU. The Danish national implementation plan for the Stockholm Convention furthermore includes an action plan for the further implementation of the provisions of the

Stockholm Convention in Denmark. TetraBDE and pentaBDE are main constituents of the commercial c-pentaBDE, while hexaBDE and heptaBDE are some of the constituents of the commercial c-octaBDE. The restriction of the substances is a *de facto* restriction of the commercial products. The substances are furthermore addressed by the CLP Regulation on classification and labelling, waste legislation, import/export restrictions, emissions legislation and environmental monitoring legislation.

The decaBDE is restricted in electrical and electronic equipment by the RoHS Directive, as are the other PBDEs and PBBs, with some exemptions and some application areas outside the scope of the directive. The exemptions for PBDE and PBBs in the RoHS directive are not included in the Danish RoHS statutory order. No harmonised classification has been established for decaBDE and the substance is not individually addressed by EU legislation, except for the electrical and electronic equipment and some ecolabelling criteria. It is however listed in the REACH Candidate List and has, on the basis of an Annex XV dossier, been proposed by ECHA for inclusion in the list of substances for authorisation. The substance has been nominated for inclusion in the list of restricted substances under the Stockholm Convention and is currently under review by the POPs Review Committee. In the USA and Canada, voluntary agreements on phasing out decaBDE have been entered into between the most of the major international manufacturers and the federal authorities.

Use - The global consumption of the PBDEs in 2001 was 56,100 t/y, of which decaBDE accounted for nearly 90%. No updated global data on the consumption of decaBDE have been available. The consumption of pentaBDE and octaBDE has more or less ceased globally today, while the consumption of decaBDE in recent years has likely been decreasing due to regulatory action (the RoHS Directive) and the above-mentioned partly voluntary phase out of production and import in North America. In the EU, the average consumption of decaBDE for the period 2010-2011 was 5,000-7,500 t/y. Approximately 1/3 was used for textiles, while the remaining part was used for plastic parts for means of transport and electrical and electronic equipment exempted from or out of the scope of the RoHS Directive. DecaBDE was not used in production processes in Denmark in significant amounts either in 1999 nor 2012, but decaBDE may be present in various imported articles e.g. cars and other means of transport. In production processes in Denmark, decaBDE was mainly replaced by TBBPA and its derivatives in the 1990s. The phase out in Denmark occurred as a consequence of the voluntary phase out by German manufacturers of plastics materials because the PBDEs could not meet the requirements of the German dioxin ordinance. At the EU level, decaBDE in electrical and electronic equipment has mainly been replaced by DBDPE and, apparently, to a smaller degree by EBTEBPI, TTBP-TAZ (1,3,5-Triazine, 2,4,6-tris(2,4,6-tribromophenoxy)-), polymeric brominated flame retardants and non-brominated flame retardants (in some cases with a change in the base resin as well).

In 2012, about 60 t/y octaBDE in polycarbonate was imported for use in the electronics industry in Denmark. The use of octaBDE is surprising, as the production of the substance has been phased out in most countries and the substance is banned for all uses in Denmark.

In terms of PBT¹ properties, hexaBB and four PBDEs are listed as persistent organic pollutants (POPs) in Annex A of the Stockholm Convention. DecaBDE has been suggested as a SVHC (Substance of Very High Concern) under REACH on the basis that it can undergo debromination in the environment to form substances with PBT or vPvB properties.

Environmental and health issues - Some PBDEs and PBBs can affect neurodevelopment and have been associated with reproductive impairment, but epidemiological evidence and toxicokinetic information are still sparse. It has become apparent that non-descended testes in young boys are

¹ PBT = Persistent, bioaccumulative and toxic to organisms in the environment. vPvB = very bioaccumulative and very persistent

linked with exposure to PBDEs and that PBBs are linked to an early age menarche and pubic hair development.

Alternatives - The successful replacement of decaBDE in EEE and the voluntary phase out in the USA clearly demonstrates that alternatives are available. The advantage of decaBDE is mainly that it is cheaper than the alternatives. Drop-in alternatives as DBDPE and EBTEBPI seem on some parameters to have a better environmental and health profile than decaBDE, but some concerns have been raised about their environmental performance. Polymeric brominated flame retardants and non-halogenated alternatives are also marketed for the main use areas, but at higher costs. For use in plastics HIPS and ABS, some of the main alternatives have been the copolymeric plastics blends PPE/HIPS and PC/ABS with non-halogenated flame retardants. While there is no single replacement flame retardant for decaBDE for textiles, the multitude of options on the market, including alternative flame retardants, inherently flame retarded fibres, fibre blends, barrier layers, nonwovens and other approaches, make it clear that viable market-ready approaches exist. The same applies to the use of HBCDD in textiles.

A restriction of decaBDE is not expected to have any negative impact on manufacturers of plastic parts, textiles or furniture in Denmark.

HBCDD

Regulatory framework - HBCDD has recently been subject to authorisation under REACH (Annex XIV to REACH) with a sunset date of 21 August 2015. HBCDD has in May 2013 been listed for restriction under the Stockholm Convention with a time-limited exemption for building materials of expanded polystyrene (EPS) or extruded polystyrene (XPS). In the EU, the restriction enters into force by May 2014. A dossier for a harmonised Classification and Labelling has been submitted.

Use - The global consumption of HBCDD has increased from 16,700 t/y in 2001 to 31,000 t/y in 2011. In the EU, the average consumption of HBCDD for the period 2010-2011 was 10,000-12,500 t/y and HBCDD is currently the BFR used in the highest quantities in the EU. Approximately 90 % of the consumption of HBCDD in the EU is used as additive flame retardant in polystyrene. PS-containing HBCDD, in the form of EPS or XPS, is mainly used as rigid thermal insulation panels/boards for buildings, and for road and railway construction to prevent frost heaves and provide a lightweight load-spreading construction material. The remaining part is used for flame retarding the plastic HIPS and for textiles.

HBCDD is used in Denmark as a flame retardant for the manufacture of EPS sheets for building applications and packaging for electronics. The total consumption for production in Denmark was about 1 tonne in 2012 as compared to 6-13 tonnes in 1999. In 1999, most of the produced flame-retarded EPS was exported. In 1999 the main consumption of HBCDD in building/construction materials was in imported flame retarded XPS, accounting for 11-29 tonnes HBCDD. The situation is likely similar at present. Currently, XPS imported from origins other than the Nordic countries contains HBCDD. For applications in buildings and construction in Denmark, flame-retardant grades of EPS and XPS are not required, as the materials are still combustible and in any case need to be covered by a non-combustible material to prevent ignition. The consumption of flame-retarded EPS in Denmark appears to be increasing for in "zero energy" houses of a new construction, wherein the walls are built of flame-retardant EPS blocks covered with a non-combustible material. The flame retarded EPS for this purpose is imported.

Environmental and health issues - HBCDD is a persistent organic pollutant. The substance is classified as toxic to reproduction.

Alternatives - Polymeric brominated flame retardants have recently been introduced as drop-in alternatives to HBCDD and the major manufacturers of brominated flame retardants are currently

increasing the production capacity for the polymeric brominated flame retardants to meet the expected demand. No independent evaluation of the health and environmental properties of the polymeric alternatives are available. According to industry information, the polymeric brominated flame retardants are potentially persistent (not biodegradable) but with low potential for bioaccumulation and low potential for toxicity. Non-halogenated alternatives for EPS/XPA are not marketed; but the flame-retardant EPS/XPS can be replaced by other insulation materials. The alternatives have different advantages and disadvantages as compared with the flame-retarded EPS, but they typically have better fire performance and contain chemical substances less problematic than HBCDD. Apart from this, the flame retarded EPS scores well in the comparison with the other materials (provided that the fire performance is acceptable), in particular if the EPS ultimately is disposed of by incinerated with energy recovery. The price of the cheapest alternatives ranges from approximately the same price as for flame retarded EPS to approximately 30% more. EPS with polymeric brominated flame retardants have not yet been compared with material alternatives.

Compared to other EU Member States, the use of flame-retardant EPS/XPS is small in Denmark because non-flammable insulation materials have been the preferred option and non-flame-retardant grades of EPS are used. A restriction of HBCDD is not expected to have a significant negative impact on manufacturers of EPS/XPS or users of the materials in Denmark.

TBBPA

Regulatory framework - A harmonised CLP classification has been agreed upon for TBBPA due to its toxicity to organisms in the aquatic environments. Otherwise, the substance is not individually addressed by any EU or Danish legislation.

Use - Globally, TBBPA is still the main BFR, accounting for about 40% of total global production and mainly used as reactive flame retardants in printed circuit boards for electronic equipment. In the EU, the average consumption of TBBPA for production of articles in 2010-2011 was 1,000-2,500 t/y; the substance thus accounts for a smaller part of the consumption of brominated flame retardants for production of articles in the EU. About 90% of the consumption in the EU is as reactive flame retardants for printed circuit boards, 5% was used as reactive flame retardant for other applications while about 5% was used as additive BFR. The majority of the amount of TBBPA in end-products sold in the EU (where the TBBPA is mainly built into the polymer structure) is imported into the EU in finished articles and components, primarily from Asia.

Environmental and health issues - Only additive use of TBBPA is mentioned as an example of brominated flame retardants included in LOUS. The rationale is that in reactive use of TBBPA, the TBBPA is not present *per se* in the final products, but has been built into the polymer structure, which may be considered a brominated plastic. The EU Risk Assessment estimated that volatile loss during service life of articles from additive flame retardants' use was approximately 15% of the total emissions of TBBPA to the air, whereas losses from the service-life of articles where TBBPA was used reactively was considered negligible. However, according to the EU Risk Assessment, direct consumer exposure to TBBPA is likely to be insignificant and EFSA concludes that the available data indicate that current dietary exposure to TBBPA in the EU does not raise a health concern. The substance is classified as toxic in the aquatic environment, but does not meet the REACH PBT criteria based on the currently available data and is not covered by any pipeline activities under REACH. TBBPA can undergo debromination under anaerobic conditions to form bisphenol-A and is thus linked to the discussion about the potential impact of that substance. The main source of releases of TBBPA to the environment was assessed to be manufacturing processes in the EU Risk Assessment. A voluntary program by manufacturers and downstream users of the substance (VECAP) has significantly reduced the total releases in recent years.

Alternatives - Alternatives to the additive use of TBBPA are in general the same as alternatives to decaBDE. Alternatives to the reactive use of TBBPA are usually non-halogenated flame retardants.

The current development of replacing TBBPA in printed circuit boards mainly appears to be part of a process whereby all halogen containing compounds and plastics are replaced in order to be able to market the equipment as halogen-free.

DBDPE and EBTEBPI

Regulatory framework - The two substances are not specifically addressed by current Danish and EU legislation, but DBDPE is included in the Community Rolling Action Plan under REACH.

Use - DBDPE appears to be the main substitute for decaBDE so far; the data indicate that DBDPE is among the main additive flame retardants in the EU, China and Japan. In the EU, the registered production and import of DBDPE is indicated as 1000+ without an upper limit. EBTEBPI is registered in the EU with a production and import in the 100-1,000 t/y tonnage band.

The two substances have application spectra in polymers quite similar to decaBDE and can be used as drop-in alternatives to decaBDE.

Environmental and health issues - DBDPE is found in sewage sludge in the Nordic Countries in concentrations of the same magnitude as decaBDE. The studies indicate that contamination of the Swedish environment with DBDPE has already approached that of decaBDE, and that this contamination is occurring primarily via the atmosphere. Further monitoring in the Arctic has been suggested for DBDPE by DCE, the Danish Centre for Environment and Energy. Very limited data on EBTEBPI are available as the substance has not been included in screenings of brominated flame retardants in the Nordic and Arctic environments.

DBDPE is persistent but does not meet the REACH PBT criteria based on the available data; however, there are currently insufficient reliable data. A UK Environment Risk Assessment considered that there was a potential for DBDPE to undergo reductive debromination by analogy with decaBDE. It has recently been shown that DBDPE may have potential to undergo photolytic debromination reactions; however, the environmental significance of such reactions is currently unknown. According to an EU expert group on identification of PBT and vPvB substances evaluation, EBTEBPI was not considered a PBT substance. Alternatives to DBDPE and EBTEBPI are either polymeric brominated flame retardants or non-halogenated flame retardants, some of which have better environmental and health profiles in screening assessments.

Alternatives – The two substances are the main alternatives to decaBDE. Polymeric brominated flame retardants and non-halogenated flame retardants which may be used as alternatives to decaBDE may be used as alternatives to the two substances.

Other BFRS

Regulatory framework - Except for the requirements of the WEEE Directive and some eco-labels, the brominated flame retardants are not addressed by any EU or Danish legislation. Pentabromoethylbenzene (PBEB) and PBB-Acr are included in the OSPAR list of Chemicals for Priority Action.

Use - For the other brominated flame retardants, information on global and EU production/consumption is more limited. The global consumption seems to have increased from about 110,000 t/y in 2001 to about 150,000 t/y in 2011.

Data on the consumption of other brominated flame retardants in the EU are scarce and uncertain. For the non-polymeric brominated flame retardants, the registrations at ECHA's website indicate total import and production (of each substance) in tonnage bands (e.g. 100-1,000 t/y), but for the polymeric brominated flame retardants no data are available as the polymers are not subject to registration under REACH. The brominated flame retardants registered in the highest tonnage (apart from the substances mentioned above) are the reactive halogenated polyetherpolyol B, 2,4,6-

tribromophenol (TBP) and the additive BFR TTBP-TAZ, which are all registered in the 1,000-10,000 t/y tonnage band. Tribromoneopentyl alcohol (TBNPA) is registered with confidential tonnage. Other additive brominated flame retardants registered with an import and production in the 100-1,000 t/y tonnage band are tris(tribromo-neopentyl)phosphate (TTBNPP), poly pentabromobenzyl acrylate (PBB-Acr) and tetrabromophthalate ester (BEH-TEBP). The main applications of the different brominated flame retardants are known and described in this survey, but detailed breakdowns of the use of each substance by end-application areas are not available.

Environmental and health issues - A screening of 16 "new" brominated flame retardants in the Nordic environment indicated that the concentrations of the "new" brominated flame retardants are, with a few exceptions, in the same order of magnitude or lower compared to the sum of BDE congeners BDE-28, -47, -99, -100, -153 and -154 addressed as priority substances under the Water Framework Directive.

Of the additive brominated flame retardants with registered import or production in the EU (i.e. production and import is above 100 t/y) the following have not been included in the recent screening of brominated flame retardants in the Nordic environment, and no data on their occurrence in the Nordic or Arctic environments have been identified: EBTEBPI, TTBP-TAZ, bis(pentabromophenoxy) benzene (4'-PeBPOBDE208) and TTBNPP. The screening of brominated flame retardants in the Nordic environment also identified some reactive brominated flame retardants in significant concentrations (DBP and TBP). Four of the registered reactive brominated flame retardants have not been included in the screening: DBNPG, HEEHP-TEBP and TEBP-Anh, halogenated polyetherpolyol B and tetrabromophthalic anhydride based diol.

Some emerging brominated flame retardants have not been studied in much detail, but the non-polymeric brominated flame retardants are supposed to have somewhat similar effects as the more studied brominated flame retardants. One of these is HBB which may be more persistent and toxic, and therefore hazardous, than the PBDEs.

Since the toxicological mechanisms of the different brominated flame retardants seem to be related, mixtures of brominated flame retardants may have additive and synergistic effects.

Alternatives – The alternatives to other brominated flame retardants are non-halogenated flame retardants and material alternatives without flame retardants. The available alternative assessments do not include an assessment of degradation products and the performance of the flame-retardant materials during fire or uncontrolled combustion. The presence of brominated flame retardants has been demonstrated to negatively affect e.g. the formation of smoke and, during thermal stress, they result in formation of hazardous substances. Most studies have however addressed the PBDEs and other brominated flame retardants with high risk of formation of hazardous substances and not as yet the polymeric brominated flame retardants, for example. The significance of formation of hazardous substances and fumes in a lifecycle perspective seems to be the main issue when comparing the impact of the non-regulated brominated flame retardants and non-halogenated flame retardants, but detailed assessments are not available yet. Data on the effect of non-halogenated flame retardants on the formation of fumes and hazardous substances are limited and comparative assessments of different types of brominated flame retardants and non-halogenated flame retardants on these parameters are missing.

The authors of a recent review of persistence, bioaccumulation and toxicity of non-halogenated flame retardants, as one of the outcomes of the EU funded ENFIRO project, conclude that large data gaps were identified for the physical–chemical properties and the PBT properties of the reviewed non-halogenated flame retardants. To assess whether the reviewed non-halogenated flame retardants are truly suitable alternatives, each compound should be examined individually by comparing its PBT values with those of the equivalent halogenated flame retardant. Until more data are

available, it remains impossible to accurately evaluate the risk of each of these compounds, including the ones that are already extensively marketed.

Ecolabelling criteria

The Nordic ecolabelling criteria for a wide range of articles contain requirements which restrict the use of some or all brominated flame retardants. The exact criteria vary among the article groups. In some groups only brominated flame retardants that are assigned specific R- phrases (e.g. phrases concerning CMR² properties) are restricted, whereas in others it is specified that certain flame retardants must not be present: either all flame retardants, all halogenated flame retardants, or all halogenated organic flame retardants. In many of the criteria for electrical and electronic equipment, some exemptions for reactive brominated flame retardants and plastic parts of less than 25 g apply.

The EU ecolabelling criteria do not generally apply to the use of reactive flame retardants. The criteria for various electrical and electronic products have restrictions on the use of additive flame retardants which meet the criteria for classification in specific hazard classes. In practice for most of the criteria, the restrictions beyond the general EU restriction of the PBDEs would mainly concern additive use of TBBPA and the use of HBCDD. The criteria for bed mattresses, textile floor coverings, textile products and furniture restrict any use of additive flame retardants in the articles.

Waste management

Disposal of BFR-containing waste – Waste electrical and electronic equipment (WEEE) represent the major part of brominated flame retardants in solid waste. Other major waste fractions are building insulation materials (EPS/XPS and PU foam) and waste from shredding of vehicles. Brominated flame retardants in textiles, furniture, paints, etc. will represent a small fraction of the total in Denmark, but may be more significant in other Member States. The WEEE Directive requires that plastics containing brominated flame retardants should be removed from the collected WEEE for selective treatment. The Danish statutory order further requires that the removed BFR-containing plastics should be disposed of to enterprises with a permit for handling of bromine-containing equipment. In Denmark, the BFR-containing plastics from WEEE are disposed of to municipal solid waste incineration. The same is the situation for BFR-containing plastics from the building sector and textiles and furniture. Plastics from shredding of vehicles are disposed of to controlled landfill.

A part of flame retarded plastics in phased out electrical and electronic in some EU Member Countries appears to end up in uncontrolled waste handling in countries outside the EU, either by illegal shipment of the WEEE or exported as second hand equipment for reuse in developing countries. The ultimate disposal of the BFR-containing plastics (possibly after recycling) is, regardless of the objective of the export, probably uncontrolled burning or waste dumping.

POP brominated flame retardants - Particular provisions for waste containing POPs are stipulated in Commission Regulation (EU) No 756/2010 amending the POPs Regulation. For hexaBB a limit value for disposal provisions of 50 mg/kg is established, but it has no practical implications for Denmark, as hexabromophenyl is likely not present in the waste. No concentration limits have been established yet for the PBDEs. Depending on the limits to be established by the European Commission, separate collection and treatment of some waste fractions may be necessary.

Incineration and uncontrolled burning - One of the main concerns about the incineration of BFR-containing plastics has been the risk of formation of brominated and mixed brominated/chlorinated dioxins and furans. The available data indicate that the destruction efficiency for brominated flame retardants in municipal waste incinerators in the Nordic countries is better than

² CMR = carcinogenic, mutagenic or reprotoxic

99,999%. Furthermore, it is indicated that the incineration of brominated flame retardants may contribute a small fraction to the total generated dioxins and furans and that the filters for control of emissions of dioxins and furans are also efficient in capturing the brominated and mixed brominated/chlorinated dioxins and furans.

Whilst the emission from incinerators with modern flue gas controls may be of little concern, much literature indicated that the emissions of dioxins and furans from fires (including incidental landfill fires) and uncontrolled burning of BFR-containing plastics may be significant.

Application of sludge on agricultural soils –The majority of the brominated flame retardants in sewage water ends up in the sludge fraction in the sewage treatment plants. DecaBDE, HBCDD and DBDPE are the dominant brominated flame retardants in municipal sewage sludge. The available data indicate that the levels of decaBDE and HCBDD levels in sewage sludge in the UK and Ireland is approximately a factor of 10 higher than in other EU Member States, indicating a link to the widespread use of these substances in textiles and furniture in the two countries. Recent analyses of 16 "new" brominated flame retardants in sewage sludge in the Nordic countries show that the concentration of DBDPE is on the same magnitude as found for decaBDE and HBCDD in other studies, whereas the concentrations for the remaining 15 brominated flame retardants are considerably lower. The results confirm that DBDPE to a large extent have substituted for decaBDE in applications that may lead to releases to wastewater.

A risk evaluation from 2012 of the application of BFR-containing sludge to agricultural land in Denmark, which included a detailed assessment of decaBDE and TBBPA, concluded that it was very unlikely that the levels of brominated flame retardants found in Danish sludge should pose a significant risk to the soil dwelling organisms and the soil quality in general, if the current application guidelines of sewage sludge were followed.

Main data gaps

Detailed data on the use of brominated flame retardants other than the PBDEs, HBCDD and TBBPA globally and in the EU are not available in the public literature. The public part of the REACH registrations provides as mentioned some indication on the production and import in the EU tonnage bands, but the polymeric brominated flame retardants are not subject to registration and no information on the market volumes of these substances are available. The consumption of some the other brominated flame retardants is expected to be increasing, but the lack of data constrain an assessment of the trends in the use of the brominated flame retardants and the monitoring of the effects of regulatory action. The lack of detailed data on the consumption by application areas furthermore constrains an assessment of the potential releases and exposure of humans and the environment.

Data on the fate, exposure and environmental and health hazards for most endpoints are missing for most brominated flame retardants.

Knowledge on the actual fate of WEEE exported for waste management outside Denmark is limited.

No data on the actual recycling of BFR-containing waste in Denmark or the EU have been identified.

The significance of the different brominated flame retardants on the formation of brominated and mixed brominated/chlorinated dioxins and furans by different types of thermal processes is not known for most brominated flame retardants.

Konklusion og sammenfatning

I perioden 2012-2015 vil alle 40 stoffer og stofgrupper på Miljøstyrelsens liste over uønskede stoffer (LOUS) blive kortlagt, og Miljøstyrelsen vil på grundlag af resultaterne vurdere behovet for yderligere regulering, substitution/udfasning, klassificering og mærkning, forbedret affaldshåndtering eller øget udbredelse af information.

Denne undersøgelse vedrører bromerede flammehæmmere. De bromerede flammehæmmere optrådte på den første udgave af LOUS i 1998 og er forblevet på listen siden da. Gruppen er angivet i LOUS som "visse bromerede flammehæmmere" med tre eksempler fra gruppen: Decabromdiphenyl ether (decaBDE), additiv brug af tetrabrombisphenol A (TBBPA) og hexabromcyclododecan (HBCDD). Det er ikke nærmere specificeret, hvilke andre bromerede flammehæmmere der anses for at være omfattet. Denne undersøgelse omhandler i et vist omfang alle bromerede flammehæmmere, men fokuserer i nogle kapitler på de tre vigtigste af stofferne: decaBDE, TBBPA og HBCDD samt to af de vigtigste bromerede alternativer til decaBDE, nemlig decabromodiphenylethan (DBDPE) og ethylenbis(tetrabromphthalimid) (EBTEBPI). Som følge heraf indeholder denne sammenfatning afsnit for hvert af fokusstofferne samt afsnit, der går på tværs af alle bromerede flammehæmmere.

Stofgruppen

Flammehæmmere tilsættes polymere materialer, både naturlige og syntetiske, for at øge materialernes flammehæmmende egenskaber. Brugen af flammehæmmere er i vid udstrækning en konsekvens af regler om brandsikkerhed. Reglerne for brandsikkerhed indeholder ikke specifikke krav om at anvende bromerede flammehæmmere eller bestemte andre typer af flammehæmmere. Reglerne definerer typisk nogle flammetests som materialer, artikler eller bygningskomponenter skal kunne leve op til, men det er op til producenten af artiklerne eller bygherren at beslutte, hvordan kravene kan opfyldes.

De bromerede flammehæmmere har til fælles, at de indeholder brom og bruges til at forhindre, at plastmaterialer og tekstiler antændes. De virker alle ved den samme grundlæggende mekanisme: Frigivelse af brombrinte når materialet antændes, som blokerer den videre forbrændingsproces. Derudover er de bromerede flammehæmmere en kompleks gruppe af stoffer: Aromatiske, cycloalifatiske, alifatiske, polymere og uorganiske stoffer, der alle indeholder brom. Nogle af stofferne anvendes som additiver, hvor stofferne ikke er kemisk bundet i polymermaterialet, mens andre bruges som reaktive stoffer, som bygges ind polymerstrukturen, og derfor ikke er til stede som det oprindelige stof i den færdige polymer (med undtagelse af spormængder af ureageret stof). I denne undersøgelse er der fundet 69 bromerede flammehæmmere, som er blevet prægistreret under REACH, eller/og er produceres og markedsføres af store internationale producenter af bromerede flammehæmmere. Desuden er der fundet 14 stoffer beskrevet i litteraturen, men som ikke er prægistrerede eller markedsføres af de store producenter.

Produktion og anvendelse af bromerede flammehæmmere

Globalt - Den samlede globale produktion af bromerede flammehæmmere er steget fra 150.000 tons/år i 1994 til ca. 360.000 tons/år i 2011. Stigningen i produktion og forbrug har først og fremmest fundet sted i Asien. På globalt plan udgør de bromerede flammehæmmere ca. 20% af det totale forbrug af flammehæmmere. Historisk set har PBDE og TBBPA (og dets derivater), været de vigtigste bromerede flammehæmmere, og de tegnede sig for næsten 2/3 af den globale produktion i

1994. Globalt fremstilles hovedparten af de bromerede flammehæmmere af fire store producenter, og stofferne fremstilles i EU kun af én virksomhed.

En detaljeret opgørelse af stoffer og anvendelsesområder på globalt plan er ikke tilgængelig. Det største anvendelsesområde er elektrisk og elektronisk udstyr, hvor bromerede flammehæmmere også er de dominerende flammehæmmere. Andre anvendelsesområder omfatter elinstallationer og eldistribution; tekstiler, tæpper og møbler; byggematerialer; transportmidler (køretøjer, tog, fly, skibe, osv.) samt maling og fugemasser.

EU – Der er detaljerede data til rådighed på EU-plan for tre af de vigtigste bromerede flammehæmmere: DecaBDE, HBCDD og TBBPA, som tegner sig for omkring 40% af det samlede forbrug. For andre ikke-polymere bromerede flammehæmmere, er der oplysninger om den samlede produktion i og import til EU i mængdeintervaller (f.eks. 100-1.000 tons/år), fra registreringsdatabasen på det Europæiske Kemikalieagenturs (ECHAs) hjemmeside. Disse data er kun tilgængelige for bromerede flammehæmmere med en samlet import og produktion i 2013 på over 100 tons/år, og der er ingen data for polymere bromerede flammehæmmere. De markedsførte mængder er yderligere beskrevet i de følgende afsnit.

Danmark - En omfattende kortlægning af brugen af bromerede flammehæmmere i Danmark blev udført i 1999. Bromerede flammehæmmere i importerede artikler og blandinger tegnede sig for omkring 90% af mængderne af de samlede mængder af bromerede flammehæmmere i slutprodukter solgt i Danmark i 1999. Af den samlede omsætning på 330-660 tons/år bromerede flammehæmmere i slutprodukter udgjorde elektrisk og elektronisk udstyr mere end 70%. Det er sandsynligvis stadig tilfældet. Bromerede flammehæmmere i artikler på det danske marked er en afspejling af det generelle brugsmønster i EU og globalt snarere end brugen af bromerede flammehæmmere i dansk industri. En fuld opdatering af opgørelsen fra 1999 har været uden for rammerne af denne undersøgelse.

I dansk industri var den vigtigste anvendelse af bromerede flammehæmmere i 1999 og 2012 reaktive bromerede polyoler, som anvendes til produktion af flammehæmmet polyuretanskum til bygningsisolering.

Lovgivningsmæssigt fokus

Det lovgivningsmæssige fokus i EU og Danmark har hidtil været på de to stofgrupper polybromerede dipenylethere (PBDE) og polybromerede biphenyler (PBB), mens HBCDD for ganske nylig er blevet autorisationspligtig i henhold til REACH, og opført under Stockholm-konventionen om persistente organiske miljøgifte (POP-stoffer). Lovgivningen er yderligere beskrevet for hver enkelt stofgruppe nedenfor. På EU-plan er der et enkelt lovgivningsmæssigt instrument, som omhandler de bromerede flammehæmmere samlet: WEEE-direktivet om affald af elektrisk og elektronisk udstyr (WEEE) kræver selektiv behandling og korrekt bortskaffelse af materialer og komponenter indeholdende bromerede flammehæmmere. De nordiske miljømærkekriterier (Svanen) for visse produktgrupper omhandler også de bromerede flammehæmmere samlet, mens både nordiske og EU- miljømærkekriterier (EU blomsten) for mange produktgrupper udelukker anvendelsen af specifikke bromerede flammehæmmere eller bromerede flammehæmmere, som er tildelt specifikke risiko-sætninger.

PBDE og PBB

Regulering - PBDE og PBB har hidtil været betragtet som de mest problematiske af de bromerede flammehæmmere. Begge grupper er additive flammehæmmere. Den danske handlingsplan for bromerede flammehæmmere fra 2001 havde som et af sine vigtigste mål en international begrænsning af brugen af PBDE og PBB. Anvendelse af hexaBB, tetraBDE, pentaBDE, hexaBDE og heptaBDE (refererer til bestemte stoffer inden for grupperne) er i dag begrænset af Stockholm-konventionen, og er i EU omfattet af POP-forordningen (forordning (EF) nr. 850/2004) og RoHS-

direktivet, som er de vigtigste instrumenter til gennemførelse af konventionens bestemmelser i EU. Den danske nationale implementeringsplan for Stockholm-konventionen omfatter desuden en handlingsplan for yderligere implementering af bestemmelserne i Stockholm-konventionen i Danmark. TetraBDE og pentaBDE er de vigtigste bestanddele af den kommercielle flammehæmmer c-pentaBDE, mens hexaBDE og heptaBDE er nogle af bestanddelene i den kommercielle flammehæmmer c-octaBDE og begrænsning af stofferne er en *de facto* begrænsning af de kommercielle produkter. Stofferne er desuden omfattet af CLP-forordningen om klassificering og mærkning, af affaldslovgivningen, import/eksport restriktioner, samt lovgivning om emissionsbegrænsning og miljøovervågning.

Anvendelse - Brug af decaBDE er, i lighed med de andre PBDE og PBB, begrænset i elektrisk og elektronisk udstyr ved RoHS-direktivet med nogle undtagelser og nogle produktkategorier, som uden for direktivets anvendelsesområde. Undtagelserne i RoHS direktivet for PBDE og PBB er ikke gældende i den danske RoHS bekendtgørelse. Der er ikke etableret en harmoniseret klassificering for decaBDE og stoffet er, med undtagelse af elektrisk og elektronisk udstyr og nogle miljømærkekriterier, ikke individuelt behandlet af EU-lovgivningen. Det er dog opført på kandidatlisten under REACH, og er på grundlag af et bilag XV-dossier blevet foreslået af ECHA for optagelse på listen over stoffer, som kræver autorisation. Stoffet er desuden blevet nomineret til optagelse på listen over begrænsede stoffer under Stockholm-konventionen, og er i øjeblikket under evaluering af Komitéen for Vurdering af Persistente Organiske Miljøgifte under konventionen. I USA og Canada er frivillige aftaler om udfasning af decaBDE indgået mellem flere af de store internationale producenter og de føderale myndigheder.

Det globale forbrug af de PBDE var i 2001 56.100 tons/år, hvoraf decaBDE tegnede sig for næsten 90%. Ingen opdaterede globale opgørelser af forbruget af decaBDE har været til rådighed. Brugen af pentaBDE og octaBDE er mere eller mindre ophørt global, mens forbruget af decaBDE i de seneste år formentlig har været faldende på grund af lovgivningsmæssige tiltag (RoHS-direktivet), og den nævnte frivillige delvise udfasning af produktion og import i Nordamerika. I EU var det gennemsnitlige forbrug af decaBDE i perioden 2010-2011 5.000-7.500 tons/år. Ca. 1/3 blev anvendt til tekstiler, mens den resterende del blev brugt til plastdele til transportmidler og elektrisk og elektronisk udstyr undtaget eller uden for RoHS-direktivets anvendelsesområde. DecaBDE blev ikke brugt i produktionsprocesser i Danmark i væsentlige mængder, hverken i 1999 eller 2012, men decaBDE kan være til stede i forskellige importerede artikler f.eks. biler og andre transportmidler. I dansk produktion blev decaBDE i 1990'erne primært erstattet af TBBPA og dets derivater. Udfasningen i Danmark var primært en følge af en udfasning af decaBDE hos tyske producenter af plastmaterialer, fordi PBDE ikke kunne opfylde kravene i den tyske dioxin bekendtgørelse. På EU-plan er decaBDE i elektrisk og elektronisk udstyr tilsyneladende primært blevet erstattet af DBDPE og i mindre grad af EBTEBPI, TTBP-TAZ (1,3,5- triazin, 2,4,6- tris (2,4,6- tribromfenoxy)-), polymere bromerede flammehæmmere og af ikke-bromerede flammehæmmere (i nogle tilfælde ved en samtidig ændring af basispolymeren).

I 2012 blev omkring 60 tons octaBDE i polycarbonat importeret til brug i elektronikindustrien i Danmark. Brugen af octaBDE er overraskende, da produktionen af stoffet er udfaset i de fleste lande, og stoffet er forbudt til alle anvendelser i Danmark.

Miljø og sundhed - I relation til PBT-egenskaber ³ er hexaBB og fire PBDE'er opført som persistente organiske miljøgifte (POP-stoffer) i bilag A til Stockholm-konventionen. DecaBDE er foreslået som et særligt problematisk stof (Substance of Very High Concern, SVHC) under REACH på det grundlag, at det kan undergå debromering i miljøet og dermed danne lavere-bromerede PBDE'er med PBT- eller vPvB-egenskaber.

³ PBT = Persistente, bioakkumulerbare and toksiske over for organismer i miljøet. vPvB = meget bioakkumulerbare og meget persistente

Nogle PBDE'er og PBB'er kan påvirke nervesystemets og er blevet knyttet til reproduktive defekter, men epidemiologisk evidens og toksikokinetiske data er stadig sparsomme. Der er undersøgelser der viser, at ikke-nedfaldne testikler hos unge drenge er forbundet med udsættelse for PBDE og at PBB er knyttet til tidlig start på menstruation og tidlig udvikling af kønsbehåring.

Alternativer - Udskiftningen af decaBDE i elektrisk og elektronisk udstyr og den frivillige udfasning i USA viser klart, at der findes brugbare alternativer. Fordelen ved decaBDE er hovedsageligt at stoffet er billigere end alternativerne. "Drop-in" alternativer som DBDPE og EBTEBPI synes på nogle parametre at have en bedre miljø- og sundhedsmæssig profil end decaBDE, men der er blevet rejst en vis bekymring om deres miljøegenskaber. Polymere bromerede flammehæmmere og ikke-halogenerede alternativer markedsføres også til de væsentligste anvendelsesområder, men prisen er tilsyneladende højere end prisen på decaBDE. Nogle af de vigtigste alternativer til brugen af decaBDE i plasttyperne HIPS og ABS har været copolymere plasttyper, PPE/HIPS og PC/ABS med ikke-halogenerede flammehæmmere. Der er ikke en enkelt flammehæmmer, som kan erstatte decaBDE i alle anvendelser i tekstiler, men der er mange muligheder på markedet, herunder alternative flammehæmmere, fibre som i sig selv er flammehæmmende, fiberblandinger, barrierelag, fiberdug og andre metoder, som viser at brugbare alternativer eksisterer. Det samme gælder for anvendelsen af HBCDD i tekstiler.

En begrænsning af decaBDE forventes ikke at have nogen negativ indvirkning på producenter af plastdele, tekstiler eller møbler i Danmark.

HBCDD

Lovgivning - HBCDD er for nylig blevet omfattet af kravene om autorisation under REACH (bilag XIV til REACH) med en solnedgangsdato ("sunset date") den 21. august 2015. HCBDD er desuden i maj 2013 blevet opført på listen over stoffer, som skal begrænses, under Stockholm-konventionen med en tidsbegrænset undtagelse for byggematerialer af ekspanderet polystyren (EPS), eller ekstruderet polystyren (XPS). Begrænsningen vil træde i kraft i EU i maj 2014. Et forslag til harmoniseret klassificering og mærkning er blevet indsendt og er under evaluering.

Anvendelse - Det globale forbrug af HBCDD er steget fra 16.700 tons/år i 2001 til 31.000 tons/år i 2011. I EU var det gennemsnitlige forbrug af HBCDD i perioden 2010-2011 10.000-12.500 tons/år og HBCDD er for øjeblikket den af de bromerede flammehæmmere, der anvendes i de største mængder i EU. Omkring 90 % af forbruget af HBCDD i EU er som additiv flammehæmmer i polystyren. Polystyren med HBCDD, i form af EPS eller XPS, anvendes hovedsageligt som isoleringsplader i bygninger og i vej- og jernbanekonstruktioner for at undgå frostskafer og fungere som et let konstruktionsmateriale, der kan fordele trykket på konstruktionen. Den resterende del anvendes til at flammehæmme plasttypen HIPS og i tekstiler.

HBCDD er i Danmark anvendt som flammehæmmer til fremstilling af EPS-plader til byggeformål og til EPS-emballage til elektronik. Det samlede forbrug til produktion i Danmark var omkring 1 ton i 2012, hvilket er et markant fald i forhold til de 6-13 tons anvendt i 1999. I 1999 blev hovedparten af den fremstillede flammehæmmede EPS eksporteret. I 1999 var det væsentligste forbrug af HBCDD knyttet til importeret flammehæmmede XPS, som tegnede sig for 11-29 tons HBCDD, og det er det sandsynligvis stadig. XPS importeret fra andre lande end de nordiske lande indeholder i dag HBCDD. Til anvendelser i bygninger og anlæg i Danmark er flammehæmmede kvaliteter af EPS og XPS ikke påkrævet, da materialerne stadig er brændbare og under alle omstændigheder skal være dækket af et ikke-brændbart materiale, som beskytter mod antændelse. Forbruget af flammehæmmede EPS i Danmark synes at være stigende i visse typer "nul-energi huse" af en ny konstruktion, hvor væggene er bygget af flammehæmmede EPS-blokke beklædt med et ikke-brændbart materiale. Det flammehæmmede EPS til dette formål importeres.

Miljø og sundhed – HBCDD er opført som persistente organiske miljøgift (POP-stof) i bilag A til Stockholm-konventionen. Stoffet er klassificeret som reproduktionstoksisk.

Alternativer - Polymere bromerede flammehæmmere er for nylig blevet indført som "drop-in" alternativer til HBCDD, og de største producenter af bromerede flammehæmmere i verden er i øjeblikket ved at øge produktionskapaciteten for de polymere bromerede flammehæmmere for at kunne imødekomme den forventede efterspørgsel. Der er ikke fundet uafhængige evalueringer af de sundheds- og miljømæssige egenskaber af de polymere alternativer. Ifølge information fra industrien, er de polymere bromerede flammehæmmere potentielt persistente (ikke bionedbrydelige), men har et lavt potentiale for bioakkumulation og et lavt potentiale for toksicitet. Der markedsføres ikke ikke-halogenerede alternativer til brug i EPS/XPS, men flammehæmmet EPS/XPS kan erstattes af andre isoleringsmaterialer. Alternativerne har forskellige fordele og ulemper i forhold til flammehæmmet EPS, men de har typisk bedre brandegenskaber og indeholder mindre problematiske kemiske stoffer. Prisen for de billigste alternativer spænder fra mere eller mindre den samme pris som for flammehæmmet EPS til omkring 30% mere. EPS med polymere bromerede flammehæmmere er endnu ikke blevet sammenlignet med de alternativer materialer.

Sammenlignet med andre EU-medlemsstater, er forbruget af flammehæmmet EPS /XPS lille i Danmark, dels fordi ikke-brandbare isoleringsmaterialer har været den foretrukne løsning og dels fordi der anvendes ikke- flammehæmmede kvaliteter af EPS/XPS. En begrænsning af HBCDD forventes ikke at have væsentlig negativ indvirkning på producenter af EPS/XPS eller brugere af materialerne i Danmark.

TBBPA

Regulering -

Anvendelse - TBBPA er den vigtigste bromerede flammehæmmer globalt set og tegner sig for omkring 40% af den samlede globale produktion. TBBPA bruges primært som reaktiv flammehæmmer i printkort til elektronisk udstyr. I EU var det gennemsnitlige forbrug af TBBPA til produktion af artikler i 2010-2011 1.000-2.500 tons/år og stoffet udgør dermed en mindre del af forbruget af bromerede flammehæmmere til produktion af artikler i EU. Omkring 90 % af forbruget i EU er som reaktiv flammehæmmer til printkort, 5% som reaktiv flammehæmmer til andre formål, mens omkring 5% blev brugt som additiv flammehæmmer i plast. Hovedparten af TBBPA i slutprodukter, der sælges i EU, (hvor TBBPA hovedsageligt er bygget ind i polymerstrukturen) importeres til EU med færdige artikler og komponenter, først og fremmest fra Asien.

TBBPA er tildelt en harmoniseret klassificering på grund af stoffets giftighed overfor organismer i vandmiljøet. Her ud over er stoffet ikke er individuelt omfattet af nogen dansk eller EU-lovgivning.

Miljø og sundhed - Kun additiv brug af TBBPA er nævnt som eksempel på bromerede flammehæmmere, der er omfattet af LOUS. Rationalet er, at TBBPA ved reaktiv anvendelse ikke som sådan til stede i de endelige artikler, men er blevet indbygget i den polymere struktur, og materialet kan betragtes som en bromeret plast. EU-risikovurderingen for TBBPA anslår, at afgivelse af TBBPA til luft fra artikler, hvor stoffet er anvendt som additiv flammehæmmer, udgjorde ca. 15 % af de samlede emissioner af TBBPA til luft, mens tab fra reaktiv brug af TBBPA i artikler blev anslået at være ubetydelige. I følge EU-risikovurderingen er den direkte forbrugereksposering for TBBPA sandsynligvis ubetydelig, og den Europæiske Fødevarerautoritet, EFSA, konkluderer, at de foreliggende data indikerer, at den nuværende eksponering for TBBPA via kosten i EU ikke giver anledning til sundhedsmæssig bekymring. Stoffet er klassificeret som giftigt i vandmiljøet, men det opfylder baseret på de tilgængelige data ikke REACH PBT-kriterierne. Der er ingen planlagte tiltag for TBBPA under REACH. Under anaerobe forhold kan TBBPA undergå debromering, hvorved der dannes bisphenol-A (BPA) og TBBPA er således knyttet til diskussionen om den potentielle effekt af BPA. Den vigtigste kilde til udslip af TBBPA til miljøet blev i EU-risikovurderingen vurderet at være fremstillingsprocesser. Som resultatet af et frivilligt program (VECAP) som omfatter producenter og

brugere af TBBPA længere nede i produktkæden (downstream-users), er de samlede udslip blevet væsentligt reduceret i de seneste år.

Alternativer - Alternativer til den additive brug af TBBPA er i store træk de samme stoffer, som kan anvendes som alternativer til decaBDE. Alternativer til reaktiv anvendelse af TBBPA er primært ikke-halogenerede flammehæmmere. Den nuværende udvikling i retning af at erstatte TBBPA i printkort synes primært at være en del af en proces, hvor alle halogenholdige stoffer og plasttyper erstattes for at kunne markedsføre udstyret som halogenfrit.

DBDPE og EBTEBPI

Regulering -

Anvendelse -DPDPE synes at være det vigtigste erstatningsstof for decaBDE, og de tilgængelige data indikerer, at DBDPE er blandt de vigtigste additive bromerede flammehæmmere i EU, Kina og Japan. I EU er den registrerede produktion og import af DBDPE angivet som 1000+, uden en øvre grænse. EBTEBPI er i EU registreret med en produktion og import i 100-1.000 tons/år intervallet.

De to stoffer er ikke specifikt omfattet af gældende dansk og EU-lovgivning, men DBDPE indgår i den løbende handlingsplan for Fællesskabet (CORAP) under REACH.

De to stoffer har anvendelsesspektre in polymerer, som helt svarer til spektret for decaBDE, og kan anvendes som "drop-in" alternativer til decaBDE. DEDPE er fundet i spildevandsslam i Norden i koncentrationerne af samme størrelsesorden som decaBDE. Undersøgelser viser, at forurening af det svenske miljø med DBDPE allerede har nået et niveau svarende til niveauet af decaBDE, og at denne forurening primært er et resultat af atmosfærisk nedfald. Yderligere overvågning af DBDPE i Arktis er blevet foreslået af DCE – Nationalt Center for Miljø og Energi. Der er meget begrænsede data vedrørende forekomsten af EBTEBPI i miljøet, da stoffet ikke har været omfattet af screeninger af bromerede flammehæmmere i de nordiske og arktiske miljøer.

Miljø og sundhed - DBDPE er persistent, men opfylder ikke REACH PBT-kriterierne, baseret på de tilgængelige data. Der er dog i øjeblikket ikke tilstrækkeligt mange pålidelige data til at komme med en endelig vurdering. En britisk miljörisikoanalyse konkluderer, at der er et potentiale for, at DBDPE kan gennemgå reaktiv debromering analog med debromeringen af decaBDE, og det er for nylig vist, at DBDPE kan have potentiale for at gennemgå fotolytiske debromeringsreaktioner. Den miljømæssige betydning af sådanne reaktioner er dog i øjeblikket ukendt. Ifølge en EU-ekspertgruppe om identifikation og evaluering af PBT og vPvB-stoffer (PBT-ekspertgruppen) kan EBTEBPI ikke betragtes som et PBT-stof. Alternativer til DBDPE og EBTEBPI er enten polymere bromerede flammehæmmere eller ikke-halogenerede flammehæmmere, hvoraf nogle har bedre miljø-og sundhedsmæssige profiler i screeningsvurderinger.

Alternativer – De to stoffer er de almindeligste alternativer til decaBDE. Alternativer er de samme polymere bromerede flammehæmmere og ikke-halogenerede flammehæmmere, som kan anvendes som alternativer til decaBDE.

Andre bromerede flammehæmmere

Anvendelse -For de øvrige bromerede flammehæmmere er information om den globale produktion og produktion og forbrug i EU mere begrænset. Det globale forbrug ser ud til at være steget fra omkring 110.000 tons/år i 2001 til omkring 150.000 tons/år i 2011.

Data om forbruget af andre bromerede flammehæmmere i EU er få og usikre. For de ikke-polymere bromerede flammehæmmere, viser registreringerne på ECHAs hjemmeside den samlede import og produktion af hvert stof i mængdeintervaller (f.eks. 100-1.000 tons/år). For polymere bromerede flammehæmmere foreligger der ikke opgørelser, da polymerer er fritaget for registrering under REACH. De bromerede flammehæmmere, som er registreret i den højeste tonnage (bortset fra de stoffer, der er nævnt ovenfor), er de reaktive flammehæmmere halogeneret polyetherpolyol B og

2,4,6-tribromphenol (TBP) samt den additive bromerede flammehæmmer TTBP-TAZ, som alle er registreret i 1.000-10.000 tons/år mængdeintervallet. Tribromneopentylalkohol (TBNPA) er registreret med fortløbig tonnage. Andre additive bromerede med en registreret samlet import og produktion i 100-1.000 tons/år intervallet er tris(tribrom-neopentyl)phosphat (TTBNPP), poly penta-brombenzylacrylat (PBB-ACR) og tetrabromphthalatester (BEH - TEBP). De væsentligste anvendelser af de forskellige bromerede flammehæmmere er kendt og beskrevet i denne kortlægning, men detaljerede opdelinger af forbruget af hvert stof på de forskellige anvendelsesområder er ikke tilgængelige.

Bortset fra kravene i WEEE-direktivet, som vedrører alle bromerede flammehæmmere, og nogle miljømærker er de øvrige bromerede flammehæmmere ikke omfattet af nogen dansk eller EU-lovgivning. Pentabrommethylbenzen (PBEB) og PBB-Acr indgår i OSPAR-listen over kemikalier med prioriteret indsats. **Miljø og sundhed** - En screening af 16 "nye" bromerede flammehæmmere i det nordiske miljø viste, at koncentrationerne af de "nye" bromerede flammehæmmere med få undtagelser var i samme størrelsesorden eller lavere end summen af BDE congenere BDE -28, -47, -99, -100, -153 og -154, som er prioriterede stoffer under EU's vandrammedirektiv.

Af de additive bromerede flammehæmmere med en registreret import eller produktion i EU (dvs. produktion og import er over 100 tons/år) er følgende stoffer ikke medtaget i den seneste screening af bromerede flammehæmmere i de nordiske miljø og ingen data om deres forekomst i de nordiske eller arktiske miljøer er blevet fundet: EBTEBPI, TTBP-TAZ, bis(pentabromphenoxy) benzen (4'-PeBPOBDE208) og TTBNPP. Screeningen af bromerede flammehæmmere i de nordiske miljø fandt også nogle reaktive bromerede flammehæmmere i betydelige koncentrationer: DBP og TBP. Fire af de registrerede reaktive bromerede flammehæmmere er ikke medtaget i screeningen: DBNPG, HEEHP-TEBP og TEBP-Anh, halogeneret polyetherpolyol B og tetrabromphthalsyreanhydrid-baseret diol.

Flere af de "nye" bromerede flammehæmmere er ikke blevet undersøgt i detaljer, men de ikke-polymere bromerede flammehæmmere formodes at have nogle af de samme virkninger som de mere velundersøgte bromerede flammehæmmere. En af disse er HBB, som formentlig er mere persistent og giftigt end PBDE.

Da de toksikologiske mekanismer af de forskellige bromerede flammehæmmere synes at være relaterede, kan blandinger af bromerede flammehæmmere have additive og synergistiske virkninger.

Alternativer - Alternativerne til andre bromerede flammehæmmere er ikke-halogenerede flammehæmmere og alternative materialer uden flammehæmmere. De tilgængelige vurderinger af alternativer omfatter ikke en vurdering af nedbrydningsprodukter eller en vurdering af, hvorledes de flammehæmmede materialer opfører sig i forbindelse med brand eller ukontrolleret afbrænding. Tilstedeværelsen af bromerede flammehæmmere har vist sig at have en negativ indflydelse på f.eks. dannelsen af røg, og under termisk stress kan de resultere i dannelse af farlige stoffer. De fleste undersøgelser har dog behandlet PBDE og andre bromerede flammehæmmere med høj risiko for dannelse af farlige stoffer, men ikke eksempelvis de polymere bromerede flammehæmmere. Betydningen af dannelse af farlige stoffer og røg i et livscyklus-perspektiv synes at være det vigtigste spørgsmål, når man sammenligner virkningen af ikke-regulerede bromerede flammehæmmere med ikke-halogenerede flammehæmmere, men detaljerede vurderinger er endnu ikke tilgængelige. Data om virkningen af ikke-halogenerede flammehæmmere på dannelsen af røg og farlige stoffer er begrænset, og sammenlignende vurderinger af forskellige typer af bromerede flammehæmmere og ikke-halogenerede flammehæmmere på disse parametre mangler.

Forfatterne til en nylig sammenfatning om persistens, bioakkumulation og giftighed af ikke-halogenerede flammehæmmere, som er et af resultaterne af det EU-finansierede ENFIRO projekt, konkluderer, at der var store datamangler for fysisk-kemiske egenskaber og PBT-egenskaber for de

ikke-halogenerede flammehæmmere. For at kunne vurdere, om de ikke-halogenerede flammehæmmere er egnede alternativer, skal hvert stof undersøges enkeltvis ved at sammenligne stoffets PBT-egenskaber med egenskaberne af de tilsvarende halogenerede flammehæmmere. Indtil flere data foreligger, er det fortsat umuligt præcist at vurdere risikoen af hver af disse forbindelser, også de som allerede markedsføres intensivt.

Miljømærkekriterier

De nordiske miljømærkekriterier for en bred vifte af produktgrupper udelukker brugen af nogle eller alle bromerede flammehæmmere i miljømærkede produkter. De nøjagtige kriterier varierer fra produktgruppe til produktgruppe. I nogle produktgrupper er det kun bromerede flammehæmmere, der er tildelt særlige risiko-sætninger (f.eks. sætninger der vedrørende CMR-egenskaber ⁴), der ikke må anvendes. I andre er det angivet, at visse flammehæmmere ikke må være til stede: Enten alle flammehæmmere, alle halogenerede flammehæmmere eller alle halogenerede organiske flammehæmmere. I mange af kriterierne for elektrisk og elektronisk udstyr er der undtagelser for reaktivt anvendte bromerede flammehæmmere og flammehæmmere i plastdele på mindre end 25 g.

EU miljømærkekriterierne omfatter generelt ikke brugen af reaktive flammehæmmere. Kriterierne for forskelligt elektrisk og elektronisk udstyr udelukker brugen af additive flammehæmmere, der opfylder kriterierne for klassificering i bestemte fareklasser. I praksis vedrører restriktionerne i de fleste af kriterierne - ud over de generelle EU begrænsninger af PBDE og PBB - hovedsagelig additiv brug af TBBPA og brugen af HBCDD. Kriterierne for madrasser, gulvbelægning, tekstilvarer og møbler udelukker enhver brug af additive flammehæmmere i artiklerne.

Affaldshåndtering

Bortskaffelse af affald indeholdende bromerede flammehæmmere - Affald af elektrisk og elektronisk udstyr (WEEE) repræsenterer den største affaldsfraktion indeholdende bromerede flammehæmmere. Andre større affaldsfraktioner er isoleringsmaterialer fra byggeri (EPS/XPS og PU skum) og affald fra ophugning af køretøjer. Bromerede flammehæmmere i tekstiler, møbler, maling osv. vil udgøre en lille del i Danmark, men kan være mere betydelige i andre EU medlemsstater. WEEE-direktivet kræver, at plast, der indeholder bromerede flammehæmmere, bør fjernes fra det indsamlede WEEE til selektiv behandling. Den danske bekendtgørelse kræver endvidere, at det fjernede plast indeholdende bromerede flammehæmmere skal afleveres til virksomheder, der er godkendt til at håndtere brom-holdigt affald. I Danmark bliver plast indeholdende bromerede flammehæmmere fra WEEE bortskaffet til almindelig affaldsforbrænding. Det samme er situationen for plast indeholdende bromerede flammehæmmere fra byggesektoren og tekstiler og møbler. Plast fra fragmentering af køretøjer, bortskaffes på kontrolleret losseplads.

En del udtjente elektriske og elektroniske produkter i nogle EU lande synes stadig at blive håndteret ukontrolleret i lande uden for EU, enten ved ulovlig eksport af WEEE, eller fordi det eksporteres som brugt udstyr til genbrug i udviklingslande. Den endelige bortskaffelse af plast indeholdende bromerede flammehæmmere (eventuelt efter genbrug) er i alle tilfælde uanset formålet med eksporten formentlig ukontrolleret afbrænding eller ukontrolleret deponering på fyldpladser.

Bromerede flammehæmmere, som er POP-stoffer - Særlige bestemmelser for affald, der indeholder POP-stoffer, er fastsat i Kommissionsforordning (EU) nr. 756/2010 om ændring af POP-forordningen. For hexaBB er der fastsat en grænseværdi for særlige bortskaffelsesforanstaltninger på 50 mg/kg, men det har ingen praktisk betydning for Danmark, da hexabromophenyl sandsynligvis ikke er til stede i affaldet. Der er endnu ikke blevet fastsat koncentrationsgrænser for de fire PBDE'er. Afhængigt af hvilke grænser, der fastsættes af EU-kommissionen, kan separat indsamling og behandling af visse affaldsfraktioner blive nødvendig.

⁴ CMR = carcinogene, mutagene eller reproduktionstoksiske

Forbrænding og ukontrolleret afbrænding - En af de vigtigste bekymringer i relation til forbrænding af plast indeholdende bromerede flammehæmmere har været risikoen for dannelse af bromerede og blandede bromerede/chlorede dioxiner og furaner. De foreliggende data viser, at destruktionseffektiviteten for bromerede flammehæmmere i forbrændingsanlæg til husholdningsaffald i nordiske lande generelt er bedre end 99,999%. Endvidere er det vist, at forbrænding af bromerede flammehæmmere kan bidrage med en mindre del af de samlede dannede dioxiner og furaner, og at filtre til kontrol af emissioner af chlorede dioxiner og furaner også er effektive til at fange de bromerede og blandede bromerede/chlorede dioxiner og furaner.

Mens emissionen fra forbrændingsanlæg med moderne røggasrensning ser ud til at være lille, er der meget litteratur der indikerer, at emissioner af dioxiner og furaner fra brande (herunder utilsigtede lossepladsbrande) og ukontrolleret afbrænding af plast indeholdende bromerede flammehæmmere kan være betydelig.

Anvendelse af slam på landbrugsjord - Størstedelen af bromerede flammehæmmere i spildevandet ender i slamfraktionen i rensningsanlæg. DecaBDE, HBCDD og DBDPE er de dominerende bromerede flammehæmmere i kommunalt spildevandsslam. De tilgængelige data viser, at niveauet af decaBDE og HCBDD i spildevandsslam i Storbritannien og Irland er ca. en faktor 10 højere end i andre EU-medlemsstater, hvilket indikerer en sammenhæng med den udbredte brug af disse stoffer i tekstiler og møbler i to lande. Nylige analyser af 16 "nye" bromerede flammehæmmere i slam fra rensningsanlæg i de nordiske lande viser, at koncentrationen af DBDPE er i samme størrelsesorden som koncentrationerne af decaBDE og HBCDD fundet i andre undersøgelser, mens koncentrationerne af de resterende 15 bromerede flammehæmmere er betydeligt lavere. Resultaterne bekræfter, at DBDPE i vid udstrækning har erstattet decaBDE i anvendelser, der kan føre til udslip til spildevand.

En risikovurdering fra 2012 om anvendelsen af slam indeholdende bromerede flammehæmmere på landbrugsjord i Danmark, som indeholdt en detaljeret vurdering af decaBDE og TBBPA, konkluderede, at det var meget usandsynligt, at niveauet af bromerede flammehæmmere i dansk slam udgør en væsentlig risiko for de jordlevende organismer og jordens kvalitet i almindelighed, hvis de aktuelle retningslinjer for anvendelse af spildevandsslam følges.

Vigtigste datamangler

Detaljerede data om brugen af andre bromerede flammehæmmere end PBDE, HBCDD og TBBPA globalt og i EU er ikke tilgængelige i den offentlige litteratur. Den offentlige del af REACH registreringer giver som nævnt en vis indikation af produktion og import i EU mængdeintervaller, men polymere bromerede flammehæmmere er ikke underlagt registrering, og der er ingen tilgængelige oplysninger om de markedsførte mængder af disse stoffer. Forbruget af nogle af de andre bromerede flammehæmmere end de gamle kendte forventes at være stigende, men manglen på data begrænser en vurdering af tendenserne i forbruget af bromerede flammehæmmere og overvågning af virkningerne af regulatoriske indgreb. Manglen på detaljerede data om forbruget af de bromerede flammehæmmere på anvendelsesområder begrænser desuden en vurdering af de potentielle udslip og eksponering af mennesker og miljø.

Data om stoffernes skæbne, eksponering samt miljø-og sundhedsmæssige effekter for de fleste "endpoints" mangler for næsten alle bromerede flammehæmmere.

Viden om den faktiske skæbne af WEEE, som eksporteres til behandling uden for Danmark, er begrænset.

Der er ikke fundet data om den faktiske genanvendelse af affald indeholdende bromerede flammehæmmere i Danmark eller EU.

Betydningen af de forskellige bromerede flammehæmmere på dannelsen af bromerede og blandede bromerede/chlorede dioxiner og furaner ved forskellige typer af termiske processer er ikke kendt for de fleste bromerede flammehæmmere.

1. Introduction to the substance group

1.1 Definition of the substance group

Flame retardants are added to polymeric materials, both natural and synthetic, to enhance the flame-retardancy properties of the polymers.

The flame retardants may be divided into several families. The grouping varies, but often the flame retardants are divided into five main families of flame-retardant chemicals:

- Inorganic flame retardants including aluminium trioxide, magnesium hydroxide, ammonium polyphosphate, and red phosphorus. This family represents about 50% of the total market volume.
- Brominated flame retardants (BFRs). The group is sometimes considered to include only the organic brominated flame retardants, but the inorganic flame retardant ammonium bromide is included in this survey.
- Chlorinated flame retardants.
- Organophosphorous flame retardants. The most important organophosphorous flame retardants are phosphate esters. Organophosphorous flame retardants with bromine content are considered to be included in the group of brominated flame retardants in this survey. The non-halogenated phosphorous-based organic and inorganic flame retardants are sometimes considered together because they represent a specific market segment.
- Nitrogen-based organic flame retardants.

According to the major manufacturers of BFRs, more than 30 bromine compounds are in use today, although only a few are used in large amounts (EBFRIP, 2011). Appendix 3 lists 30 CAS numbers of BFRs, and 8 BFRs with proprietary CAS numbers (non-disclosed CAS numbers), manufactured and marketed by the major global manufacturers of flame retardants.

Over time more than 70 different BFRs have been marketed. Several of the BFRs are banned today, but may still be present in products in use in society or in the environment.

A gross list of BFRs has been populated on the basis of:

- A list of BFRs marketed by major manufacturers shown in Appendix 3.
- BFRs evaluated by the European Food Safety Authority (EFSA). EFSA has in recent years published a number of assessments reports addressing BFRs.
- A review paper suggesting a novel abbreviation standard for organobromine (and other) flame retardants (Bergman *et al.*, 2012a);
- A substance flow analysis of BFRs in Denmark from 1999 which identified 14 BFRs used for production processes in Denmark (Lassen *et al.*, 1999);

- A survey of brominated flame retardants in the Nordic environment (Schlabach *et al.*, 2011).

For all substances in the gross list it has been checked if they are pre-registered or registered under REACH. For substances imported or manufactured in the 100-1000 t/y range the deadline for registration was 1 June 2013. The registered volume is based on the update of the registration database of 13 June 2013.

The BFRs from the gross list has been divided into two tables.

Table 1 includes a list of 69 identified BFRs, which have been pre-registered under REACH and/or are produced by the major manufacturers of BFRs. Some of the proprietary BFRs (with non-disclosed CAS Number) may in fact consist of the same substances (the total number would consequently be less than 69) and HBCDD is represented by two CAS numbers, so the total may actually be about 65 BFRs.

The manufacturing and use of the BFRs are further described in chapter 0, but the registered tonnages are indicated in Table 1 with the aim of prioritization of the substances for the survey. The substances are either registered by an individual or a joint submission. In the case of a joint submission, the indicated tonnage band is the total of all manufactured and/or imported volumes. The registration of HBCDD is, for instance, a joint submission by 7 companies with a total registered tonnage of 10,000-100,000 t/y. In some cases the substances are registered by more than one individual submission; in these instances, each of the individual tonnage bands are indicated, i.e. the total registered tonnage is the sum of the individual submissions.

The present study concerns all BFRs, but in some chapters more focus is put on the substances manufactured in larger volumes and, therefore, currently of greater concern. For some of the manufactured BFRs the CAS numbers are indicated as proprietary (not disclosed) and it has not been possible to identify these substances in the REACH databases. Furthermore, some of the polymeric flame retardants are polymers and, as such, are not subject to pre-registration and registration under REACH. For at least one CAS number, the substance has been introduced after the pre-registration deadline and is consequently not included in the database of pre-registered substances (and still not registered).

The abbreviations used in this report are in accordance with a novel abbreviation standard for organobromine (and other) flame retardants suggested by Bergman *et al.* (2012a). The abbreviations used are the so-called practical abbreviations (PRAB). The International Organizing Committee for the bi-annual international symposia for BFRs recommends that authors follow this abbreviation system in order to facilitate communication and minimize confusion. In all tables derived from the literature, the abbreviations have been changed to be consistent throughout the report. Original abbreviations from the cited literature are listed together with the abbreviations used in this report in Appendix 2, which includes chemical and physical properties of the substances.

Appendix 2 also indicates the common names for the substances, which are generally used in this report. The substance names indicated in Table 1 are the names as they appear in pre-registrations and registrations.

TABLE 1
IDENTIFIED BFRS WHICH ARE EITHER PRE-REGISTERED AND/OR PRODUCED BY MAJOR MANUFACTURERS WITH
INDICATION OF REGISTERED TONNAGE (AS UPDATED BY ECHA 26 JULY 2013)

CAS No	EC No	Substance name *1	Abb. *4	R/A *5	Registered, tonnage band, t/y *2 Preregistered	Supplied by major manufacturers *3	Evaluated by EFSA
1163-19-5	214-604-9	Bis(pentabromophenyl) ether	decaBDE	A	10,000 - 100,000	x	EFSA, 2011b
118-79-6	204-278-6	2,4,6-Tribromophenol	TBP	A/R	1,000 - 10,000	x	EFSA, 2012b
126-72-7	204-799-9	tris(2,3-dibromopropyl) phosphate	TDBPP	A	-		EFSA, 2012a
135229-48-0	*603-911-7	Pratherm EC 20 (as indicated in the preregistration)	-	A	-	x	
13654-09-6	237-137-2	Decabromo-1,1'-biphenyl	DecaBB	A	-	-	EFSA, 2010
148993-99-1		Polydibromo-styrene copolymer	-	A	Not pre-registered (polymer)	x	
155613-93-7	*605-018-8	1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-, octabromo deriv.	OBTMPI	A	-	-	EFSA, 2012a
158725-44-1	500-399-6	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol, oligomeric reaction products with 1-chloro-2,3-epoxypropane and 2,4,6-tribromophenol	-	A	-	x	-
183658-27-7	-	2-ethylhexyl-2,3,4,5-tetrabromobenzoate	EH-TBB	A	Not preregistered	x	
19186-97-1	606-254-4	Tri[3-bromo-2,2-bis(bromomethyl)propyl]phosphate.	TTBNPP	A	100 - 1,000 1-10	x	-
20566-35-2	243-885-0	2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	HEEHP-TEBP	A	100 - 1,000	x	EFSA, 2012a
21850-44-2	244-617-5	1,1'-(Isopropylidene) bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene]	TBBPA-BDBPE	R	100 - 1,000	x	EFSA, 2011c
23488-38-2	245-688-5	2,3,5,6-Tetrabromo-p-xylene	TBX	A	-	-	EFSA, 2012a
25327-89-3	246-850-8	1,1'-Isopropylidenebis[4-(allyloxy)-3,5-dibromobenzene]	TBBPA-bAE	A/R	-	x	EFSA, 2011c

CAS No	EC No	Substance name *1	Abb. *4	R/A *5	Registered, tonnage band, t/y *2 Preregistered	Supplied by major manufacturers *3	Evaluated by EFSA
25637-99-4	247-148-4	1,2,5,6,9,10-Hexabromocyclododecane	HBCDD	A	10,000 - 100,000	x Mainly indicated as CAS No 3194-55-6	EFSA, 2011a
25713-60-4	*607-784-9	1,3,5-Triazine, 2,4,6-tris(2,4,6-tribromophenoxy)-	TTBP-TAZ	A	1,000 - 10,000	x	EFSA, 2012a
26040-51-7	247-426-5	Bis(2-ethylhexyl) tetrabromophthalate	BEH-TEBP	A	100 - 1,000	x	EFSA, 2012a
3072-84-2	221-346-0	2,2'-[(1-Methylethylidene)bis[(2,6-dibromo-4,1-phenylene)oxymethylene]]bisoxirane	TBBPA-BGE	R	-	x	EFSA, 2011c
31780-26-4	250-802-1	Dibromostyrene	DBS	A/R	-	-	EFSA, 2012a
3194-55-6	221-695-9	1,2,5,6,9,10-Hexabromocyclododecane	HBCDD	A	Preregistered – HBCDD registered under CAS No 25637-99-4	x	EFSA, 2011a
32534-81-9	251-084-2	Diphenyl ether, pentabromo derivative	pentaBDE	A	-	-	EFSA, 2011b
32536-52-0	251-087-9	Diphenyl ether, octabromo derivative	octaBDE	A	-	-	EFSA, 2011b
32588-76-4	251-118-6	N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide)	EBTEBPI	A	100 - 1,000	x	EFSA, 2012a
3278-89-5	221-913-2	2-(allyloxy)-1,3,5-tribromobenzene	TBP-AE	A/R	-	x	EFSA, 2012b
3296-90-0	221-967-7	2,2-bis(bromomethyl)propane-1,3-diol	DBNPG	R	100 - 1,000	x	EFSA, 2012a
3322-93-8	222-036-8	1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane	DBE-DBCH	A	-	-	EFSA, 2012a
33798-02-6	251-681-8	4,4'-isopropylidenebis[2,6-dibromophenyl] diacetate	TBBPA-bOAc	A	-	-	EFSA, 2011c

CAS No	EC No	Substance name *1	Abb. *4	R/A *5	Registered, tonnage band, t/y *2 Preregistered	Supplied by major manufacturers *3	Evaluated by EFSA
34571-16-9	252-097-6	1,2,3,4,7,7-Hexachloro-5-(tetrabromophenyl)bicyclo[2.2.1]hept-2-ene	HCTBPH	A	-	-	EFSA, 2012a
35109-60-5	252-372-0	1,3,5-tribromo-2-(2,3-dibromopropoxy)benzene	DPTE	A	-	-	EFSA, 2012b
3555-11-1	222-610-8	Allyl pentabromophenyl ether)	PBPAAE	A/R	-	-	EFSA, 2012b
36355-01-8	252-994-2	Hexabromo-1,1'-biphenyl	HexaBB	A	-	-	EFSA, 2010
36483-57-5	253-057-0	2,2-dimethylpropan-1-ol, tribromo derivative	TBNPA	R	Tonnage Data Confidential Intermediate Use Only	x	-
37853-59-1	253-692-3	1,1'-[ethane-1,2-diylbisoxy]bis[2,4,6-tribromobenzene]	BTBPE	A	-	x	EFSA, 2012a
37853-61-5	253-693-9	Benzene, 1,1'-(1-methylethylidene) bis[3,5-dibromo-4-methoxy	TBBPA-BME	R	-	-	-
39569-21-6	254-522-0	Benzene, 1,2,3,4-tetrabromo-5-chloro-6-methyl	TBCT	A	-	-	-
39635-79-5	254-551-9	4,4'-sulphonylbis[2,6-dibromophenol]	TBBPS	A/R	-	-	EFSA, 2012b
4162-45-2	224-005-4	4,4'-isopropylidenebis(2-(2,6-dibromophenoxy)ethanol)	TBBPA-BHEE	A/R	-	-	EFSA, 2011c
42757-55-1	255-929-6	bis[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl] sulphone	TBBPS-BDBPE	A	-	-	EFSA, 2012b
51936-55-1	257-526-0	7,8-Dibromo-1,2,3,4,11,11-hexachloro-1,4,4a,5,6,7,8,9,10,10a-decahydro-1,4-methanobenzocyclooctene	DBHCTD	A	-	-	EFSA, 2012a
52434-90-9	257-913-4	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	TDBP-TAZTO	A	-	-	EFSA, 2012a

CAS No	EC No	Substance name *1	Abb. *4	R/A *5	Registered, tonnage band, t/y *2 Preregistered	Supplied by major manufacturers *3	Evaluated by EFSA
58965-66-5	261-526-6	1,2,4,5-tetrabromo-3,6-Bis(pentabromophenoxy) benzene	4'-PeBPOB-DE208	A	-	-	EFSA, 2012a
59447-55-1	261-767-7	(Pentabromophenyl)methyl acrylate	PBB-Acr	R	100 - 1,000	x	EFSA, 2012a
59447-57-3	-	Poly (pentabromobenzyl) acrylate	-	R	not preregistered	x	
615-58-7	210-436-5	2,4-dibromophenol	DBP	A/R	-	-	EFSA, 2012b
608-71-9	210-167-3	Pentabromophenol	PBP	A/R	-	-	EFSA, 2012b
632-79-1	211-185-4	Tetrabromophthalic anhydride	TEBP-Anh	R	100 - 1,000	x	-
66710-97-2	266-455-4	2-Propenoic acid, 1,1'[(1-methylethylidene)bis[(2,6-dibromo-4,1phenylene)oxy-2,1-ethanediyl]] ester	TBBPA-BHEEBA	R	-	-	-
68441-62-3	614-503-3	2-butyne-1,4-diol, polymer with 2-(chloromethyl)oxirane, brominated, dehydrochlorinated, methoxylated	-	R	1,000 - 10,000	x	-
68928-70-1	*614-817-0	Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with 2,2'-[(1-methylethylidene)bis[(2,6-dibromo-4,1-phenylene)oxymethylene]]bis[oxirane]	-	A	-	x	-
71342-77-3	*615-282-6	Carbonic dichloride, polymer with 4,4'-(1-methylethylidene)bis[2,6-dibromophenol], bis(2,4,6-tribromophenyl) ester	RDT-7	A	-	x	-
79-94-7	201-236-9	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol	TBBPA	A/R	1,000 - 10,000	x	EFSA, 2011c

CAS No	EC No	Substance name *1	Abb. *4	R/A *5	Registered, tonnage band, t/y *2 Preregistered	Supplied by major manufacturers *3	Evaluated by EFSA
84852-53-9	284-366-9	1,1'-(Ethane-1,2-diyl)bis[pentabromobenzene]	DBDPE	A	1,000 +	x	EFSA, 2012a
85-22-3	201-593-0	2,3,4,5,6-Pentabromoethylbenzene	PBEB	A	-		EFSA, 2012a
87-82-1	201-773-9	Hexabromobenzene	HBB	A	-		EFSA, 2012a
87-83-2	201-774-4	2,3,4,5,6-Pentabromotoluene	PBT	A/R	-		EFSA, 2012a
88497-56-7	*618-171-0	Benzene, ethenyl-, homopolymer, brominated [Brominated Polystyrene]	-	A	-	x	-
94334-64-2	*619-012-8	Carbonic dichloride, polymer with 4,4'-(1-methylethylidene)bis[2,6-dibromophenol] and phenol	-	A	-	x	-
1195978-93-8	-	Benzene, ethenyl-, polymer with 1,3-butadiene, brominated	-	A	Not identified in preregistration database (polymer)	x	
Proprietary		Physical blend of brominated polystyrene and a polyester resin	-	A	Not identified in preregistration database	x	
Proprietary		Reactive diol blend	-	R	"-"	x	
Proprietary		Aromatic reactive diol	-	R	"-"	x	
Proprietary		Brominated polymer	-	A	"-"	x	
Proprietary		Tetrabromophthalic Anhydride Based Diol	-	R	"-"	x	
Proprietary		Phosphorus-Bromine Flame Retardant	-	?	"-"	x	
Proprietary		Phosphorus-Bromine Flame Retardant	-	?	"-"	x	

* Substances without an EC number – the number is a list number applied for the pre-registration.

*1 Chemical name according to pre-registration/registration.

*2 Substances registered with ECHA: The database on registered substances includes as of June 2013:

- substances manufactured or imported at 100 tonnes or more per year,
- carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year.

Substances which are pre-registered but not registered are indicated by a "-"

*3 Identified at web-sites of major manufacturers March 2012. Substances and products listed in Appendix 3.

*4 Practical abbreviations, PRABs (Bergman *et al.*, 2012a).

*5 R: reactive, A: additive; see main text for description for additive vs. reactive use of BFRs. Source: Bergman *et al.* (2012) – for substances not included in this review paper information is searched in the technical literature.

Substances from the gross list, which are not pre-registered or produced by the major manufacturers, are included in Table 2. The substances are listed separately as most of the substances are probably not currently manufactured or imported into the EU, but are rather manufactured outside the EU (not by the major global manufacturers).

One of the substances in Table 2 has been demonstrated to be present in the environment in a survey of brominated flame retardants in the Nordic environment (Schlabach *et al.*, 2011): TBA (CAS No. 607-99-8).

TABLE 2
IDENTIFIED BROMINATED FLAME RETARDANTS WHICH ARE NOT PRE-REGISTERED OR SUPPLIED BY MAJOR MANUFACTURERS

CAS No	EC No	Substance name *1	Abb.	Evaluated by EFSA	Source
1084889-51-9 1025956-65-3 893843-07-7	-	Octabromotrimethyl-phenyl indane	OBTMPI	x	EFSA, 2012a
1522-92-5	-	Tribromoneopentyl alcohol [same substance as CAS No 36483-57-5]	TBNPA	x	EFSA, 2012a
168434-45-5	-	Phenol, 2,4,6-tribromo3-(tetrabromopentadecyl)	TBPD-TBP	x	EFSA, 2012b
25495-98-1	-	Hexabromocyclodecane	HBCYD	x	EFSA, 2012a
3194-57-8	-	Cyclooctane, 1,2,5,6-tetrabromo	TBCO	-	Bergman <i>et al.</i> , 2012a
37419-42-4	-	Phenol, 4,4'-(1-methylethylidene)bis[2,6dibromo-, dipropionate (9CI)	TBBPA-BP	-	Bergman <i>et al.</i> , 2012a
38521-51-6	253-985-6	Benzene, 1,2,3,4,5-pentabromo6-(bromomethyl)	PBBB	-	Bergman <i>et al.</i> , 2012a
497107-13-8	-	Benzene, 1,1'-[oxybis(methylene)]bis[2,3,4,5,6-pentabromo(9CI)	DBDBE	-	Bergman <i>et al.</i> , 2012a
55205-38-4	-	2-Propenoic acid, 1,1'-[(1-methylethylidene) bis(2,6-dibromo-4,1-phenylene)] ester	TBBPA-BA	-	Bergman <i>et al.</i> , 2012a

CAS No	EC No	Substance name *1	Abb.	Evaluated by EFSA	Source
57829-89-7	-	1-(2,3-Dibromopropyl)-3,5-diallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	DBP-TAZTO	x	EFSA, 2012a
58495-09-3	-	Benzene, 1,2,3,4,5-pentabromo6-(chloromethyl)	PBBC	-	Bergman <i>et al.</i> , 2012a
607-99-8	-	2,4,6,-tribromoanisol	TBA	-	Bergman <i>et al.</i> , 2012a
70156-79-5	-	Benzene, 1,1'-sulfonylbis[3,5-dibromo-4-methoxy	TBPPS-BME	x	EFSA, 2012b
75795-16-3	-	1,3-Bis(2,3-dibromopropyl)-5-allyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	BDBP-TAZTO	x	EFSA, 2012a

The brominated flame retardants, as defined in this survey, can be divided into five classes:

- Aromatic BFRs (with a double carbon ring structure), such as tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs): the largest group of BFRs;
- Cycloaliphatic BFRs (with a single carbon ring structure), primarily hexabromocyclododecane (HBCDD);
- Aliphatic BFRs (with carbon chains without ring structures), a few flame retardants which are used in relatively small quantities;
- Polymeric BFRs (with repeating carbon units) such as brominated polystyrene;
- Inorganic BFRs (without carbon), includes ammonium bromide only.

In some contexts only the three first classes are considered to be included in the group of brominated flame retardants.

Most common BFRs

The most common BFRs are decabromodiphenyl ether (decaBDE), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD), according to information from the major manufacturers, and confirmed by the registered volumes (EBFRIP, 2011). DecaBDE and HBCDD are both registered with a total production + import in the 10,000 - 100,000 t/y range, while TBBPA are registered in the 1,000 - 10,000 t/y range.

Besides these substances, four BFRs are registered with a production + import of more than 1,000 t/y:

- 1,1'-(Ethane-1,2-diyl)bis[pentabromobenzene (DBDPE, additive BFR);
- 1,3,5-Triazine, 2,4,6-tris(2,4,6-tribromophenoxy) (TTBP-TAZ, additive BFR);
- 2,4,6-Tribromophenol (TBP, reactive BFR);
- 2-butyne-1,4-diol, polymer with 2-(chloromethyl)oxirane, brominated, dehydrochlorinated, methoxylated (halogenated polyetherpolyol B, reactive BFR).

Focus of the survey

LOUS 2009 includes “Certain brominated flame retardants “ with three examples from the group: Decabromodiphenyl ether (decaBDE), additive use of tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD). These are also the BFRs currently used in the highest quantities and some of the BFRs which are given most attention as concerns possible legislative actions. Some alternatives to decaBDE, primarily DBDPE, have drawn some attention as well as upcoming high-volume BFRs. Within the limits of this survey, a decision was made to describe the environmental and health properties of these substances in more detail and focus the assessment of alternatives on alternatives to these substances. The additive FR TTBP-TAZ with a registered volume in the 1,000 - 10,000 t/y range was not indicated as registered at ECHA's website until the update of 26 July 2013, and was not included in the list of substances with particular focus, as the review of environmental and health hazards were finalized at that time.

For the other BFRs, available information on their use and presence in environment as well as potential human exposure is briefly reviewed in order to identify upcoming issues and major data gaps.

PBDEs and PBBs

Historically, the polybrominated diphenyl ethers or PBDEs, together with TBBPA and its derivatives, have been the main groups of BFRs. The polybrominated diphenyl ethers (PBDEs) with three to ten bromine atoms were used in commercial additive flame retardants.

Three different PBDEs were commercially available, but the commercial products were not pure substances. They were referred to as commercial penta-, octa- and decabromodiphenyl ether, but each product was a mixture of brominated diphenyl ethers. The commercial products are often abbreviated c-pentaBDE, c-octaBDE and c-decaBDE. The exact composition of the commercial products varied and according to the EU Risk Assessment Report for decaBDE "*The actual composition of the products from different producers/suppliers is regarded as confidential information*" (ECB, 2002). In 1995, the producers in the USA and Europe committed themselves to producing c-deca-BDE with an average purity of 97% or better (Lassen *et al.*, 2006). Typical contents, as reported in the EU Risk Assessment for decaBDE, are shown in Table 3.

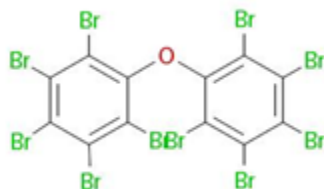
TABLE 3
TYPICAL COMPOSITION OF COMMERCIAL PBDES (BASED ON ECB, 2002)

Component	Number of bromine atoms	Commercial product, % by weight		
		c-pentaBDE *1	c-octaBDE *2	c-decaBDE *2
Tribromodiphenylethers	3	0.2		
Tetrabromodiphenylethers	4	36.0		
Pentabromodiphenylethers	5	55.1		
Hexabromodiphenylethers	6	8.6	5.5	
Heptabromodiphenylethers	7		42.3	
Octabromodiphenylethers	8		36.1	
Nonabromodiphenylethers	9		13.9	2.5
Decabromodiphenylethers	10		2.1	97.4
Total		99.9	99.9	99.9

*1 Data from 2000; *2: data from 1997.

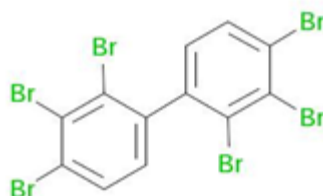
Today, mainly c-decaBDE is in commercial use. The production of pentaBDE and octaBDE has ceased by the major global manufacturers of brominated flame retardants (see Section 3.1.3), but the substances may still be produced by minor producers (e.g. in China) or present in products in use in society, or in recycled materials. Some import of pentaBDE into the EU is reported in statistics, and information on the use of octaBDE in Denmark has been obtained (see Chapter 3).

The PBDEs consist of many different congeners, each representing a specific configuration of the bromine atoms on the biphenyl group, and in monitoring they are referred to by a specific congener number e.g. BDE-47. DecaBDE, with only one possible configuration, is referred to as BDE-209.



Decabromodiphenyl ether, *decaBDE*, CAS No 1163-19-5

The manufacturing of brominated biphenyls (PBBs) which have a structure similar to PCBs but with bromine substituting for hydrogen in the biphenyl, have ceased, but the substances may still be present in products used in society. The commercial products of the brominated biphenyls, c-hexaBB and c-decaBB, consisted of a mixture of different PBBs.

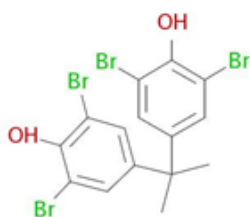


Hexabromobiphenyl, *hexaBB*, CAS No 36355-01-8

The PBBs and PBDEs are the most well described of the substances, and much information on human health and environmental effects as well as monitoring data is available. As the use of penta- and octaBDE is highly restricted today, the description of environmental and health impacts of the PBDEs will, as well as description of alternatives, mainly focus on decaBDE, which is still used. The other substances are described in the context of their presence in the environment, in products in society and in waste streams.

TBBPA and derivatives

Tetrabromobisphenol A (TBBPA) and derivatives are a group of aromatic BFRs in which four hydrogens in the bisphenol structure are replaced by bromine. From a global perspective, TBBPA and derivatives have been the most important group of brominated flame retardants for decades.



Tetrabromobisphenol A, *TBBPA*,
CAS No 79-94-7



Tetrabromobisphenol A bis(allyl ether)
TBBPA-bAE,
CAS No 25327-89-3

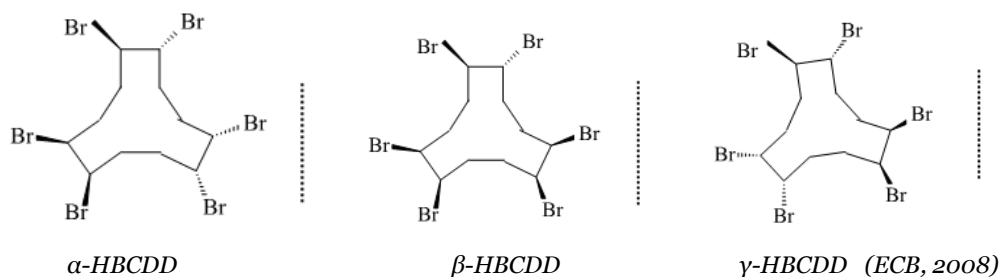
Tetrabromobisphenol A (TBBPA) can be used both as an additive BFR and as a reactive BFR. TBBPA is used as reactive flame retardant in the production of epoxy resins, replacing bisphenol A, partially or totally, in the reaction with epichlorhydrin. When TBBPA is used as a reactive flame retardant, the chemical identity of the compound is lost in the process of polymerisation. This means that TBBPA *per se* is not present in the final product except for a trace content of unreacted TBBPA. TBBPA can be used as an additive flame retardant in acrylonitrile-butadiene-styrene (ABS), polystyrene (PS) and phenolic resin. In this case the substance is present in the polymer and can be released from the surface. As mentioned in the preface, it is stated in the LOUS that only the additive use of TBBPA is included in the list.

Besides TBBPA, a number of BFRs are used reactively, including 2,4,6-tribromophenol (2,4,6-TBP), tetrabromophthalic anhydride and reactive diol blends.

HBCDD

Hexabromocyclododecane, HBCDD, is a cycloaliphatic compound with six bromine atoms and the most common non-aromatic BFR. The bromine atoms can have different configurations, and commercial HBCDD is made up of three “chiral diastereomers” which complicates a risk assessment (ECB, 2008). The three diastereomers, α -, β - and γ -HBCDD, shown in the figure below, are all chiral and exist as pairs of enantiomers in technical HBCDD. After release to the environment, the enantiomers may interact differentially with other chiral molecules in biological systems (ECB, 2008).

The sum of the diastereomers are commonly referred to as Σ HBCDD.

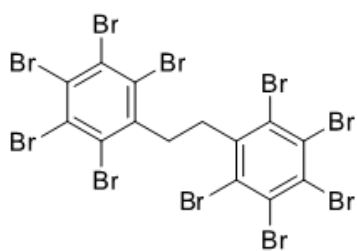


Hexabromocyclododecane, HBCDD, CAS 25637-99-4, the line indicates the mirror plane

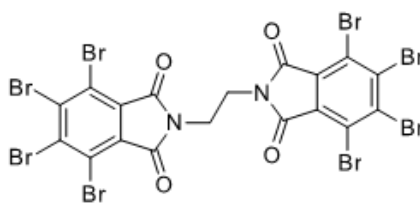
Stereomerism is also an issue for other cycloaliphatic BFRs such as 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (DBE-DBCH).

DecaBDE alternatives

DecaBDE has been replaced to a large extent by other BFRs e.g. in electrical and electronic equipment, and some of the substitutes are themselves of some concern and increasingly included in surveys and studies. Examples are the aromatic BFRs: decabromodiphenyl ethane, (DBDPE), ethylenebis(tetrabromophthalimide) (EBTEBPI) and TBBPA and derivatives. The two first are shown below. As they are alternatives to decaBDE with a nearly similar application profile, the consumption of these substances may increase significantly in the future.

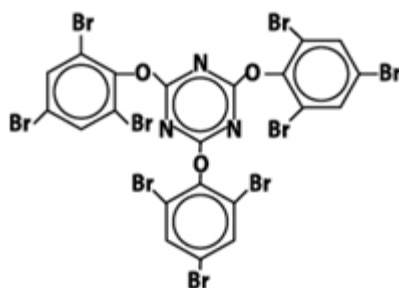


Decabromodiphenyl ethane, DBDPE,
CAS No 84852-53-9



Ethylenebis(tetrabromophthalimide),
EBTEBPI,
CAS No 32588-76-4

2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) is registered in the tonnage band of 1,000-10,000 t/y by one company which represents Asian manufacturers. The substance is indicated to be used in the polymers HIPS and ABS in electronics and may be one of the main alternatives to the regulated octaBDE in ABS, and alternative to decaBDE for HIPS and other polymers. Very limited information on the use of the substance is available.

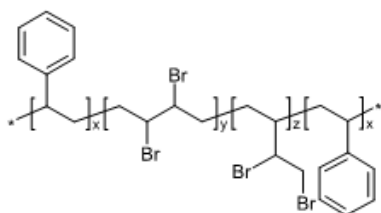


ICL, 2012

1,3,5-Triazine, 2,4,6-tris(2,4,6-tribromophenoxy), TTBP-TAZ, CAS No 25713-60-4

Brominated polymers

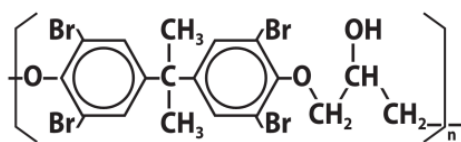
Brominated polymers have been used for certain applications for many years, but have in recent years been increasingly marketed as "green" alternatives to e.g. regulated BFRs. Examples are the proprietary polymeric BFRs GreenArmor™ and GreenCrest™ from the manufacturer Albemarle which are marketed as alternatives to decaBDE and HBCDD, respectively, and the Emerald Innovation™ series from Chemtura. The structure of a recently introduced polymeric alternative to HBCDD, which is manufactured by three of the major manufacturers, is shown below.



US EPA, 2011a

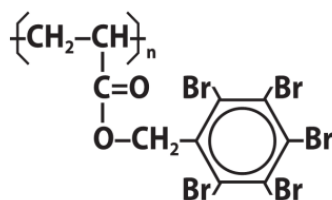
Benzene, ethenyl-, polymer with 1,3-butadiene, brominated
CAS No 1195978-93-8

Other examples of polymeric BFRs are brominated epoxy and brominated polyacrylate, shown below. The brominated epoxy has brominated benzene rings in the backbone, whereas the brominated polyacrylate polymers contain brominated aromatic side chains.



ICL, 2012

Brominated epoxy, CAS No 3072-84-2



ICL, 2012

Brominated polyacrylate, CAS No 59447-57-3

For the assessment of these polymeric substances it may be of importance as to what extent the degradation of the polymers leads to the formation of brominated aromatic compounds.

Antimony trioxide

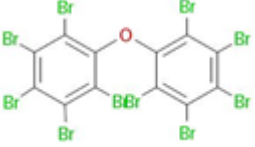
Many of the additive brominated flame retardants are used together with antimony trioxide (Sb_4O_6 , CAS No 1309-64-4) which acts as a synergist (Troitzsch, 2004). Antimony trioxide is classified as carcinogenic according to the CLP Regulation (Carc. 2, H351).

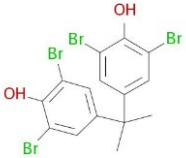
1.2 Physical and chemical properties of selected brominated flame retardants

The names, other identifiers, physical and chemical properties of the three high-volume BFRs are shown in Table 4. A list with selected physical and chemical properties of all BFRs is included in Appendix 3.

The listed properties mainly refer to the registration dossiers available at ECHA's website. The registration dossiers may include different values for the same parameter; in this case, all values are indicated. Please consult the registrations for the original references.

TABLE 4
PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED BROMINATED FLAME RETARDANTS

	Bis(pentabromophenyl) ether	Reference
EC number	214-604-9	Joint submission registration at ECHA's website
CAS number	1163-19-5	-“-
Synonyms	Decabrominated diphenyl ether, decaBDE, 1,1'-oxybis(pentabromobenzene)	-“-
Molecular formula	$\text{C}_{12}\text{Br}_{10}\text{O}$ 	-“-
Physical state	Solid, at 20°C and 1013 hPa	-“-
Melting/freezing point	304 °C, measurement performed at sea level and room temperature	-“-
Boiling point	No data	-“-
Relative density	2.63, at 20 °C	-“-
Vapour pressure	0.00000463 Pa at 21 °C	-“-

Surface tension	No data	-“-
Water solubility (mg/l)	< 0.1 µg/l at 25 °C	-“-
Log P (octanol/water)	6.625 at 25 °C	-“-
Molecular weight range		
	2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol (TBBPA)	Reference
EC number	201-236-9	Joint submission registration at ECHA's website
CAS number	79-94-7	-“-
Synonyms	Tetrabromobisphenol A, TBBPA, TBBP-A, 2,2-Bis(3,5-dibromo-4-hydroxyphenyl)propane, Phenol, 4,4'-(1-methylethylidene) bis[2,6-dibromo	Bergman <i>et al.</i> , 2012
Molecular formula	 $C_{15}H_{12}Br_4O_2$	-“-
Physical state	Solid, at 20 °C and 1013 hPa	-“-
Melting/freezing point	304 °C, measurement performed at sea level and room temperature	-“-
Boiling point	No data	-“-
Relative density	2.17 1.750 kg/l 2.2 kg/l at 4 °C	-“-
Vapour pressure	< 0.0000119 Pa at 20 °C	
Surface tension	no data	-“-
Water solubility (mg/l)	Slightly soluble (0.1-100 mg/l) <= 0.08 mg/l at 20 °C and pH >= 7.6 <= 8.1 0.72 mg/l at 15 °C 4.16 mg/l at 25 °C 1.77 mg/l at 35 °C	-“-
Log P (octanol/water)	5.903 at 25 °C 4.54	-“-
Molecular weight range	543.87	Bergman <i>et al.</i> , 2012
	Hexabromocyclododecane	Reference
EC number	247-148-4; 221-695-9	Joint submission registration at ECHA's website
CAS number	25637-99-4 (mixture of mainly three dia-	-“-

	stereomers) 3194-55-6 (not registered)	
Synonyms	HBCDD, HBCD, cyclododecane, 1,2,5,6,9,10-hexabromo	Bergman <i>et al.</i> , 2012
Molecular formula	C ₁₂ H ₁₈ Br ₆	-“-
Physical state	Solid, at 20°C and 1013 hPa	-“-
Melting/freezing point	185.9 ± 0.04 °C (95% confidence interval). 182.7 °C (results for HBCDD 2) 201 -205 °C (for highest melting version) Melting points of pure isomers of HBCD: HBCDD 1 (γ-isomer) = 208 - 210°C HBCDD 2 (β-isomer) = 169 - 170°C HBCDD 3 (α-isomer) = 171 - 173°C	-“-
Boiling point	No data	-“-
Relative density	2.403 kg/l	-“-
Vapour pressure	6.27 x 10E-5 Pa at 21°C	-“-
Surface tension	No data	-“-
Water solubility (mg/l)	α-HBCDD 48.8±1.9 µg/l β-HBCDD 14.7±0.5 µg/l γ-HBCDD 2.1±0.2 µg/l HBCDD technical product, sum of above, approximately 65 µg/l 3.4 µg/l at 25°C Slightly soluble (0.1-100 mg/l)	-“-
Log P (octanol/water)	5.625 at 25°C The Log Kow of HBCDD is within the range of 5.07-5.47 (α-HBCDD = 5.07 ± 0.09, β-HBCDD = 5.12 ± 0.09, γ-HBCDD = 5.47 ± 0.10) under the conditions of the calculations presented.	-“-
Molecular weight range	641.7	Bergman <i>et al.</i> , 2012

1.3 Function of the substances for main application areas

The brominated flame retardants are used to prevent the ignition of plastic materials and textiles.

A fire starts with an ignition source (for example a match) setting combustible material (for example a piece of plastic) on fire. The fire spreads, heats up the surroundings and once the materials in the room have formed enough flammable gases and are sufficiently hot, flashover takes place. This is the start of the fully developed fire whereby temperatures up to 1,200 °C can be reached. (EFRA, 2013).

Depending on their nature, flame reactants can act chemically and/or physically in the solid, liquid, or gas phases (Troitzsch, 2004). They interfere with combustion during a particular stage of this process, for example during heating, decomposition, ignition, or flame spread (Troitzsch, 2004).

The brominated flame retardants and other halogenated flame retardants (generally chlorinated) act mainly through gas phase mechanisms (Troitzsch, 2004). Due to the release of hydrogen halide during decomposition, halogen compounds act by replacing the highly reactive OH and H radicals by the less reactive halogen radical. By dissipating the energy of the ·OH radicals by trapping, the thermal balance is modified and this strongly reduces the combustion rate. (Troitzsch, 2004)

Brominated flame retardants dehydrogenate polymers by virtue of abstracting hydrogen atoms needed to produce hydrogen bromide. This process enhances charring of the polymer at the expense of volatile combustible products, thus contributing to the flame retardancy of the polymer. (EFRA, 2013)

The overall flame retardancy mechanism of all the halogenated FRs is consequently the same. The choice of halogenated FR depends on the type of polymer to be made flame retardant, for example in relation to the behaviour of the halogenated flame retardant under processing conditions (stability, melting, distribution). (Troitzsch, 2004)

In the series of aliphatic, cycloaliphatic, and aromatic halogen compounds, the strength of the bond between the halogen and the basic structure of the molecule increases, which means that the temperature stability also rises, but that the flame retardancy effectiveness may decrease. Polybrominated diphenyl ethers (for instance decaBDE), being aromatic compounds, have more temperature stability than cycloaliphatic bromine compounds (such as, for instance, hexabromocyclododecane: HBCD), and can therefore be utilized with plastics that must be processed at relatively high temperatures. However, they do require antimony trioxide as a synergist to raise their effectiveness (Leisewitz *et al.*, 2001).

Often the addition of metallic compounds such as zinc or antimony oxides enhance the efficiency of BFRs, by allowing the formation of transition species, “metal oxohalides”, which allow the deposit of a protective layer of metal oxides on the surface of the material. Antimony trioxide Sb_2O_3 does not have flame retardant properties on its own, but is an effective synergist for bromine- and chlorine-based flame retardants. It acts as a catalyst, facilitating the breakdown of these halogenated flame retardants to active free radicals. It also reacts with the halogens to produce volatile antimony halogen compounds, which are themselves directly effective in removing the high energy H· and OH· radicals that feed the gas phase of the fire, thus strengthening the flame-suppressing effect of the flame retardants. (EFRA, 2013; Troitzsch, 2004).

The application of the BFRs, loading in different plastic types, etc. is further described in section 3.3.1

2. Regulatory framework

This chapter gives an overview of how BFRs are addressed in existing and upcoming EU and Danish legislation, international agreements and by EU and Nordic eco-label criteria.

In Appendix 1, a brief overview of legal instruments in the EU and DK and how they are related is presented. The appendix also gives a brief introduction to the chemicals legislation, explains the lists referred to in section 2.1.2 on REACG, and provides a brief introduction to international agreements and the EU and Nordic ecolabelling schemes.

2.1 Legislation

This section will first list existing legislation addressing BFRs and then give an overview of on-going activities, focusing on which substances are in the pipeline in relation to various REACH provisions.

2.1.1 Existing legislation

Table 5 provides an overview of existing legislation addressing BFRs. For each area of legislation, the table first lists the EU legislation (if applicable) and then (as concerns directives) existing transposition into Danish law and/or other national rules. The latter will only be elaborated upon in case of Danish rules differing from EU rules.

In Denmark, the Danish EPA published an action plan for brominated flame retardants in 2001 (Danish EPA, 2001). The target of the action plan was to internationally eliminate the use of PBDEs and PBBs in the short term and to identify and eliminate other problematic BFRs in the longer term. It was stated that BFRs, which can migrate from products, shall not be used if they are persistent, are bioaccumulative and harmful effects on human health or the environment are suspected. Some actions initiated on the basis of the action plan were dissemination of information on BFRs and alternatives, and a number of studies on the feasibility of phasing out selected brominated flame retardants, as well as assessments of human health and environmental effects of alternatives to the BFRs.

The first measures for reducing the emission of BFRs at EU level were introduced in 2003 with the RoHS Directive, restricting PBDEs in electrical and electronic equipment placed on the EU market, and with Directive 2003/11/EC (an amendment to Directive 76/769/EEC), which introduced a general restriction on pentaBDE and octaBDE in concentrations above 0.1%.

Table 5 illustrates that current EU legislation mainly focuses on the PBDEs and PBBs and includes strict restrictions on the use of these substances, a requirement for export notification procedure and listing as possible priority substances under the Water Framework Directive.

HexaBB, tetraBDE, pentaBDE, hexaBDE and heptaBDE, are strictly restricted by the POPs regulation (Regulation (EC) No 850/2004) which is the main implementing instrument of the Stockholm Convention in the EU. The tetraBDE and pentaBDE are main constituents of the commercial pentaBDE, whereas hexaBDE and heptaBDE are some of the constituents of the commercial octaBDE. The exemptions generally allow very low concentrations in substances, preparations and the addressed articles. The European Commission is currently working on setting specific concentration limits in waste for the covered brominated flame retardants and other new substances under the Stockholm Convention.

For PBDEs in electrical and electronic equipment, the restrictions are currently effectively an interplay between the POPs Regulation, the REACH Regulation and the RoHS Directive. The POPs Regulation and the REACH Regulation have an exemption for electrical and electronic equipment within the scope of the RoHS Directive. The RoHS Directive (and the Danish RoHS Statutory Order) applies to articles placed on the EU market, whereas production for export is outside the scope of the Directive and is therefore regulated by the POPs Regulation and the REACH Regulation. This also applies to electrical and electronic parts for a range of applications including large-scale stationary tools and fixed installations, means of transport, photovoltaic panels, and military equipment. For such type of equipment, the decaBDE can still be applied, whereas other PBDEs and PBBs will be restricted by the POPs Regulation and the REACH Regulation. The RoHS Directive includes some exceptions for medical devices and monitoring and control instruments and spare parts (see Table 5 for details). For the excepted equipment and some spare parts octaBDE and pentaBDE may still be used. For this equipment and some spare parts, the EU legislation does not appear to be in accordance with the Stockholm Convention. Contrary to this, the Danish RoHS statutory order do not have a general exemption for medical devices and monitoring and control instruments, but substance/applications specific exemptions for this equipment. PBB and PBDE are not among the substances exempted for use in this equipment in Denmark.

The European Commission has put forward a proposal for a regulation on ship recycling on 23 March 2012 (COM(2012) 188, final). PBBs and PBDEs are included in a list of items for inventory of hazardous substances.

Fire regulations

Fire safety regulations are the driver for using flame retardants to a large extent. The annex XV report for decaBDE (UK, 2012) lists examples of fire regulation in different EU Member States and fire safety standards applicable for various application areas of BFRs.

Fire safety regulations in general do not include any specific requirements for the use of BFRs. The regulations typically define some fire tests which the materials, article or building component should pass, but it is up to the manufacturer/user to decide how the requirements can be met.

A detailed description of fire safety standards in Denmark, Germany and UK is provided in Lassen *et al.* (1999). It has been beyond the scope of this report to provide an updated description of fire regulations and fire standards in Denmark and internationally. Fire tests are performed by DBI - Danish Institute of Fire and Security Technology and other authorities in Denmark. Information on requirements and test methods is available from the institute's website (DBI, 2013).

Fire safety regulation is mentioned here with the scope of identifying potential application areas of the BFRs. Section 3.3.2 discusses the necessary loadings of BFRs in different materials in order to meet the fire safety standards. In Chapter 0 on alternatives, it is discussed to what extent the fire safety requirement can be met by the use of other flame retardants or use of other materials. It is beyond the scope of this report to discuss to what extent the fire safety regulation and standards are able to reduce the risk of fire and reduce the number of fatalities from fires. It is furthermore beyond the scope to discuss to what extent the benefits of using the BFRs is counterbalanced by the environmental and health impacts of the flame retardants. Fire statistics for different Member States and the correlation between number of fire deaths and fire regulation has recently been reviewed in a study for the European Commission, Health and Consumers DG (Arcadis, 2011).

The fire safety standards that are applicable to plastics/polymers will depend on the end-use. Legislation that sets safety goals for goods supplied to the EU market includes the General Product Safety Directive (2001/95/EEC), the Toy Safety Directive (88/378/EEC now replaced by 2009/48/EC), the Radio and Telecommunications Terminal Equipment Directive (1999/5/EC), the Machinery Directive (2006/42/EC) and the Construction Products Directive (89/106/EEC) (UK, 2012). These pieces of legislation do not specify particular levels of fire safety performance within

the legal text but in some cases, e.g. the Construction Products Regulation, very general requirements for fire performance (referred to as “essential requirements”) are described in the legal text. These essential requirements are clarified by reference to harmonised fire performance standards and classifications. (UK, 2012)

For the electrical and electronic equipment and means of transportation, the requirements are to a large extent the same across the EU, but major differences exist as concerns textiles/furniture and building materials, resulting in differences in the use of BFRs among EU Member States.

There are no harmonised fire safety standards within the EU that are applicable to the use of flame retardants in textiles. Instead a patchwork of fire safety requirements has developed with some Member States placing requirements on domestic furniture and some on furniture used in public buildings (UK, 2012). This means that there are differences in the fire performance required for textiles depending on the country to which they are supplied and their intended end use. The most stringent requirements for domestic furniture have been introduced in the UK and in Ireland. This legislation is particularly demanding because it requires the performance of upholstery textiles to be assessed when the textile is placed over untreated foam. This means that in addition to its own fire performance, the textile must provide protection to the filling below.

A compilation of international building regulations relevant for EPS/XPS insulation panels describes the requirements applied in different EU Member States and in other parts of the world. (Blomquist *et al.*, 2010). In the EU, the Euroclass System for classification of building products defines a range of fire classes. The Euroclass system implements Article 20 of the Construction Products Directive. Furthermore, a number of European products standards define requirements regarding reaction-to-fire performance of the products. The building regulations in the individual Member States are decided nationally. In some countries (e.g. Germany) the requirements are set at material level, whereas in others the requirements concern the fire safety performance of the building (e.g. in Sweden for some applications) which does not result in a formal requirement that the building materials used are flame retardant. This situation results in different use patterns for flame retarded EPS/XPS building insulation material across the EU.

The fire regulations mainly concern the following areas:

- **Electrical and electronic equipment.** This is regulated in Denmark by the National Electrical Code Standard Handbook (Danish: Stærkstømsbekendtgørelsen) which is a framework of separate Statutory Orders for the different areas covered. The requirements are mainly based on international IEC- and CENELEC standards with some specific Danish additions.
- **Wiring.** Also regulated by the National Electrical Code Standard Handbook.
- **Building materials.** Building materials are regulated by the 2010 Building Regulations, BR10 (Danish: Bygningsreglementet). Combustible insulation materials can be used for some specific applications provided that the combustible material is protected against ignition sources (details specified in the regulations). The regulations do not require that combustible insulation materials are flame retardant.
- **Protective clothing.** In Denmark, there are no fire requirements for clothing textiles except for some types of protective clothing, which are regulated by different Danish/European standards. (Lassen *et al.*, 1999)
- **Furniture.** Specific requirements apply to furniture used in ships and building rooms intended for more than 150 persons (DBI, 2013).
- **Carpets.** Carpets used in escape routes and other areas with requirements for fire and smoke shall meet the European fire class Dfl-s1 and be tested using international standards (Gulvbranchen, 2013).
- **Means of transport.** Specific fire regulations apply to vehicles, trains, ships and aircraft which are based on international standards. The requirements apply to a range of compo-

nents/materials. In ships, for example, specific requirements apply to primary deck coverings, vertically supported textiles and films, upholstered furniture, bedding components among other materials/components (DBI, 2013).

TABLE 5
EU AND DANISH LEGISLATION ADDRESSING BROMINATED FLAME RETARDANTS (AS OF JULY 2013)

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns BFRs
Legislation addressing products			
Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes I and III (POPs Regulation) The BFRs are added by Commission regulation No 757/2010 amending Regulation (EC) No 850/2004 as regards Annexes I and III	EU	HexaBB (CAS No 36355-01-8)	Production, marketing and use of the five BFRs are prohibited.
	EU	TetraBDE, C ₁₂ H ₆ Br ₄ O PentaBDE, C ₁₂ H ₅ Br ₅ O HexaBDE, C ₁₂ H ₄ Br ₆ O HeptaBDE, C ₁₂ H ₃ Br ₇ O	By way of derogation, production, marketing and use of the following is allowed for the four PBDEs: 1. Concentrations of the substances equal to or below 10 mg/kg (0,001 % by weight) when it occurs in substances, preparations, articles or as constituents of the flame-retarded parts of articles. 2. Production, placing on the market and use of the following shall be allowed: (a) articles and preparations containing concentrations below 0.1 % of by weight when produced partially or fully from recycled materials or materials from waste prepared for re-use; (b) electrical and electronic equipment within the scope of Directive 2002/95/EC of the European Parliament and Council (*). 3. Use of articles already in use in the Union before 25 August 2010 containing Tetrabromodiphenyl ether as a constituent of such articles shall be allowed. Article 4(2), third and fourth subparagraphs shall apply in relation to such articles. Waste management provisions are mentioned under legislation addressing waste below.
Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)	EU	Tris (2,3 dibromopropyl) phosphate (CAS No 126-72-7) PBBs (CAS No 59536-65-1)	Subject to <u>restriction (Annex XVII)</u> 1. Shall not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin. 2. Articles not complying with paragraph 1 shall not be placed on the market.
		OctaBDE C ₁₂ H ₂ Br ₈ O	1. Shall not be placed on the market, or used: — as a substance, — as a constituent of other substances, or in mixtures, in concentrations greater than 0.1 % by weight. 2. Articles shall not be placed on the market if they, or flame-retardant parts thereof, contain this substance in concentrations greater than 0.1 % by

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns BFRs
			weight. 3. By way of derogation, paragraph 2 shall not apply: – to articles that were in use in the Community before 15 August 2004, – to electrical and electronic equipment within the scope of Directive 2002/95/EC (RoHS).
		HBCDD (CAS No 3194-55-6, 25637-99-4, 134237-50-6, 134237-51-7, 134237-52-8)	Subject to <u>authorisation (Annex XIV)</u> Latest application date: 21 February 2014 Sunset date: 21 August 2015
Regulation 649/2012 concerning the export and import of hazardous chemicals	EU	OctaBDE (CAS No 32536-52-0) PBBs (CAS No 13654-09-6, 27858-07-7, 36355-01-8 and others) Tris (2,3-dibromopropyl) phosphate (CAS No 126-72-7) PentaBDE (CAS No 32534-81-9 and others) TetraBDE (CAS No 40088-47-9 and others) HexaBDE (CAS No 36483-60-0 and others) HeptaBDE (CAS No 68928-80-3 and others)	Subject to <u>export notification procedure</u> : Octabromodiphenyl ether, Polybrominated biphenyls (PBB) except hexabromobiphenyl, Tris (2,3-Dibromopropyl) phosphate Subject to <u>export ban</u> : Hexabromobiphenyl, tetrabromodiphenyl ether, pentabromodiphenyl ether, hexabromodiphenyl ether, heptabromodiphenyl ether Included in list of chemicals <u>qualifying for PIC notification</u> : Octabromodiphenyl ether, polybrominated biphenyls (PBB), tris (2,3-dibromopropyl) phosphate
Directive 2011/65/EU on the restriction of the use of certain hazardous substances in electrical and electronic equipment (recast) (RoHS Directive)	EU	PBBs PBDEs	Electrical and electronic equipment (EEE) placed on the market, including cables and spare parts for its repair, its reuse, updating of its functionalities or upgrading of its capacity, shall not contain PBB and PBDE in concentrations above 0.1 mg/kg. The following application areas are <u>outside the scope</u> of the directive: (a) equipment which is necessary for the protection of the essential interests of the security of Member States; (b) equipment designed to be sent into space; (c) equipment which is specifically designed, and is to be installed, as part of another type of equipment that is

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns BFRs
			<p>excluded or does not fall within the scope of this Directive;</p> <p>(d) large-scale stationary industrial tools;</p> <p>(e) large-scale fixed installations;</p> <p>(f) means of transport for persons or goods, excluding electric two-wheel vehicles which are not type-approved;</p> <p>(g) non-road mobile machinery made available exclusively for professional use;</p> <p>(h) active implantable medical devices;</p> <p>(i) photovoltaic panels intended to be used in a system that is designed, assembled and installed by professionals for permanent use at a defined location to produce energy from solar light for public, commercial, industrial and residential applications;</p> <p>(j) equipment specifically designed solely for the purposes of research and development only made available on a business-to-business basis.</p> <p>The restriction shall <u>not</u> apply to:</p> <ol style="list-style-type: none"> 1. Medical devices and monitoring and control instruments which are placed on the market before 22 July 2014, to in vitro diagnostic medical devices which are placed on the market before 22 July 2016 and to industrial monitoring and control instruments which are placed on the market before 22 July 2017 2. cables or spare parts for the repair, the reuse, the updating of functionalities or upgrading of capacity of the following: <ol style="list-style-type: none"> (a) EEE placed on the market before 1 July 2006; (b) medical devices placed on the market before 22 July 2014; (c) in vitro diagnostic medical devices placed on the market before 22 July 2016; (d) monitoring and control instruments placed on the market before 22 July 2014; (e) industrial monitoring and control instruments placed on the market before 22 July 2017; (f) EEE which benefited from an exemption and which was placed on the market before that exemption expired as far as that specific exemption is concerned. 3. Reused spare parts, recovered from EEE placed on the market before 1 July 2006 and used in equipment placed on the market before 1 July 2016, provided that reuse takes place in auditable closed-loop business-to-business return systems, and that the reuse of parts is notified to the consumer.
Bekendtgørelse om be-	National	PBBs	The Danish Statutory Order differs from the RoHS di-

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns BFRs
grænsning af import og salg samt fremstilling til eksport inden for EU af elektrisk og elektronisk udstyr, der indeholder visse farlige stoffer (RoHS-bekendtgørelsen) [Statutory Order on the restriction of the import and marketing as well of manufacturing within the EU for export of electrical and electronic equipment containing certain hazardous substances] BEK nr 1041 af 30/10/2012		PBDEs	rective in the way that the Statutory Order does not include general exemptions for medical equipment and other equipment exempted from the RoHS directive. The exemptions only concern specific substances in the equipment exempted in the RoHS directive e.g. "Lead used in x-ray tubes" in medical equipment. The use of PBB and PBDE is not exempted in any equipment.
Regulation (EC) No 1223/2009 of 30 November 2009 on cosmetic products (apply from 11 July 2013)	EU	OctaBDE (CAS No 32536-52-0)	Included in list of substances prohibited in cosmetic products
Bekendtgørelse om kosmetiske produkter [Statutory Order on cosmetic products] BEK nr 422 af 04/05/2006 This will be repealed following the full transition of all provision from the old cosmetics directive to the cosmetics regulation 1223/2009	National	OctaBDE (CAS No 32536-52-0)	Included in list of substances prohibited in cosmetic products
Executive Order on Working with Substances and Materials (chemical agents) No. 292; 26 April 2001	National	Brominated flame retardants (BFRs)	All work with brominated flame retardants is covered by this executive order
Executive Order on Measures to Protect Workers from the Risks related to Exposure to Carcinogenic Substances and Materials at Work, Appendix 1, No. 908; 27 September 2005	National	Products with ≥ 0.1 % of 2,2-bis (bromethyl)-1,3-probandiol (CAS-no. 3296-90-0)	Specifies the labelling requirement: "Contains a substance regulated by the Danish occupational health regulations concerning cancer risk"
Legislation addressing waste			
Commission regulation	EU	HexaBDE (CAS No	Waste management provisions:

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns BFRs
(EU) No 756/2010 amending Regulation (EC) No 850/2004 as regards Annexes IV and V (Amending the POPs Regulation)		36355-01-8) TetraBDE, C ₁₂ H ₆ Br ₄ O PentaBDE, C ₁₂ H ₅ Br ₅ O HexaBDE, C ₁₂ H ₄ Br ₆ O HeptaBDE, C ₁₂ H ₃ Br ₇ O	The substances shall be disposed of in such a way as to ensure that the persistent organic pollutant content is destroyed or irreversibly transformed so that the remaining waste and releases do not exhibit the characteristics of persistent organic pollutants. Hexabromobiphenyl Limit value for disposal provisions: 50 mg/kg. Permanent storage shall be allowed only when specified conditions are met :5,000 mg/kg: Concentration limits for the four PBDEs in the context of waste management are not set yet.
Directive 2012/19/EU on waste electrical and electronic equipment (recast) (WEEE-Directive)	EU	Brominated flame retardants (BFRs)	Plastic containing brominated flame retardants is subject to selective treatment for materials and components of waste electrical and electronic equipment (WEEE). Proper treatment, other than preparing for re-use, and recovery or recycling operations shall, as a minimum, include the removal and a selective treatment. Equipment outside the scope: From 13 August 2012 to 14 August 2018 (transitional period), subject to paragraph 3, EEE falling outside the categories set out in Annex I. (industrial tools, stationary equipment, etc.) (a) Equipment which is necessary for the protection of the essential interests of the security of Member States, including arms, munitions and war material intended for specifically military purposes; (b)Equipment which is specifically designed and installed as part of another type of equipment that is excluded from or does not fall within the scope of this Directive, which can fulfil its function only if it is part of that equipment; (c) filament bulbs.
Bekendtgørelse om markedsføring af elektrisk og elektronisk udstyr samt håndtering af affald af elektrisk og elektronisk udstyr (WEEE Bekendtgørelsen) [Statutory Order on placing on the market of electrical and electronic equipment	National	Brominated flame retardants (BFRs)	Plastics containing brominated flame retardants must be delivered to companies that are authorized to handle brominated waste under the Environmental Protection Act § 33 or similar legislation abroad. Plastic with bromine content of less than 5 ppm (mg/kg) can be returned for reprocessing and recycling by companies that have been approved under the Environmental Protection Act § 33 or similar legislation abroad

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns BFRs
<p>and management of waste of electrical and electronic equipment]</p> <p>BEK nr 1296 af 12/12/2011</p>			<p>Printed circuit boards that are not recycled, shall follow- ing dismantling of capacitors, batteries, accumulators and mercury containing components, including LCD displays with gas discharge lamps, be delivered to plants that are approved for treatment of metallic waste con- taining brominated flame retardants, PCBs and berylli- um under the Environmental Protection Act § 33 or similar legislation abroad.</p> <p>The scope of the Danish statutory order is wider than the WEEE Directive</p>
Legislation addressing emissions			
<p>Regulation (EC) No 166/2006 concerning the establishment of a Europe- an Pollutant Release and Transfer Register (PRTR Regulation)</p>	EU	<p>PBDEs (total of penta- BDE, octa-BDE and deca-BDE.)</p> <p>HexaBB</p>	<p>The operator of a facility that undertakes one or more of the activities specified in the Regulation above the appli- cable capacity thresholds shall report the amounts annu- ally to its competent authority if the releases are above the following threshold for releases:</p> <p>To air: - To land: 1 kg/year To water: 1 kg/year</p> <p>To air: 0.1 kg/year To land: 0.1 kg/year To water: 0.1 kg/year</p>
<p><i>Bekendtgørelse om visse virksomheders afgivelse af miljøoplysninger (PRTR-bekendtgørelsen) [Statutory Order on certain companies' delivery of environmental infor- mation]</i></p> <p>BEK no 210 of 03/03/2010</p>	National	Same	Same
<p>Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (Water Framework Di- rective)</p>	EU	<p>PBDEs</p> <p>PentaBDE (congener number -28, -47, -99, - 100, -153 and -154)</p>	<p>Included in Annex X: "List of priority substances in the field of water policy".</p> <p>Only pentaBDE is included in the list of priority hazard- ous substances</p>
<p>As amended by Directive 2008/105/EC on environmental quality standards in the field of</p>	EU	PBDEs	<p>Annual Average Ecological Quality Standards (AA-EQS) and Maximum Allowable Concentration (MAC) in µg/l for pentaBDE</p> <p>AA-EQS, Inland surface waters: 0.0005</p>

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns BFRs
water policy			AA-EQS, Other surface waters: 0.0002 MAC-EQS, Inland surface waters: not applicable MAC-EQS, Other surface waters: not applicable
			(New proposal (COM(2011), 876 final): PBDEs should as regards EQS cover tetra-, penta-, hexa- and heptaBDE only Hexabromocyclododecane included in Annex X.
<i>Bekendtgørelse om miljøkvalitetskrav for vandområder og krav til udledning af forurenende stoffer til vandløb, søer eller havet [Statutory Order on environmental quality standards for the aquatic environments and requirements regarding discharges of pollutants to streams, lakes and the sea]</i> <i>BEK nr 1022 af 25/08/2010</i>	National	PBDEs	Same as Directive 2008/105/EC
<i>Bekendtgørelse om kvalitetskrav til miljømålinger [Statutory Order on quality requirement to environmental analyses]</i> <i>BEK no 900 of 17/08/2011</i>	National	PBDEs PentaBDE (congener number -28, -47, -99, -100, -153 and -154)	Sets requirements concerning quality control of chemical analyses of environmental and product samples and requirements concerning standard deviation on the measurements. Concerns analyses prepared as part of the authorities' enforcement of the Danish Environmental Protection Act, the Chemical Substances and Products Act and other legal instruments in the field of the environment and analysis prepared as part of environmental monitoring programmes.

*1 Unofficial translation of name of Danish legal instruments.

Standard conditions for industrial installations or activities

None of the standard conditions for industrial installations or activities listed in Annex II to the Danish Order of Environmental permitting (Godkendelsesbekendtgørelsen, BEK No 1454 of 20/12/2012) specifically address brominated flame retardants (cf. Annex 5 to BEK No 486 of 25/05/2012).

CLASSIFICATION AND LABELLING

Table 6 lists brominated flame retardants for which a harmonised CLP classification and labelling have been agreed upon (as of 30 July, 2013). It shows that harmonised classification has been established for octaBDE, pentaBDE and TBBP.

TABLE 6
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s) *1
602-094-00-4	Diphenylether; octabromo derivate (octaBDE)	32536-52-0	Repr. 1B	H360Df
602-083-00-4	Diphenyl ether, pentabromo derivative pentabromodiphenyl ether (pentaBDE)	32534-81-9	STOT RE 2 * Lact. Aquatic Acute 1 Aquatic Chronic 1	H373 ** H362 H400 H410
604-074-00-0	Tetrabromobisphenol-A; 2,2', 6,6'-tetrabromo-4,4'-isopropylidenediphenol (TBBPA)	79-94-7	Aquatic Acute 1 Aquatic Chronic 1	H400 H410
602-109-00-4	Hexabromocyclododecane 1,2,5,6,9,10-hexabromocyclododecane (HBCDD)	25637-99-4 3194-55-6	Repr. 2 Lact.	H361 H362

* The classification shall be considered as a minimum classification.

** The classification under 67/548/EEC indicating the route of exposure has been translated into the corresponding class and category according to this Regulation, but with a general hazard statement not specifying the route of exposure as the necessary information is not available.

*1 H360Df: May damage the unborn child. Suspected of damaging fertility.
H361: Suspected of damaging fertility or the unborn child
H362: May cause harm to breast-fed children
H373: May cause damage to organs through prolonged or repeated exposure
H400: Very toxic to aquatic life
H410: Very toxic to aquatic life with long lasting effects

Self classification

Industry classifications for substances without harmonised classifications and labelling agreements are summarised in Appendix 6 and taken into account in Chapters 0 and 0 on environment and human health assessments.

2.1.2 REACH

This section concerns pipeline activities under REACH, whereas existing regulation is included in Table 5.

Community rolling action plan (CORAP)

One brominated flame retardant, DBDPE, is included in the Community rolling action plan (CORAP) (ECHA, 2012a) for 2012, whereas no BFRs are included in the most recent draft Community Rolling Action Plan, 2013-2015 (ECHA, 2013e).

TABLE 7
SUBSTANCES IN THE COMMUNITY ROLLING ACTION PLAN FOR 2012-2014 (ECHA, 2012A)

CAS No	EC No	Substance Name	Year	Member State	Initial grounds for concern
84852-53-9	284-366-9	1,1'-(ethane-1,2diyl)bis[pentabromo benzene], DBDPE	2012	United Kingdom	Environment/Suspected PBT; Exposure/Wide dispersive use, high aggregated tonnage

Registry of Intentions

Table 8 shows Registry of Intentions by ECHA and Member States' authorities for restriction proposals, proposals for harmonised classifications and labelling and proposals for identifying brominated flame retardants as Substances of Very High Concern (SVHC).

DecaBDE has been recommended by ECHA for inclusion in the authorisation list and a public consultation is on-going until 23 September 2013,

TABLE 8
BROMINATED FLAME RETARDANTS IN REGISTRY OF INTENTIONS (AS OF 30 JULY 2013)

Registry of:	CAS No	Substances	Scope (reproduced as indicated in the Registry of intentions)	Dossier intended by:	Date of submission:
Harmonised Classification and Labelling intentions					
Annex XV dossiers submitted	25637-99-4 3194-55-6	Hexabromocyclododecane, HBCDD	Proposed classification according to CLP: Repr. 2 H361fd (Suspected of damaging fertility. Suspected of damaging the unborn child.) Lact. Effects H362 (May cause harm to breast-fed children)	Sweden	Submitted: 10/06/2008 [slightly different classification has been agreed upon]
SVHC intentions					
Annex XV dossiers submitted	1163-19-5	Decabromodiphenylether, decaBDE	PBT	United Kingdom	06/08/2012
	25637-99-4	Hexabromocyclododecan, HBCDD	PBT	Sweden	30/06/2008

Candidate list

As of March 2013 decaBDE and HBCDD have been included in the candidate list with the scope of being PBT substances (and vPvB for decaBDE). Please note that HBCDD has been included in Annex XIV to REACH (and is consequently not a "candidate" anymore).

TABLE 9

BROMINATED FLAME RETARDANTS ON THE CANDIDATE LIST (ECHA, 2013B; LAST UPDATED: 20/06/2013)

CAS No	EC No	Substance Name	Date of inclusion	Reason for inclusion	Decision number
1163-19-5	214-604-9	Bis(pentabromophenyl) ether, decaBDE	2012/12/19	PBT (Article 57 d); vPvB (Article 57 e)	ED/169/2012
25637-99-4 3194-55-6 (134237-50-6) (134237-51-7) (134237-52-8)	221-695-9 247-148-4	Hexabromocyclododecane (HBCDD) and all major diastereoisomers identified: Alpha-hexabromocyclododecane; Beta-hexabromocyclododecane; Gamma-hexabromocyclododecane	2008/10/28	PBT (article 57d)	ED/67/2008

Annex XIV recommendations

The latest list of Annex XIV recommendations does not include any BFRs.

2.1.3 Other legislation/initiatives

VECAP

The Voluntary Emissions Control Action Programme (VECAP) is a voluntary initiative of member companies of the European Flame Retardant Association (EFRA) together with the industry's global organisation, the Bromine Science and Environmental Forum – BSEF (VECAP, 2011). The programme aims to reduce emissions of decaBDE, HBCDD and TBBPA through the promotion of environmental management and manufacturing process best practices throughout the value chain, from producers to downstream users. The programme publishes an annual progress report for Europe and North America, respectively.

Norway

The legislation in Norway on brominated flame retardants goes beyond the legislation in the EU as Norway has a general ban on production, import, export and placing on the market of substances, mixtures and articles containing decaBDE in concentrations above 0.1 % w/w (FOR 2004-06-01 nr 922:). The use in vehicles and most other means of transport is exempted.

U.S.A.

On December 17, 2009, as the result of negotiations with US EPA, the two U.S. producers of decabromodiphenyl ether (decaBDE), Albemarle Corporation and Chemtura Corporation, and the largest U.S. importer, ICL Industrial Products, Inc., announced commitments to phase out decaBDE in the U.S.A. (US EPA, 2012). The companies have committed to end production, importation, and sales of decaBDE for most uses in the U.S.A. by December 31, 2012, and to end all uses by the end of 2013.

Canada

In North America the first restriction was adopted in Canada in 2008 with a ban on manufacture of PBDEs, including decaBDE, under the The Polybrominated Diphenyl Ethers Regulations (Environment Canada 2008 as cited by Norway, 2013). A voluntary agreement between Environment Canada and three large worldwide producers of decaBDE include a phase-out of decaBDE exports and sales for electrical and electronic equipment by the end of 2010, for transportation and military uses by the end of 2013 and for all other uses by the end of 2012 (Environment Canada 2010 b, as cited by Norway, 2013). According to the announcement, Environment Canada is also considering a ban on PBDE use in articles (Environment Canada 2010 b as cited by Norway, 2013).

2.2 International agreements

Table 10 gives an overview of how brominated flame retardants are addressed by various international agreements.

TABLE 10
INTERNATIONAL AGREEMENTS ADDRESSING BROMINATED FLAME RETARDANTS

Agreement	Substances	How the selected brominated flame retardants are addressed
OSPAR Convention	Brominated flame retardants PBDEs and PBBs 2,3,4,5,6-Pentabromoethylbenzene, PBEB (Pentabromophenyl)methyl acrylate, PBB-Acr	Included in list OSPAR List of Chemicals for Priority Action (Revised 2011) For PBEB and PBB-ACR it is indicated that no background document is prepared because there is no current production and use interest) The OSPAR background document on certain brominated flame retardants addresses PBDEs, PBBs and HBCDD (OSPAR 2009), but it is not clear from the list if "Brominated flame retardants" only include those BFRs covered by the background document. Lead country for BFRs: Sweden
	Decabromodiphenyl ether, decaBDE Benzene, 1,2,3,4,5-pentabromo-6-(bromomethyl), PBBB Decabromobiphenyl, DecaBB Pentabromodiphenyl ether, pentaBDE Octabromodiphenyl ether, octaBDE 2-(allyloxy)-1,3,5-tribromobenzene, TBP-AE 1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, TDBP-TAZTO	Included in Section A of list of substances of possible concern: Substances which warrant further work by OSPAR because they do not meet the criteria for Sections B – D and substances for which, for the time being, information is insufficient (it is not indicated which of the substances are listed due to insufficient information)
	Hexabromo-1,1'-biphenyl, hexaBB Nonabromobiphenyl, nonaBB Octabromobiphenyl, octaBB Tetrabromophthalic anhydride, TEBP-Anh	Included in Section C of list of substances of possible concern: Substances which are not produced and/or used in the OSPAR catchment or are used in sufficiently contained systems making a threat to the marine environment unlikely
HELCOM (Helsinki Convention)	Pentabromodiphenyl ether, pentaBDE Octabromodiphenyl ether, octaBDE Decabromodiphenyl ether, decaBDE Hexabromocyclododecane, HBCDD (not indicated if it is the substances or the commercial products which are addressed)	Included in list of HELCOM priority hazardous substances (HELCOM Recommendation 31E/1 of May 2010)
	Hexabromobiphenyl	Selected substance for immediate priority action (HELCOM Recommendation. 19/5 of March 1998)
	Brominated and antimony-containing flame retardant used in leather processing industry	BAT measures: Substitution HELCOM Recommendation 25/2 of March 2004)
Rotterdam Convention (PIC Convention)	PBBs Tris(2,3-dibromopropyl) phosphate	Included in Annex III to the Convention and subject to the PIC procedure

Stockholm Convention	Hexabromobiphenyl, hexaBB Tetrabromodiphenyl ether, tetraBDE Pentabromodiphenyl ether, pentaBDE Hexabromodiphenyl ether, hexaBDE Heptabromodiphenyl ether, heptaBDE	Listed in Annex A, "List of restricted substances". The requirements are transposed into the EU POPs Regulation (Regulation (EC) No 850/2004) and reference is made to Table 3
	Hexabromocyclododecane, HBCDD	At the sixth meeting of the Conference of the Parties, May 2013 the Parties decided to include HBDD in Annex A to the Convention with specific exemptions for production and use in expanded polystyrene and extruded polystyrene in buildings (SC-6/13). Each Party that uses the exemption shall register the exemption by the secretariat. All registrations of specific exemptions shall expire five years after the date of entry into force of the Convention with respect to HBCDD. The restriction will enter into force in the EU by May 2014
	Octabromodiphenyl ether, octaBDE	The substance has been suggested by the European Community for inclusion in the relevant annexes. It has been reviewed by the POPs Review Committee of the Convention, which has suggested that the risk of octaBDE is managed by inclusion of the congeners of commercial octaBDE (c-octaBDE) with POPs characteristics i.e. the hexaBDE and the heptaBDE. OctaBDE is consequently not included in Annex A.
	Decabromodiphenyl ether, decaBDE	The substance has been suggested by the Norway for inclusion in the relevant annexes (Norway, 2013). Is currently (October 2013) under review by the POPs Review Committee of the Convention.
Basel Convention	PBBs	Included in Category Y10 of waste to be controlled: "Waste substances and articles containing or contaminated with polychlorinated biphenyls (PCBs) and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs)". Addressed by technical guidelines for the environmentally sound management of wastes consisting of the substances (Basel, year not indicated).
	Other BFRs	Not specifically addressed by a waste category but may be included in various categories: Y45 " Organohalogen compounds other than substances referred to in this Annex", waste metal cables, or "waste electrical and electronic assemblies or scrap...." Under the convention technical guidelines for the environmentally sound management of the "new" BFR POPs substances are developed.
Convention on Long-range Trans-	Hexabromobiphenyl, hexaBB	Included in Annex 1, substances scheduled for elimination. Elimination of production and use.

boundary Air Pollution (CLRTAP)	Tetrabromodiphenyl ether, tetraBDE Pentabromodiphenyl ether, pentaBDE Hexabromodiphenyl ether, hexaBDE Heptabromodiphenyl ether, heptaBDE	Elimination of production and use. A Party may allow recycling and final disposal of articles that may contain these substances provided that the recycling and final disposal is carried out in an environmentally safe manner and does not lead to the recovery of any of these substances for the purpose of their reuse.
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2.2.1 The Stockholm Convention implementation plan

HexaBB, and four of the PBDEs, tetra-, penta-, hexa- and heptabromodiphenyl ether, are included in the list of restricted substances (Annex A) of the Stockholm Convention (with exemptions) and in the list of substances for elimination in the POPs Protocol under the UNECE LRTAP Convention. It is the individual substances (each consisting of several congeners) which are covered by the convention. As the commercial products consists of mixtures of these substances, the inclusion of the four substances means that the commercial products c-pentaBDE and c-octaBDE *de facto* are restricted by the Convention. The convention further restricts the use of HBCDD (with exemptions) and hexabromobiphenyl, hexaBB. DecaBDE has recently been suggested by Norway for inclusion in Annex A.

Action plan for reduction of hexaBB and the four PBDEs in Denmark

As part of the updated Danish national implementation plan for Stockholm Convention submitted to the secretariat for the Convention in August 2012, an action plan for the reduction of hexaBB and tetraBDE, pentaBDE, hexaBDE and heptaBDE in Denmark was developed.

The following table indicates the new initiatives that will be taken in relation to the release of the substances throughout their life cycle.

As Party to the Convention the EU has prepared an updated community implementation plan for the Stockholm Convention as well, but the updated plan is not yet published (as of July 2013).

TABLE 11
ACTION PLAN FOR REDUCTION OF hexaBB, tetraBDE, pentaBDE, hexaBDE AND heptaBDE IN DENMARK

No.	Initiative	Description	Responsible institution	Time frame
1	Validation of destruction of technical pentaBDE	Encourage the European Commission to prepare a study to validate whether technical pentaBDE is sufficiently destroyed in ordinary waste incineration. On the basis of the results, the need for treatment of waste containing pentaBDE in Denmark will be assessed. [As mentioned elsewhere in this report the European Commission has answered on this subject]	Danish EPA	Not set
2	Possible separation of household waste containing pentaBDE	Depending on the results of Initiative 1, any requirements for separating important fractions of household waste containing pentaBDE will be prepared.	Danish EPA	Not set
3	Guidelines concerning articles which must not be reused and recycled	Prepare guidelines concerning articles which must not be reused and recycled as a consequence of a content of pentaBDE exceeding the set limit values.	Danish EPA	Not set

No.	Initiative	Description	Responsible institution	Time frame
4	Examine the possibilities of identifying pentaBDE in shredder waste	<p>In 2011, the Danish EPA established an innovation partnership for shredder waste, thus putting focus on improved exploitation of resources from waste, managing substances of concern (including POPs) and reducing the amounts for landfilling, e.g. by establishing treatment requirements for shredder waste.</p> <p>Through the Action plan to promote eco-efficient technology, the Danish EPA has supported several projects on shredder waste, including a project aimed at identifying potential substances of concern in shredder waste (e.g. pentaBDE) and investigating the possibilities of using sensor-based technology to identify and separate materials containing such substances before or after the shredder process. The results from these projects are included in the work of the innovation partnership.</p>	Danish EPA	Not set

2.3 Eco-labels

Table 12 gives an overview of how brominated flame retardants are addressed by the EU and Nordic eco-labelling schemes, with an indication of requirements beyond existing restrictions in the EU (RoHS Directive, REACH Annex XVII, etc.)

The Nordic ecolabelling criteria for a wide range of articles contain requirements which restrict the use of some or all brominated flame retardants. The exact criteria vary among the article groups. In some groups only BFRs that are assigned specific R-phases (e.g. phases concerning CMR properties) are restricted, whereas in others it is specified that certain FRs must not be present: all FRs, all halogenated FRs, or all halogenated organic FRs. In many of the criteria for electrical and electronic equipment, some exemptions for reactive BFRs and plastic parts of less than 25 g applies.

The EU ecolabelling criteria generally do not apply to the use of reactive flame retardants. The criteria for various electrical and electronic products have restrictions on the use of additive flame retardants which meet the criteria for classification in specific hazard classes. In practice, for most of the criteria, the restrictions (beyond general EU restrictions) would mainly concern additive use of TBBPA and the use of HBCDD. The criteria for bed mattresses, textile floor coverings, textile products and furniture restrict any use of additive flame retardants in the articles.

TABLE 12
ECO-LABELS TARGETING SELECTED BROMINATED FLAME RETARDANTS

Eco-label	Articles	Criteria relevant for BFR (beyond general EU restrictions)	Document title/number
Nordic Swan	Audiovisual equipment	Flame retardants containing organohalogen compounds are not permitted. Exemptions from the requirement are: Plastic parts does not include cables Reactive flame retardants in printed wired boards (PWB) i.e. those which upon use change their properties (i.e. are actually not contained in the final product in a concentration > 0.1%) such that the identified R-phases above no longer apply. Plastic parts weighing less than 25g. Process-induced technologically unavoidable impurities. The maximum allowable concentrations are 0.1 w-% in homogenous material.	Nordic Ecolabelling of Audiovisual equipment, Version 4.2 • 15 December 2009 – 31 October 2014
	Computers	More or less the same as above	Nordic Ecolabelling of Computers, version 6.4 • 8 June 2009 – 30 June 2014
	Imaging equipment	More or less the same as above	Nordic Ecolabelling of Imaging equipment, Version 5.4 • 14 June 2007 – 30 June 2014
	Dish washers	Plastic parts heavier than 25 grams shall not contain additive flame retardant substances that are assigned any of the risk phrases which concern CMR properties. In practice this restricts the presence of HBCDD.	Nordic Ecolabelling of Dishwashers, Version 3.6 14 March 2007 – 31 July 2014
	Washing machines	The same as above	Nordic Ecolabelling of Washing machines, Version 4.7 • 18 March 2004 – 31 July 2014
	Refrigerators and freezers	The same as above	Nordic Ecolabelling of Refrigerators and freezers, Version 5.5 • 29 May 2008 – 31 July 2014
	Machines for parks and gardens	HBCDD and TBBPA may not be actively added to the product. Other halogenated organic flame retardants which has been classified with some or combinations listed R-phases may not be added in components weighing more than 25 g	Nordic Ecolabelling of Machines for Parks and Gardens, Version 5.0 • 13 March 2013 – 31 March 2017
	Rechargeable batteries	Battery charger may not contain flame retardants with risk classification as CMR substances. Restricting in practice the use of HBCDD.	Nordic Ecolabelling of Rechargeable batteries, Version 4.2 • 7 December 2010 – 31 December 2015
	Textile services	Halogenated flame retardants must not be present in laundry chemicals	Nordic Ecolabelling of Textile services, Version 3.0 • 12 December 2012 – 31 December 2016

Eco-label	Articles	Criteria relevant for BFR (beyond general EU restrictions)	Document title/number
	Textiles, hides/skins and leather	Flame retardants shall not be present. This also applies to flame retardants that are integrated in the product or material	Nordic Ecolabelling of Textiles, hides/skins and leather. Includes products for apparel and furnishings, Version 4.0 • 12 December 2012 – 31 December 2016
	Toys	Halogenated organic flame retardants shall not be present	Nordic Ecolabelling of Toys, Version 2.0 • 21 March 2012 – 31 March 2016
	Furniture and fitments	More or less the same as above	Nordic Ecolabelling of Furniture and fitments, Version 4.4 • 17 March 2011 – 30 June 2015
	Outdoor furniture and playground equipment,	More or less the same as above	Nordic Ecolabelling of Outdoor furniture and playground equipment, Version 3.0 • 17 March 2011 – 30 June 2015
	Laundry detergents	Halogenated flame retardants must not be present	Nordic Ecolabelling of Laundry detergents for professional use, Version 2.2 • 15 December 2009 – 31 December 2014
	Windows and exterior doors	The same as above	Nordic Ecolabelling of Windows and Exterior Doors, Version 3.4 • 4 November 2008 – 31 December 2014
	Disposable bags, tubes and accessories for health care	General restriction of substances with CMR and PBT properties would restrict some of the BFRs in the articles	Nordic Ecolabelling of Disposable bags, tubes and accessories for health care, Version 1.4 • 13 December 2007 – 31 December 2015
	Printing companies, printed matter, envelopes and other converted paper products	More or less the same as above	Nordic Ecolabelling of Printing companies, printed matter, envelopes and other converted paper products, Version 5.0 • 15 December 2011 – 31 December 2014
	Remanufactured OEM Toner Cartridges	More or less the same as above	Nordic Ecolabelling of Remanufactured OEM Toner Cartridges, Version 5.1 • 15 June 2012 – 30 June 2016
	Panels for the building, decoration and furniture industries	Plastic parts should not contain hazardous substances meeting the criteria for classification in listed hazard classes. Would restrict the use of HBCDD	Nordic Ecolabelling of Panels for the building, decoration and furniture industries, Version 5.2 • 17 March 2011 – 30 June 2015
	Sanitary products	Flame retardants must not be added	Nordic Ecolabelling of Sanitary products, Version 5.4 • 5 March 2008 – 31 October 2015

Eco-label	Articles	Criteria relevant for BFR (beyond general EU restrictions)	Document title/number
	Small houses, apartment buildings and pre-school buildings	Brominated flame retardants must not be present	Nordic Ecolabelling of Small houses, apartment buildings and pre-school buildings, Version 2.5 • 15 December 2009 – 31 December 2014
EU Flower	Notebooks	The product should not contain hazardous substances meeting the criteria for classification in listed hazard classes. The use of substances or mixtures which change their properties upon processing (e.g. become no longer bioavailable, undergo chemical modification) so that the identified hazard no longer applies is exempt from the above requirement. Additive use of TBBPA and HBCDD meets these criteria and would therefore be restricted.	Commission decision 2011/330/EU
	Personal computers	The same as above	Commission decision 2011/337/EU
	Televisions	Plastic parts should not contain hazardous substances meeting the criteria for classification in listed hazard classes. This requirement shall not apply to reactive flame retardants i.e. those which upon use change their properties (i.e. are actually not contained in the final product in a concentration > 0.1 %). Additive use of TBBPA and HBCDD meets these criteria and would therefore be restricted.	Commission decision 2009/300/EC
	Bed mattresses	Only flame retardants that are chemically bound into mattress materials or onto the materials' surfaces (reactive flame retardants) may be used in the product. Less than 0.1 % of the flame retardant may remain in the form as before application, if the flame retardants used have any of R-phrases listed in the decision.	Commission decision 2009/598/EC
	Textile floor coverings	The same as above	Commission decision 2009/967/EC
	Textile products	The same as above	Commission decision 2009/567/EC
	Furniture	The same as above	Commission decision 2009/894/EC

2.4 Summary and conclusions

BFRs in general - One legal instrument at the EU level addresses the BFRs as a whole: The WEEE Directive on waste electrical and electronic equipment (WEEE) requires selective treatment and proper disposal for materials and components of WEEE with brominated flame retardants. Furthermore, some of the ecolabels address all BFRs in common.

PBDEs and PBBs - The main legal focus has so far been on the PBDE and the PBBs. HexaBB, tetraBDE, pentaBDE, hexaBDE and heptaBDE are strictly restricted by the Stockholm Convention on Persistent Organic Pollutants (POPs), and are addressed by the POPs Regulation (Regulation

(EC) No 850/2004) and the RoHS Directive which are the main implementing instruments for the provisions of the convention in the EU. The Danish national implementation plan for the Stockholm Convention includes an action plan for the implementation of the provisions of the Stockholm Convention in Denmark. The tetraBDE and pentaBDE are the main constituents of the commercial c-pentaBDE, whereas hexaBDE and heptaBDE are some of the constituents of the commercial c-octaBDE and the restriction of the substances is a *de facto* restriction of the commercial products. The substances are furthermore addressed by the CLP Regulation (classification and labelling), waste legislation, import/export restriction, emission legislation and environmental monitoring legislation.

Together with the other PBDEs and PBBs, decaBDE is restricted in electrical and electronic equipment by the RoHS Directive with some exemptions (but not in Denmark) and some application areas outside the scope of the directive. No harmonised classification has been established for decaBDE and the substance is not addressed by EU legislation except for the electrical and electronic equipment and some ecolabelling criteria. It is listed in the REACH Candidate List and has been proposed by ECHA for inclusion in the list of substances for authorisation on the basis of an Annex XV report. The substance has been nominated for inclusion in the list of restricted substances under the Stockholm Convention. In the US and Canada, voluntary agreements on phasing out decaBDE have been entered between the major international manufacturers and the federal authorities.

DecaBB is restricted in electrical and electronic equipment within the scope of the RoHS Directive, but otherwise not restricted. According to the available information, the substance is not manufactured anymore in any country of the world.

HBCDD - HBCDD has recently been listed for restriction under the Stockholm Convention with a time-limited exemption for building materials of EPS/XPS, but the POPs Regulation has still not been amended as of August 2013. A dossier for harmonised Classification and Labelling has been submitted. HBCDD is subject to authorisation (Annex XIV to REACH) with a sunset date: 21 August 2015.

TBBPA - A harmonised CLP classification has been agreed upon for TBBPA. Otherwise, the substance is not specifically addressed by any EU or Danish legislation.

DBDPE and EBTEBPI - The two substances are not specifically addressed by current Danish and EU legislation, but DBDPE is included in the Community Rolling Action Plan under REACH.

Other BFRs - Except for the requirements of the WEEE Directive, the BFRs are not addressed by any EU or Danish legislation. PBEB and PBB-ACR are included in the OSPAR list of Chemicals for Priority Action.

Ecolabel schemes - The Nordic ecolabelling criteria for a wide range of articles contain requirements which restrict the use of some or all brominated flame retardants. The exact criteria vary among the article groups. In some groups only BFRs that are assigned specific Risk-phrases (e.g. phrases concerning CMR properties) are restricted, whereas in others it is specified that certain FRs must not be present: all FRs, all halogenated FRs, or all halogenated organic FRs. In many of the criteria for electrical and electronic equipment, some exemptions for reactive BFRs and plastic parts of less than 25 g apply.

The EU ecolabelling criteria generally do not apply to the use of reactive flame retardants. The criteria for various electrical and electronic products have restrictions on the use of additive flame retardants which meet the criteria for classification in specific hazard classes. In practice for most of the criteria, the restrictions (beyond general EU restrictions) would mainly concern additive use of

TBBPA and the use of HBCDD. The criteria for bed mattresses, textile floor coverings, textile products and furniture restrict any use of additive flame retardants in the articles.

Voluntary agreement on emission reduction - A voluntary European emission reduction programme has been introduced for the three main BFRs: decaBDE, TBBPA and HBCDD. The programme addresses emissions from the manufacture of BFRs and industrial downstream uses.

3. Manufacture and uses

3.1 Manufacturing

The market for BFRs is dominated by relatively few major global manufacturers: Albemarle Corporation (U.S.A.), ICL Industrial Products (Israel), Chemtura (U.S.A.) and Tosoh Corporation (Japan). The companies each manufacture a range of different BFRs. The four companies established Bromine Science and Environment Forum (BSEF) in 1997 to commission research on BFRs and bromine and disseminate information to decision-makers and other stakeholders. Until 2011, three of the manufacturers of BFRs were further organised in The European Brominated Flame Retardant Industry Panel (EBFRIP), but in 2011, the members decided to dissolve the panel and integrate the industry's advocacy activities into EFRA, the European Flame Retardant Association, which brings together and represents the leading organisations which manufacture, market or use flame retardants in Europe.

Besides these four manufacturers, BFRs are manufactured by a number of companies which typically produce a limited range of BFRs.

Information on manufacturers in China and Korea is limited. For the REACH registering of the BFRs in the EU, the Asian manufacturers are assisted by representatives including (as indicated in registrations): KTR Europe GmbH Germany (established by Korea Testing and Research Institute), NetSun EU B.V. (representative of Weifang Yucheng Chemical Co., Ltd., China) and Chemical Inspection and Regulation Service (CIRS) Limited (headquarters based in Hangzhou, China).

3.1.1 Manufacturing processes

BFRs are manufactured using different processes. Processes used for the main types of BFRs are briefly described below on the basis of the EU Risk Assessments for the substances.

PBDEs are produced by direct bromination of diphenyl ether using a Friedel-Crafts catalyst. Information reported in the Risk Assessment (ECB, 2002) indicates that production of decaBDE is carried out by using bromine as both the reactant and reaction medium. Diphenyl ether is added to the bromine in the presence of a catalyst and the rate of addition of diphenyl ether effectively controls the rate of reaction. The reaction is a batch process and the temperature of the reaction is around the boiling point of the bromine solvent (~59 °C) (ECB, 2002).

Tetrabromobisphenol-A is produced by the bromination of bisphenol-A in the presence of a solvent. The bromination reaction may be conducted in the presence of hydrocarbon solvent only or with water, 50% hydrobromic acid or aqueous alkyl monoethers. When methanol is used as the solvent the fumigant methyl bromide is produced as a co-product. The production process is largely conducted in closed systems (ECB, 2006).

The production of HBCDD is a batch process. Elementary bromine is added to cyclododecatriene in the presence of a solvent (ECB, 2008a). The process temperature is 20 to 70 °C, and the reaction takes place in closed systems. The suspension obtained is filtered, the solvent is removed with water, and the product is dried, stored in a silo and packed. According to one producer, production and transportation of the material to silo and the packaging are done in a closed system. The product is delivered as powder or pellets.

3.1.2 Manufacturing sites

According to a presentation by PINFA, which represents the European manufacturers of non-halogenated phosphorus, inorganic and nitrogen (PIN) flame retardants, brominated flame retardants are produced at one site in the EU (in The Netherlands) (PINFA, 2010). According to the EU Risk Assessment Report for HBCDD, the manufactured volume of HBCDD at the site in The Netherlands was 6,000 tonnes in 2005. TBBPA and PBDEs were not manufactured in the EU according to the EU Risk Assessment Reports. No data on the manufacturing of other BFRs in the EU have been obtained.

BFRs are not manufactured in Denmark.

3.1.3 Manufacturing volumes The global flame retardants market

The worldwide production and consumption of flame retardants (FRs) amounts to around 2 million tonnes a year (Clariant, 2013). BFRs accounted for 19.7% of the total in 2011 (Figure 1) which would correspond to approximately 360,000 tonnes.

Fink *et al.* (2008, as cited by Harju, 2009) estimated the total BFR market in 2005 at 311,000 tonnes.

According to a 2012 market study by Townsend (as cited by Clariant, 2013), the consumption of flame retardants has grown substantially in the past 4 years, notably in electronics, and is expected to continue to grow at a global annualized rate of 4-5%. Use in plastics accounts for approximately 85% of all flame retardants used, with textiles and rubber products accounting for most of the remaining fraction (Clariant, 2013).

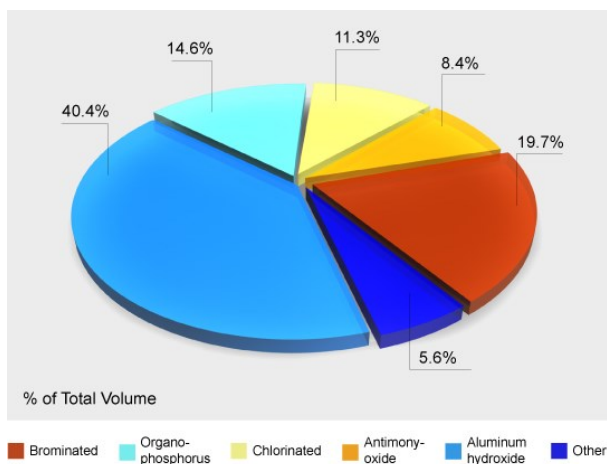


FIGURE 1
GLOBAL CONSUMPTION OF FLAME RETARDANTS IN PLASTICS BY TYPE IN 2011 (CLARIANT, 2013 CITING TOWNSEND SOLUTIONS ESTIMATE)

The global market of BFRs

The global demand for BFRs has been increasing as a consequence of the increasing usage of polymeric materials in construction, electronic and computer equipment. The global market demand for BFRs in 1990 was 145,000 tonnes and grew to more than 310,000 tonnes in 2000 (Alaee *et al.*, 2003) while the demand in 2011 was approximately 360,000 tonnes as estimated above.

Updated information on the global use of BFRs by substances has not been available. The global market demands for PBDEs, TBBPA and HBCDD in 2001 is shown in Table 13. Compared to the estimate of the total BFR market of 310,000 tonnes in 2000, it can be estimated that the five listed BFRs accounted for about 2/3 of the total global market at that time. These data indicate that the

total market for other BFRs was about 100,000 t/y in 2001. In accordance with this, Harju *et al.* (2009) reach an estimate of about 100,000 t/y for other brominated flame retardants based on data from 2005. According to OECD (1994), in 1992 other BFRs accounted for 36% of the total BFR market volume (OECD, 1994); the percentage of other BFRs seems to have been fairly stable over time.

As shown in Table 13, the consumption of the main BFRs in Asia is more than four times the consumption in Europe, reflecting the fact that a major part of the electrical and electronic articles are produced in Asia.

In Denmark, imported articles accounted for about 90% of the consumption in end products in 1999, and today the percentage is likely even higher as the majority of electrical and electronic products are produced in Asia. It means that the BFRs in the end products reflect the use pattern of the BFRs in Asia to a much higher extent than the use of BFRs in production processes in Denmark.

TABLE 13
MARKET DEMAND FOR PBDES AND TWO OTHER MAJOR BROMINATED FLAME RETARDANTS, BY REGION, IN 2001 (TONNES) (BSEF 2006, AS CITED BY LASSEN *ET AL.*, 2006)

Flame re- tardant	Market demand (tonnes/year)				
	Americas	Europe	Asia	Rest of the World	Total
C-pentaBDE	7,100	150	150	100	7,500
C-octaBDE	1,500	610	1,500	180	3,790
C-decaBDE	24,500	7,600	23,000	1,050	56,100
HBCD	2,800	9,500	3,900	500	16,700
TBBPA	18,000	11,600	89,400	600	119,700
TOTAL	53,900	29,460	117,950	2,430	203,790

PBDEs

C-pentaBDE - Based on the information provided by the bromine industry for the POPs Review Committee under the Stockholm Convention, the estimated cumulative use of c-pentaBDE since 1970 was 100,000 tonnes (POPRC, 2006). The total market demand decreased from 8,500 tons in 1999 to 7,500 tons in 2001 (BSEF, 2001). As of 2007 c-pentaBDE was not manufactured in Europe, Japan, Canada, Australia and the U.S.A., but no information on the status of the production in China was available (POPRC, 2007a). It is possible that c-pentaBDE is not produced in any country at present.

C-octaBDE -Information provided by the bromine industry for the POPs Review Committee indicates that c-OctaBDE has been produced in The Netherlands, France, USA, Japan, UK and Israel, but since 2004, it was no longer produced in the EU, USA and the Pacific Rim (lands around the edges of the Pacific Ocean e.g. Japan and China). No information was available that indicates it was being produced in developing countries (POPRC, 2007b). OctaBDE was commercialized sometime in the mid-1970s. By the early 2000s, global production was <4,000 tonnes/year and by the time production ceased, demand was <500 tonnes. Assuming 30 years of production at 6,000 tonnes per year, total production volume would be around 180,000 tonnes (POPRC, 2007b). As mentioned later in this chapter, octaBDE was still imported to Denmark in 2013 with polycarbonate raw materials, demonstrating that the substance is still produced in at least one country (details not provided).

C-decaBDE - According to VECAP (2011) a range of 5,000-7,500 t/y of c-decaBDE was sold in the EU on average in the years 2009-2011 (described further in the next section). These figures do not include decaBDE imported in preparations or articles. The production/import volume of decaBDE in the U.S.A. is reported to be in the range of 25,000 – 50,000 t/y in 2002 and in 2006 (US EPA Inventory Update Reporting as cited by Norway, 2013). The VECAP reports for North America do not include information on volumes sold. As described in section 2.1.3, the two U.S. manufacturers and the largest importer have committed to ending production, import, and sales of c-decaBDE for all uses by the end of 2013. The current global use must consequently be expected to be well below the 25,000-50,000 tonnes in 2006. Among the Asian countries, c-decaBDE is produced mainly in China, where its production was up to 13,500 t/y in 2001 and up to 30,000 t/y in 2005 (Xia *et al.*, 2005; Zou *et al.*, 2007 as cited by Norway, 2013).

PBBs. – HexaBB has not been produced since the 1970s, but decaBB (not covered by the Stockholm Convention) but was produced in France until 2000 (OSPAR, 2009). It is possible that the PBBs are currently not produced in any country.

HBCDD

According to the risk management evaluation of HBCDD prepared by the POPs Review Committee, HBCDD is produced in China, Europe, Japan, and the USA (POPRC, 2011). The known annual production in 2011 was approximately 31,000 tonnes per year (18,000 tonnes in China and 13,426 tonnes in Europe and the U.S.A.) (data for China updated from POPRC, 2012). Available information suggests that use of HBCDD may be increasing. From 2001 to 2011 the global market demand increased from 16,700 t/y to 31,000 t/y (POPRC, 2011, 2012). The main share of the market volume is used in Europe and China (POPRC, 2011). Of the 18,000 tonnes produced in China in 2011, 5,500-6,000 tonnes were exported (POPRC, 2012).

TBBPA and derivatives

According to the OSPAR background document on TBBPA, the substance is produced in the USA, Israel, Jordan and Japan, but not in the EU (OSPAR, 2011). The total global production volume in 2011 was estimated to be in the range 120,000-150,000 t/y. (OSPAR, 2011)

Other BFRs

As indicated above, until recently the total global market volume of other BFRs have been about 100,000 t/y, but may have been increasing in recent years. A breakdown of the global market for other BFRs by substance has not been available. The following sections include scattered information on the global market of individual substances, while a more detailed description of the consumption of other BFRs in the EU is provided in section 3.3.1.

DBDPE - DBDPE was introduced as an alternative to decaBDE and has been on the market for more than 20 years. The market for DBDPEs is probably increasing due to the restriction on decaBDE in electrical and electronic equipment in the EU and the general phase out of production in the U.S.A. Information on the global production of DBDPE has not been available. The total consumption of the DBDPE in Western Europe in 1998 was about 2,500 tonnes while, according to ECHA's registration database, the total import to the EU in 2011 was in the 1,000+ tonnes range (upper limit not indicated, see Table 18). In China, DBDPE was the second most used BFR in 2006 after decaBDE (Shi, 2009). The estimated domestic production volumes in China were 20,000, 12,000, 4,500, and 4,000 t/y for decaBDE, DBDPE, HBCD, and TBBPA-DBPE, respectively. In Japan, the consumption of DBDPE surpassed the consumption of c-decaBDE in 1997-1998 according to Watanabe and Sakai (2003), as cited by Ricklund *et al.* (2008).

EBTEBPI - EBTEBPI has a similar application profile as decaBDE (OECD, 1994) and has been on the market for more than 20 years. Information on the global production of EBTEBPI has not been

available. The total consumption of EBTEBPI in Western Europe in 1998 was about 5,250 tonnes, but the substance has not been registered and the import statistics indicate an import of a few hundred tonnes only (Table 18).

BTBPE - According to Ahi *et al.* (2008), BTBPE is produced and used in China, but information on its production and consumption is not available.

3.2 Import and export

3.2.1 Import and export of brominated flame retardants in Denmark

Data on import and export of brominated flame retardants on their own are shown in Table 14 based on data from Statistics Denmark. The only BFR for which the statistics provide specific data is EBTEBPI, which is listed together with another BFR (CAS No 52907-07-0). The latter has not been pre-registered and it is therefore assumed that the reported import/export concern EBTEBPI only. The net import of EBTEBPI to Denmark in 2011 was 2 tonnes.

TABLE 14
DANISH PRODUCTION, IMPORT AND EXPORT OF BROMINATED FLAME RETARDANTS (STATISTICS DENMARK, 2013)

CN8 code	Text	Import, t/y		Export, t/y		Production	
		Average 2006-2010	2011	Average 2006-2010	2011	Average 2007-2011	2012
290.93031	Pentabromodiphenyl ether; 1,2,4,5-tetrabromo-3,6-bis"pentabromophenoxy"benzene [pentabDE]	0	0	0	0	0	0
2909.3035	1,2-bis"2,4,6-tribromophenoxy"ethane for the manufacture of acrylonitrile-butadiene-styrene [abs] [BTBPE]	0	0	0	0	0	0
2909.3038	Brominated derivatives of aromatic ethers (excl. Pentabromodiphenyl ether, 1,2,4,5-tetrabromo-3,6-bis"pentabromophenoxy"benzene and 1,2-bis"2,4,6-tribromophenoxy"ethane for the manufacture of acrylonitrile-butadiene-styrene [abs])	0	0	0	0	0	0
2917.3920	Ester or anhydride of tetrabromophthalic acid; benzene-1,2,4-tricarboxylic acid; isophthaloyl dichloride, containing by weight 0.8% or less of terephthaloyl dichloride; naphthalene-1,4,5,8-tetracarboxylic acid; tetrachlorophthalic anhydride; sodium 3,5-bis(methoxycarbonyl)benzenesulphonate	61	168	0	0	0	0
2925.1920	3,3',4,4',5,5',6,6'-octabromo-n,n'-ethylenedipthalimide [EBTEBPI]; n,n'-ethylenebis(4,5-dibromohexahydro-3,6-methanophthalimide) [CAS No 52907-07-0]	1	2	0	0	0	0

3.2.1 Import and export of brominated flame retardants in the EU

EU external trade of the BFRs is shown in Table 15.

The average net import of the BFRs can be summarised as follows:

- PentaBDE and/or 4'-PeBPOBDE208 : 216 tonnes in 2011 (average 125 t/y for 2006-2010). Considering that pentaBDE is restricted for nearly all purposes it is most likely that the reported import concerns 4'-PeBPOBDE208.
- Other PBDEs; mainly decaBDE: 5,499 t/y in 2011 (average 9,389 t/y for 2006-2010)
- BTBPE: confidential tonnes in 2011 (average 82 t/y for 2006-2007)
- EBTEBPI: 98 tonnes in 2011 (average 166 t/y for 2009-2010)
- Other BFRs: part of 4,674 tonnes in 2011 (part of average 6,656 for t/y for 2009-2010).

TABLE 15

EU27 EXTERNAL IMPORT AND EXPORT OF SELECTED BROMINATED FLAME RETARDANTS (EUROSTAT, 2012A) *1

CN code	Text	Import, t/y		Export, t/y	
		Average 2006-2010	2011	Average 2006-2010	2011
2909.3031	Pentabromodiphenyl ether (pentaBDE); 1,2,4,5-tetrabromo-3,6-bis"pentabromophenoxy"benzene (CAS No 58965-66-5)	125	216	12.7	0.9
2909.3035	1,2-Bis(2,4,6-tribromophenoxy) ethane, for the manufacture of acrylonitrile-butadiene- styrene (ABS) [BTBPE, CAS No 37853-59-1]	82 (average 2006-2007)	confidential	9.6 (average 2006-2007)	0
2909.3038	Brominated derivatives of aromatic ethers (excl. pentabromodiphenyl ether, 1,2,4,5-tetrabromo-3,6-bis"pentabromophenoxy"benzene and 1,2-bis"2,4,6-tribromophenoxy"ethane for the manufacture of acrylonitrile-butadiene-styrene [abs])	9,389	5,499	492	105
2917.3920	Ester or anhydride of tetrabromophthalic acid; benzene-1,2,4-tricarboxylic acid; isophthaloyl dichloride, containing by weight 0.8% or less of terephthaloyl dichloride; naphthalene-1,4,5,8-tetracarboxylic acid; tetrachlorophthalic anhydride; sodium 3,5-bis(methoxycarbonyl)benzene-sulphonate	6,656	4,674	1,123	2,320
2925.1920	3,3',4,4',5,5',6,6'-octabromo-n,n'-ethylenedipthalimide [EBTEBPI]; n,n'-ethylenebis(4,5-dibromohexahydro-3,6-methanophthalimide) [CAS No 52907-07-0]	100 (average 2009-2010)	181	2.5 (average 2009-2010)	15.2

*1 Data from other years are confidential.

For many of the BFRs, a significant part of the import of the substances would be in imported articles, primarily electrical and electronic equipment imported from Asia.

Data on import of BFRs in articles are generally not available. The EU Risk Assessment for decaBDE (ECB, 2004) estimates that net import of decaBDE in articles around 2000 was probably small compared to consumption in the EU.

For TBBPA, the EU Risk Assessment (ECB, 2007) estimated import to be significant whereas the EU Risk Assessment for HBCDD (ECB, 2008) does not provide data, but indicates that HBCDD contained in expanded polystyrene (EPS) and extruded polystyrene (XPS) for the construction industry is not likely to be transported long distances. It should be noted that even though the net import of decaBDE in articles is considered relatively small, decaBDE in imported articles may still account for a major part of the decaBDE in articles sold on the EU market, because a significant part of the decaBDE used in the EU may be incorporated into articles exported from the EU.

A majority of the TBBPA (indicated as the TBBPA used to produce the TBBPA flame retarded plastics) was imported into the EU in finished articles and components in 2003/2005, as shown in Table 16. According to the EU Risk Assessment, the import of TBBPA on its own ("as the substance") decreased from 13,800 t/y in the late 1990s to 6,500 t/y in 2003/2005. The import of TBBPA in finished articles and components in 2003/2005 accounted for 69% of the total import, and the percentage is likely higher today. As indicated in section 3.3.1, the import of TBBPA on its own has further decreased to 1,000-2,500 t/y in 2010.

The change reflects the fact that an increasing fraction of electrical and electronic equipment sold in the EU is imported.

TABLE 16
IMPORT OF TBBPA IN THE EU IN 2003 TO 2005 (ECB, 2007)

	Import (t/y)
	2003/2005 data
TBBPA imported into the EU as "the substance"	6,500
TBBPA imported into EU as partly finished products (e.g. masterbatch, epoxy resins)	6,000
Amount of TBBPA imported into the EU in finished articles and components	27,500
Total	40,000

3.3 Uses of brominated flame retardants

3.3.1 Consumption of BFRs in the EU

EFRA, the European Flame Retardant Association, has been contacted in order to obtain updated information on the use of BFRs in Europe, but the organisation has not submitted any information.

Data on the use of decaBDE, TBBPA and HBCDD in the EU are available from the reporting of the Voluntary Emissions Control Action Programme (VECAP), which was developed and first implemented in 2004 by three producers of flame retardants in partnership with user industries. The VECAP programme addresses decaBDE, TBBPA and HBCDD and prepares annual reports on used volumes and emissions from manufacturers and industrial downstream users in Europe. The reported volumes sold and emissions for the period 2008 to 2010 are shown in Table 17 (VECAP, 2011). In 2011, in total 13,500- 20,000 tonnes of the three BFRs were sold for industrial down-

stream uses in Europe, a decrease as compared to the 2007 figures. The exact figure for 2007 is 20,829 tonnes (VECAP, 2009). The VECAP programme covers North America and the Asia-Pacific regions as well, but data on the volumes sold in those regions are not reported.

TABLE 17
TOTAL VOLUME SOLD BY MEMBERS OF THE VECAP PROGRAMME (VECAP, 2012)

Substance	Total volume sold in Europe, t/y *1					Coverage 2011 *2
	2007	2008	2009	2010	2011	
DecaBDE	5,000-7,500	5,000-7,500	5,000-7,500	7,500-10,000	2,500-5,000	84%
HBCDD	10,000- 12,500	7,500-10,000	7,500-10,000	10,000-12,500	10,000-12,500	98%
TBBPA	2,500-5,000	2,500-5,000	1,000-2,500	1,000-2,500	1,000-2,500	95%

*1 The volumes sold in a specific year are referred to in the report as the survey results of the subsequent year. In this table, the volume data from the 2011 survey are consequently referred to as 2010 volume.

* Indicates the percentage of the total volumes sold by EFRA member companies covered by the survey.

The only published detailed market analysis of the consumption of BFRs in Western Europe is reported in a Danish substance flow analysis from 1999 (Lassen *et al.*, 1999). The data, representing 1998, are shown in Table 18 together with an updated estimate based on information from registrations (Table 1), import/export statistics (section o) and data from VECAP (Table 17).

Due to the wide ranges indicated in the registration, the total consumption can only be estimated with high uncertainty at 21,000-71,000 t/y. To this uncertainty, substances should be added which are not registered and or that have confidential CAS numbers (which have not been included in the search at ECHA's web site). For the non-polymeric substances, the total is expected to be small, as all substances manufactured or imported in volumes of more than 100 t/y should now be registered. The total reported consumption of BFRs in the EU in 2006 was approximately 47,000 t/y (Stevens *et al.*, 2010).

As indicated in Table 18, the total consumption of TBBPA as a substance on its own has decreased markedly from 13,150 t/y in 1998 to 1,000-2,500 t/y in 2010. About 90% of the TBBPA was used as reactive BFR in the production of printed circuit boards (VECAO, 2012). It is not indicated whether the remaining part is used as reactive BFR for other applications or as additive BFR. The additive use of TBBPA in the EU would be 250 t/y as a maximum, indicating that it represents a small part of the additive use of BFRs.

The brominated polyols, which are BFRs used reactively, accounted in 1999 for 8,400 t/y, and the consumption may still be of the same magnitude as halogenated polyetherpolyol B as the main BFR, with a registered import/manufacture in the 1,000-10,000 t/y range.

Among the additive BFRs, decaBDE and HBCDD were the main BFRs both in 1998 and in 2010. The use of DBDPE may have increased from 2,500 t/y consumption in 1999, but the registered volume is only indicated as 1000+ t/y without an upper limit of the range. TTBP-TAZ is registered in the 1,000 - 10,000 t/y range. The consumption of EBTEBPI in the EU seems to have decreased significantly from about 5,000 t/y in 1998 to a few hundred tonnes in 2010.

Two of the BFRs showing substantial consumption in 1999, polybrominated polystyrenes (4,175 t/y) and poly(2,6-dibromophenylene oxide) (3,250 t/y), are not registered; the latter is also not preregistered, indicating that it is not marketed in the EU anymore.

The polymeric BFRs are not subject to registering and therefore not included in the 2010 estimate. The total consumption of the polymeric BFRs in 1998 was about 9,000 t/y and may have been of the same magnitude in 2010. One polymeric BFR (brominated polystyrene) has been preregistered, but none of the polymeric BFRs have been registered.

TABLE 18
CONSUMPTION OF BROMINATED FLAME RETARDANTS IN WESTERN EUROPE 1998 AND IN THE EU IN 2010

Substance (1998) As indicated in Lassen <i>et al.</i> (1999)	1998 *1		2010
	Market volume, t/y Western Europe	% of total	Market volume, t/y EU27+2 *6
Reactive:			
TBBPA	13,150	21	1,000-2,500 *3
TBBPA polycarbonate oligomer (RDT-7 and other)	2,150	3	Not registered
TBBPA bis(2,3-dibromopropyl ether) (TBBPA-BDBPE)	1,500	2	100-1,000
Brominated polyols	8,400	13	HEEHP-TEBP: 100 - 1,000 TEBP-Anh: 100-1,000 Halogenated polyetherpolyol B: 1,000 - 10,000
Brominated epoxy oligomers	1,250	2	Relevant substances not registered (e.g. TBBPA-BGE and end-capped brominated epoxy)
Dibromoneopentyl glycol (DBNPG)	1,150	2	100-1,000
Other reactive	250	0.4	TBP: 1,000-10,000 (partly used for other applications) TBNPA: Confidential PBB-Acr: 100-1000
Subtotal, reactive	28,800	45	3,000 – 26,000 + non registered + confidential
Additive:			
PBDEs	7,050	11	decaBDE: 5,000-7,500
PBBs	600	1	Not pre-registered
HBCDD	8,950	14	10,000-12,500
Ethylene bis(tetrabromophthalimide), (EBTEBPI)	5,250	8	100 - 1,000 Imp: 181 (2011)
Polybrominated polystyrenes	4,175	7	Not registered (polymers)
Poly (2,6-dibromophenylene oxide) *4	3,250	5	Not pre-registered (polymer)
Saytex 8010 proprietary product (DBDPE)	2,500	4	1,000 +
Polybrominated imides*5	850	1	Not registered

Substance (1998) As indicated in Lassen <i>et al.</i> (1999)	1998 *1		2010
	Market volume, t/y Western Europe	% of total	Market volume, t/y EU27+2 *6
Brominated phenylindane (OBTMPI)	750	1	Not registered
Poly(pentabromobenzyl) acrylate	500	0.8	Not pre-registered (polymer)
Other additive	775	1	TTBP-TAZ: 1,000 - 10,000 TTBNPP: 100-1000 BEH-TEBP: 100-1000 Substances not registered but covered by the statistics: 4'-PeBPOBDE208: import: 216 (2011, together with pentaBDE) BTBPE: Import confidential (2011) 82 (average 2006/2007)
Subtotal, additive	34,700	55	18,000-45,000 +non registered *2
Total (additive + reactive)	62,500	100	21,000-71,000 + non registered + confidential*2

*1 Source: Lassen *et al.*, 1999. Substances names as indicated in Lassen *et al.* with abbreviations used in this survey in brackets.

*2 The 1000+ for DBDPE is calculated as 1000-10,000.

*3 A part may be used as additive BFR.

*4 CAS No 69882-11-7. Not pre-registered (polymer) or produced by major manufacturers. Marketed by Chinese manufacturers via the Internet.

*5 Not clear which specific substances are covered by this.

*6 EU27 + Norway and Switzerland

3.3.2 Applications of BFRs

The BFRs are a complex group of substances with a wide range of applications. As mentioned before, the mechanism of flame retardancy is basically the same for all BFRs.

The optimal BFR for a specific application depends mainly on the polymers/textiles/coating to be provided with flame retarded properties, the processing conditions (e.g. processing temperature), desired characteristics of final polymer (e.g. UV stability and colour) and the price of the BFRs.

The application spectra of the main BFRs from one of the major manufacturers are shown in Appendix 5 (Table A5-2) The other major manufacturers have similar portfolios of BFRs for a range of polymers, textiles and coatings.

DecaBDE, with a high degree of bromination, has traditionally been the cost-effective allround BFR used as additives in a wide range of thermoplastics. DBDPE, EBTEBPI and a newly introduced polymeric BFR have, as mentioned earlier, nearly the same application spectrum as decaBDE and have been used as substitutes for decaBDE. Most of the other BFRs have relatively narrow spectra and are optimised for specific polymers or textiles. For the reactive flame retardants, specific BFRs are used for the different thermosets e.g. tetrabromophthalic anhydride diester/etheriol is used as a reactive component in polyurethane. The application of each of the BFRs is described in more detail below.

The flame retardant polymers may be used for different applications; generally, the same flame retardants are used in a polymer regardless of the end application e.g. the same types of BFR are

used to manufacture flame retardant polyamides used in electrical and electronic equipment, transportation or building applications.

The global production of polymers with BFRs in 2000 is shown in the table below with an indication of the typical content of BFR. The polymer with the highest volume was flame retardant polystyrene foams used mainly for building insulation, with a global production of 600,000 t/y. Other polymers with a narrow application spectrum are FR epoxy (mainly printed circuit boards) and FR polyurethanes (mainly insulation panels), whereas the other polymers are used for production of various articles.

TABLE 19
GLOBAL ANNUAL PRODUCTION OF POLYMERS IN 2000 AND THEIR BFR CONTENT (BASED ON ALAEE *ET AL.*, 2003)

Polymer	Abbreviation *1	Typical BFR content (%)	A/R*1	Type of BFR	Annual production of polymer (1000 t/y)	Main application areas *2
Polystyrene foam	EPS, XPS	0.8–4	A	HBCDD	600	Building insulation panels
High-impact polystyrene	HIPS	11–15	A	decaBDE, brominated polystyrene	350	Housing and other moulded parts for EEE, sheets *3
Epoxy resin	Epoxy	19–33	R	TBBPA	300	Printed circuit boards for EEE
Polyamides	PA	13–16	A	decaBDE, brominated polystyrene	200	Switchgear, fuse boxes, terminal blocks, print connectors, etc. for EEE
Polyolefins	PE, PP	5–8	A	decaBDE, propylene dibromostyrene	200	Cable covering, pipes, sheets for transportation and construction; various EEE applications
Polyurethanes	PU	10–18	A	decaBDE, esters of TBBPA	150	Insulation panels
Polyterephthalate	PET, PBT	8–11	A	brominated polystyrene, TBBPA derivatives	150	Relays, motors, switchgear and other EEE components
Unsaturated polyesters	UPE	13–28	R/A	TBBPA	150	Transportation, roof sheets, sanitary ware, switchgear and other EEE components
Polycarbonate	PC	4–6	R/A	Brominated polystyrene, TBBPA-derivatives	100	EEE components
Styrene copolymers	ABS and others	12–15	A	octaBDE, brominated polystyrene	50	Housing and other moulded parts for EEE

*1 Information added in this survey. A=additive; R= reactive

*2 Information added in this survey, based on Lassen *et al.*, 1999

Concentrations of BFRs in materials

The concentration of BFRs added to the different polymers depends on:

- The efficacy of the BFR (e.g. determined by the bromine content of the BFR) and synergists;
- The desired level of flame retardancy (tested by different flammability tests);
- The flammability of the base resin (expressed by the "limiting oxygen index" or "LOI" of base resin).

A further description of the concentrations of BFRs in different plastic materials is included in Appendix 4.

Main application areas

The main application areas of materials with BFRs as flame retardants are:

- Electrical and electronic equipment;
- Wiring and power distribution;
- Textiles, carpets and furniture;
- Building materials;
- Means of transportation (vehicles, trains, airplanes, ships, etc.);
- Paint and fillers.

A breakdown of the total market volume by application area at global or EU level is not available, but a detailed breakdown of the use of BFRs by application area in Denmark in 1999 is shown in Table 22 in section 3.3.3.

A list of applications of decaBDE is shown in Appendix 5 (Table A5-1). Apart from the uses in insulation materials (mainly HBCDD), the list of decaBDE applications covers the main application areas of the additive BFRs. The application of decaBDE is therefore described in more detail in the following.

DecaBDE

A breakdown of the consumption of decaBDE by application area in the EU is not available. In the U.S.A., around 2010, the consumption of decaBDE could be broken down as follows (excluding import in articles): Automotive and transportation 26%, building and construction 26%, textiles 26%, electrical and electronic equipment (EEE) 13% and others 9%. As a consequence of the restriction of decaBDE in the RoHS Directive, the use in electrical and electronic equipment would be lower in the EU. DecaBDE may still be used for manufacturing of some types of EEE which are outside the scope of the RoHS Directive or applications currently exempted.

The 2010 VECAP report stated that textiles account for one third of the volume of decaBDE sold (VECAP, 2010). Based on the supply figures from the 2010 VECAP report, this suggests that around 4,500 tonnes per annum are used in plastics/polymers and 2,250 tonnes per annum are used in textiles (UK, 2012).

Polymeric applications - According to the Annex XV report for decaBDE (UK, 2012), the following range of polymers has been identified as possible applications for decaBDE (please note that this is not a definitive list):

1. Polyolefins – decaBDE may be used in polypropylene (PP), polyethylene (PE), polypropylene ether (PPE) and ethylene vinyl acetate (EVA) polymers. Examples of end uses where decaBDE may be present include power cables and wires insulation, conduits, stadium seating, electrical connectors, electrical boxes, heat shrinkable material, shipping pallets and roofing membranes. DecaBDE may also be used in polyethylene wood composites used in construction.

2. Styrenics – decaBDE can be used in high-impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS) and polyphenylene oxide/polystyrene blends (PPO/PS). RoHS restricts the use of decaBDE for end uses of these polymers in consumer electrical and electronic goods.
3. Engineering thermoplastics – decaBDE may be used in the following:
 - polyesters such as polybutylene terephthalate (examples include circuit breakers, sockets and electrical connectors) and polyethylene terephthalate (PET);
 - polyamides, e.g. nylon (used for injection moulding applications in transport e.g. wheel covers and handles, chair and seat belt mechanisms, under-hood applications);
 - polycarbonate (PC) (used to make window housings in trains and aircraft, as well as automotive components such as headlamps and bumpers) and polycarbonate blends, e.g. PC/ABS;
 - polyimides (used for bearings in aircraft, seals and gaskets) and
 - melamine (textile finishing applications).
4. Thermosets – decaBDE is used in unsaturated polyester resins (UPS) (used to make a variety of articles for construction including modular building parts, roofing materials, porch canopies and decorative mouldings) and epoxy resins (these have applications in electronics, construction and aerospace).
5. Elastomers – decaBDE may be used in ethylene propylene diene monomer (EPDM) rubber (automotive radiator hoses and seals, roofing membranes, cable and wire insulation), styrene-butadiene rubber (SBR), thermoplastic polyurethanes (TPUs) (automotive and wire and cable applications) and ethylene vinyl acetate (EVA) elastomers often used for wire and cable insulation.
6. Waterborne emulsions and coatings such as acrylic emulsions, polyvinyl chloride emulsions, ethylene vinyl chloride emulsions and urethane emulsions. These are used for coating, impregnation and saturation of fibrous materials such as paper, nonwovens (e.g. felt) and woven textiles.

For many of these polymers, other FRs will also be used. The choice of FRs will depend on the fire performance that is required and the cost (both of the raw materials and the sale price to the end user). Typically, decaBDE is used in plastics/polymers at loadings of 10-15% by weight, though in some cases loadings as high as 20% may be required (stakeholder communication, 2011). The amount of flame retardant that is required for any given application depends on a number of factors; the fire performance required for the finished product (in some cases determined by fire safety standards), the effectiveness of the flame retardant (and synergist) and the physical properties required for the end product (e.g. colour, density, stability, etc.) (see Appendix 5 for more information).

Textile applications - DecaBDE is a versatile flame retardant that can be used to treat a wide range of synthetic, blended and natural fibres. The versatility of decaBDE makes it particularly suitable for the most popular textile fabrics used in the upholstery market at present: blends of polyester, acrylic and viscose fibres. End-uses identified in 2003 for textiles treated with decaBDE are listed in Table 15. The main end-uses were upholstery, window blinds, curtains (e.g. for public occupancy areas including hospitals), mattress textiles (some Member States have specific fire performance requirements for mattresses used in public buildings, e.g. prisons), tentage (e.g. military tents and textiles also commercial marquees, tents and canvasses) and transport (e.g. interior fabrics in cars, rail passenger rolling stock and aircraft) (UK, 2012). It was suggested in the EU RAR that upholstery accounts for three quarters of the total UK textiles usage of decaBDE (EC, 2002). It is possible that decaBDE is also used in synthetic latex foam in mattresses, but no further details of this use are available (UK, 2012).

DecaBDE is not used in applications with the potential for prolonged contact with skin e.g. clothing textiles, bedding, or protective clothing. In 2003, EBFRIIP indicated that decaBDE does not play an important role as a flame retardant for carpets (as cited by RPA, 2003) and recent information confirms that it is not used for commercial and residential carpets (UK, 2012). However, some aircraft manufacturers have identified carpets as a possible application for decaBDE (UK, 2012).

TABLE 20
USE OF DECA BDE IN TEXTILES (RPA 2003, AS CITED BY UK, 2012)

Material	Domestic sector		Contract sectors					
	Upholstery	Filters for cookers	Blinds	Blackout curtains	Upholstery (hospitals, theatres, etc.)	Automotive textiles	Geotextiles and wall coverings *1	Other
Cotton	✓		✓	✓				
Polyester	✓	✓	✓	✓	✓	✓		
Acrylic	✓							
Viscose	✓							
Polyamide (nylon)	✓							
Polypropylene	✓							
Blends of all above	✓							
Polyester cotton	✓		✓	✓	✓			✓
Glass		✓	✓				✓	

*1 'Geotextiles' are textiles used in civil engineering to replace natural stabilisation of (for example) earthworks while natural materials grow and they are usually positioned underground (possible areas of application include tunnels) (UK, 2012).

C-octaBDE and c-pentaBDE

According to the EU Risk Assessment for octaBDE, in Europe c-octaBDE was primarily used in acrylonitrile-butadiene-styrene (ABS) polymers at 12-18% weight loadings in the final product. Around 95% of the total octaBDE supplied in the EU is used in ABS (ECB, 2003). Other minor uses, accounting for the remaining 5% usage, include high impact polystyrene (HIPS), polybutylene terephthalate (PBT) and polyamide polymers, at typical loadings of 12-15% weight in the final product. Other uses that have been reported for octaBDE include nylon and low density polyethylene polycarbonate, phenol-formaldehyde resins and unsaturated polyesters (OECD, 1994), and in adhesives and coatings (WHO, 1994).

As indicated elsewhere, the use of octaBDE is assumed to have ceased worldwide, but a use of the octaBDE in polycarbonate in Denmark has been confirmed for this survey.

Flame retarded ABS with octaBDE has predominantly been used for enclosures and structural parts of electrical and electronic equipment and may be present in recycled plastics from electrical and electronic waste.

It is considered that between 90% and 95% of the use of c-PentaBDE globally was for the treatment of polyurethane (PU) foam (UNEP, 2012a). These foams were mainly used in automotive and upholstery applications. Minor uses included textiles, printed circuit boards, insulation foam, cable sheets, conveyer belts, lacquers and possibly drilling oils (UNEP, 2012a). The total amount of c-PentaBDE used for these minor uses is estimated to account for 5% or less of the total usage. An approximate distribution of global c-PentaBDE use of 36% in transport, 60% in furniture and a 4% residual in other articles is considered by UNEP (2012) to be reasonable and is generally consistent with the analytical data for different waste streams. The average content of c-PentaBDE in PUR foam is reported to be around 3-5 % (w/w) for upholstery, cushions, mattresses, and carpet padding used in particular in countries with flammability standards for these applications (e.g. United States, United Kingdom). PUR foam in the transport sector might have been used in lower concentrations for applications such as seats or arm/head rests at 0.5-1 % (w/w) (UNEP, 2012a).

HBCDD

The main part (90 %) of HBCDD used in the EU is used as a flame retardant in polystyrene (PS). PS-containing HBCDD, in the form of Expanded PS (EPS) or Extruded PS (XPS), is mainly used as rigid thermal insulation panels/boards for buildings and for road and railway constructions to prevent frost heaves and provide a lightweight load-spreading construction material. HBCDD is also used to provide flame retardant properties to textiles (for furniture, automobile interiors. etc.) and in smaller quantities in high-impact PS (HIPS). The latter polymer material is typically used in electronic and electrical equipment. Some other minor uses have been reported, but it is not clear whether they are relevant for the EU.

Use in EPS and XPS. - Nearly all EPS-containing HBCDD is used in the building and construction industry, with smaller quantities used in (non-food) packaging.

According to an Annex XV report for HBCDD, in Europe some 420,000 tonnes of EPS is used for construction applications; 170,000 tonnes of this is used in Eastern Europe (Sweden, 2008). In Western Europe approximately 70 % of this EPS is in flame-retardant grades, while in Eastern Europe it is more than 99 %. Packaging uses some 250 000 tonnes of EPS in Western Europe, of which approximately 10 % is flame-retardant grade. HBCDD is incorporated as an integral and encapsulated component within the polymer matrix with uniform concentration throughout the bead. The maximum concentration of HBCDD in EPS beads is assumed to be 0.7 %. (IOM, 2009) EPS foam is produced from EPS beads through pre-expansion of the beads with dry saturated steam, drying with warm air and shaping in shape moulds or in a continuous moulding machine.

XPS with HBCDD is used in the construction industry as rigid insulation boards in constructions and in road and railway embankments to protect against frost damage and as thermal insulation. It is also used as insulation in sandwich constructions in vehicles such as caravans and lorries for cold or warm transport of goods. (Sweden, 2008)

Use in HIPS - It is believed that the use of HBCDD in HIPS is small (less than 10% of total use) and that its use in textiles is also small (IOM, 2008). HIPS containing HBCDD is used mainly in electronic and electrical equipment such as video and stereo equipment, distribution boxes in electrical lines, and refrigerator lining.

Use in textiles -For the use in textiles, HBCDD is formulated to polymer-based dispersions (e.g. acrylic or latex) in water (IOM, 2008). This dispersion is then applied to the textile. The dispersion is applied to the textile by back coating, either as a paste which is applied to the textile and a scratch knife defines the final thickness, or as a foam layer which is pressed on the textile through a rotating screen. The use of rotation screen is limited. Flame-retarded textiles treated with HBCDD are typically technical textiles and furniture fabric. HBCDD has certain particular advantages when used on synthetic fibres, although this does not exclude its use on cotton. Typical end products are uphol-

stered furniture, draperies, interior textiles and automobile interior textiles. Draperies would only be treated by back-coating in specific (institutional) end-uses, and then typically only when there are specific fabric-related reasons for using HBCDD. The HBCDD particles used for textile back-coating need to be very small and micronised. DecaBDE is the BFR of choice for back coating, as HBCDD is more expensive (IOM, 2008). According to industry information (as cited by IOM, 2008), the concentration of HBCDD in the dispersion may range from 5 to 48 %. However, additional product information indicates that a likely concentration of HBCDD in the coated layer may be about 25 %, corresponding to 10 - 15 % in the final dilution of the dispersion. Water and solvents will leave the preparation when dried and concentrations of flame-retardants in the coating layer will be higher than in the preparation. The formulated product is used on technical textile and furniture fabric, on cotton fabrics, and on cotton polyester blends. For the calculations of exposure, the RAR assumed that the backcoating layer of the finished textile contains 25 % HBCDD. HBCDD is usually applied with antimony trioxide as a back-coating in a mass ratio of 2:1 (i.e. about 6-15 % HBCDD and 4-10 % antimony oxide by weight) (National Research Council, 2000). (IOM, 2009)

TBBPA and derivatives

According to the EU RAR, the primary use of TBBPA, accounting for approximately 90% of TBBPA used, is as a reactive BFR in the manufacture of epoxy and polycarbonate resins (ECB, 2006). When used as a reactive BFR it becomes covalently bound in the polymer and is only present in trace concentrations as unreacted monomer. When used as a flame retardant in the production of epoxy resins, TBBPA along with bisphenol-A is reacted with epichlorohydrin. Commercial flame retardant epoxy resins contain up to approximately 20% bromine (the maximum bromine content that can be achieved in epoxy resins is 48% if no bisphenol-A is used in the formulation). The main use of these resins is in the manufacturing of rigid epoxy-laminated printed circuit boards. The FR4-type laminate is by far the most commonly used laminate and is typically made by reaction of around 15-17% TBBPA in the epoxy resin (ECB, 2006). The bromine content of these circuit boards is around 18-20% on a resin weight basis or 9-10% on a laminate weight basis (the resin makes up around 50% of the total weight of the laminate). The most commonly used laminate is approximately 1.6 mm thick and the TBBPA content has been estimated at around 0.42 kg/m² (Lassen *et al.*, 1999). This type of laminate is typically used in computers and telecommunications equipment. TBBPA is used in more than 90% of FR-4 printed circuit boards. (VECAP, 2011) Antimony oxide is generally not used in conjunction with tetrabromobisphenol-A in reactive flame retardant applications.

As well as use in the printed circuit board laminate itself, epoxy resins containing TBBPA are also used to encapsulate certain electronic components (e.g. plastic/paper capacitors, microprocessors, bipolar power transistors, IGBT (Integrated Gate Bipolar Transistor) power modules, ASICs (Application Specific Integrated Circuits) and metal oxide varistors) on the printed circuit board (ECB, 2006). The concentration of TBBPA in the production of the resins used for encapsulation is relatively low, approximately 2%.

TBBPA is also used as a reactive flame retardant in polycarbonate (PC) and unsaturated polyester resins. Polycarbonates are used in communication and electronics equipment, electronic appliances, transportation devices, sports and recreation equipment, lighting fixtures and signs. Unsaturated polyesters are used for making simulated marble floor tiles, bowling balls, glass reinforced panels, furniture parts, sewer pipes coupling compounds, automotive patching compounds, buttons, and for encapsulating electrical devices.

Where TBBPA is used as an additive flame retardant, it is generally used with antimony oxide. ABS resins are used in automotive parts, pipes and fittings, refrigerators, business machines and telephones and other appliances.

TBBPA is also used in the manufacture of derivatives. According to the EU RAR, the main derivatives produced from TBBPA are TBBPA dimethylether, TBBPA dibromopropylether (TBBPA-

BDBPE), TBBPA bis(allylether), TBBPA bis(2-hydroxyethyl ether), TBBPA brominated epoxy oligomer, and TBBPA oligomers (ECB, 2066). The main use of these derivatives is as flame retardants, usually in niche applications. The total amount of tetrabromobisphenol-A derivatives used is less than the amount of TBBPA used (approximately 25% on a weight basis) (ECB, 2006). As indicated above, TBBPA-BDBPE is the only TBBPA derivative registered in the EU (indicating that it is the only derivative used in volumes of more than 100 t/y).

DBDPE

Polymer applications - According to UK Environmental Risk Assessment, the major use of DBDPE in Europe and the UK (accounting for at least 90% of the tonnage supplied) was as an additive flame retardant for polymers (Environment Agency, 2007). The properties of DBDPE make it suitable for applications involving high temperature, a requirement for colour stability or where recycling is anticipated. The substance can be used with a variety of polymers, similar to decaBDE. A summary of applications is provided by Environment Agency (2007) and includes adhesives, building insulation and roofing materials, cables, coatings, electronic components and transportation. It has not been possible to obtain a breakdown of the amounts of DBDPE used in each application. Typical loading rates are similar to decaBDE. DBDPE has also been detected in a water pipe insulating tube consisting of two different types of plastics (an inner insulating layer and an outer protective layer) (Kierkegaard *et al.*, 2004).

Textile applications - DBDPE is an additive flame retardant for textiles used for furniture and furnishings (Environment Agency, 2007). The quantities are relatively low compared to polymer applications and account for less than 10% of the total volume. No information was available to the Environment Agency (2007) about specific applications, but they are likely to be similar to those for decaBDE (i.e. latex-based backcoatings for drapery and upholstery fabric). Typical loadings for various fabrics are thought to be in the range of 30-80 g dry coating per m² of fabric; the brominated flame retardant makes up around 30-40% of the dry coating weight (Environment Agency, 2007).

Polymeric flame retardants

A number of polymeric BFRs are marketed covering the major application areas of additive BFRs. Some brominated polymers, such as brominated polystyrene and brominated epoxy polymers, have been used for many years, whereas others have been introduced as alternatives to decaBDE and HBCDD only in recent years.

The polymeric BFRs are introduced by industry as the safest and most “elegant” flame retardants of high molecular weight man-made materials. According to manufacturers, due to their low solubility in water, polymeric flame retardants, once incorporated into the end-product plastic matrix, become integrated with the plastic and leaching is not expected to occur. (ICL, 2012) Furthermore, they do not migrate to the surface of the plastic during aging, thus eliminating any potential blooming in the finished product.

As an example ICL-IP promotes several ranges of brominated polymeric flame retardants for most applications, and the other major manufacturers have similar portfolios of polymeric BFRs:

- **FR-1025:** brominated polyacrylate (molecular weight: 600,000 dalton; 71% Br) is especially suitable for applications in engineering thermoplastics (PET, PBT, nylon and styrenic copolymers). Marketed for use in the automotive and electronics industry.
- **F-2000 series:** brominated epoxy polymers with a wide range of molecular weight. As an example the F-2100 (molecular weight: 20,000 dalton; 52% Br) is suitable for PBT and PET used in electronics.
- **F-3000 series:** end-capped brominated epoxy polymers with various molecular weights. As an example the F-3100 (molecular weight: 15,000 dalton; 52-54% Br) is recommended for use in

engineering thermoplastics such as PBT, styrenic copolymers and their alloys ⁵and polyamides used in the automotive industry.

- FR-803P: brominated polystyrene (molecular weight: 600,000 dalton; >66% Br) is most suitable for application in engineering thermoplastics such as polyamide, PET, PBT and their alloys in the automotive and electronics industry.
- FR-122P, a proprietary polymeric flame retardant (molecular weight: 600,000 dalton; >66% Br) (ICL, 2012) is recommended for use in EPS and XPS.

No data on the actual uses of the polymeric BFRs and the used volumes have been available. As mentioned elsewhere, the polymeric BFRs are not subject to REACH registrations; consequently, no information in their use is available from ECHA's registration web-site.

Other BFRs

Information on the application of other BFRs is briefly listed in Table 21. If no reference is indicated, the information builds on data provided in Annex 3 or elsewhere in this report.

TABLE 21
APPLICATION OF OTHER BROMINATED FLAME RETARDANTS AND AN INDICATION OF THE EXTENT TO WHICH THE SUBSTANCES HAVE BEEN REPORTED IN THE NORDIC OR ARCTIC ENVIRONMENT

Abbreviation	Common name/description	Application	Registered import /production t/y	Manufactured by major manufacturers
Additive BFRs				
4'-PeBPOBDE208	Bis(pentabromo-phenoxy) benzene	No data on application	import: 216 (2011, together with pentaBDE) not registered	
BEH-TEBP	Tetrabromophthalate ester	Primary replacement for pentaBDE in polyurethane foam together with EH-TBB (CECBP, 2008) Flame retardant plasticizer for PVC applications such as wire and cable insulation, coated fabrics, film and sheeting.	100-1000	x
BTBPE	Bis (tribromophenoxy) ethane	Has been the main substitute for octaBDE with a wide application profile. Flame retardant for HIPS, ABS, polycarbonate, thermoplastic, elastomers, unsaturated polyesters, adhesives, coatings, and textiles	import 82 (average 2006/2007; conf. for 2011)	x
DBDPE	Decabromodiphenyl ethane	Has a similar application profile as decaBDE. Is the main substitute for decaBDE in electrical and electronic products in which the use of decaBDE is restricted.	1,000 +	x

⁵ Alloys are made by mixing traditional polymers which have already been formed whereas copolymers are made by mixing of monomers

Abbreviation	Common name/description	Application	Registered import /production t/y	Manufactured by major manufacturers
DBE-DBCH	1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane	The substance was formerly marketed under the trade name Saytex BCL-462 (Albemarle), but is not marketed by any of the major manufacturers today. Reported to be used primarily in expandable polystyrene beads (used for thermal insulation in housing). It was also used as a flame retardant for extruded polystyrene foam and for adhesives in fabric and vinyl lamination, electrical cable coatings, high-impact plastic parts of appliances and some construction materials (CECBP, 2008)		
DBHCTD	Hexachlorocyclopentadienyl-dibromocyclooctane	No updated information on use identified Reported to be used as a flame retardant is reportedly in “styrenic polymers” (ICPS, 1997)		
DPTE	1,3,5-tribromo-2-(2,3-dibromopropoxy)benzene	No updated information on use identified. Reported to be used as flame retardant in extrusion grade polypropylene (ICPS, 1997)		
EBTEBPI	Ethylenebis(tetrabromophthalimide)	Has a similar application profiles as decaBDE. Used as alternative to decaBDE in particular in electrical and electronic equipment.	100 - 1,000 Imp: 181 (2011)	x
EH-TBB	Ethylhexyl tetrabromobenzoate	Primary replacement for pentaBDEs in polyurethane foam together with BEH-TEBP. (CECBP, 2008)		x
HBB	Hexabromobenzene	No updated information on use identified. Reported to be used been used as a flame retardant in polymers, plastics, textiles, wood and paper. Its primary uses have been reported in the plastics, paper and electrical industries (CECBP, 2008)		
PBEB	Pentabromoethylbenzene	No updated information on use identified Reported to be used for textiles; adhesives; polyurethane foam. Thermoset polyester resins, coatings. Additive for unsaturated polyesters. (ICPS, 1997)		

Abbreviation	Common name/description	Application	Registered import /production t/y	Manufactured by major manufacturers
PBT	Pentabromotoluene	No updated information on use identified. Reported to be used for unsaturated polyesters; polyethylene; polypropylenes; polystyrene; SBR-latex, textiles, rubbers; ABS (ICPS, 1997)		
RDT-7 (partly)	Phenoxy-terminated carbonate oligomer of TBBPA	Flame retardant for thermoplastic resin systems		x
TBA	Tribromoanisole	No information on actual uses identified		
TBBPA-bAE	TBBPA- bis (allyl ether)	Additive flame retardant for EPS and in foam polystyrene. The unsaturated end groups provide the unique function of initiating FR performance.		x
TBBPA-BDBPE	TBBPA- bis (2,3-dibromopropyl ether)	Suitable for polyolefin and styrenic resins. End use in EEE.		x
TBBPA-BGE	Brominated epoxy	Used to stabilize plastic compositions containing active halogen atoms such as flame retardant Polystyrene foam (XPS). It can also be used as a FR in epoxy formulation		x
TBP-AE	Tribromophenyl allyl ether	Additive flame retardant for EPS and foamed polystyrene		x
TTBNPP	Tris(tribromo-neopentyl)phosphate	Additive flame retardant developed for applications such as PP and HIPS. With high UV and light stability. End use in EEE.		x
TTBNPP	Tris(tribromo-neopentyl)phosphate	Additive flame retardant developed for applications such as PP and HIPS. Good UV and light stability.	100-1000	x
TTBP-TAZ	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine	Major use of TTBP-TAZ is in ABS and HIPS	1,000 - 10,000	x
-	Phenoxy-terminated carbonate oligomer of TBBPA	For thermoplastic resin systems	not subject to registration	x
-	Brominated Butadiene/Styrene Block Copolymer	Alternative to HBCDD marketed by three major manufacturers of BFR. For expanded polystyrene (EPS/XPS) for thermal insulation applications.	not subject to registration	x

Abbreviation	Common name/description	Application	Registered import /production t/y	Manufactured by major manufacturers
-	End Capped Brominated Epoxy	Suitable for use in HIPS and ABS including electronics applications	not subject to registration	x
-	Polydibromo-styrene copolymer	Designed for polyamides and thermoplastic polyesters (PBT and PET) which are used in EEE and means of transport	not subject to registration	x
-	Physical blend of brominated polystyrene and a polyester resin	Designed specifically for injection-molding grades of polybutylene terephthalate (PBT). Additive that works well in unfilled, fiberglass and fiberglass/mineral-reinforced PBT composites	not subject to registration	x
-	Ammonium bromide	Mainly used as flame retardant for chipboard.		x
Reactive BFRs				
DBNPG	Dibromoneopentyl glycol	Used in CFC-free foam systems designed to meet more stringent standards of flame retardancy.	100-1,000	x
DBP	2,4-dibromophenol	No updated information on use identified Reported to be used for epoxy resins; phenolic resins; intermediates (ICPS, 1997)		
HEEHP-TEBP	Mixture of the diester/ether diol of tetrabromophthalic anhydride and phosphate ester.	Reactive diol for rigid polyurethane and polyisocyanurate foams, urethane elastomers and coatings	100 - 1,000	x
PBB-Acr	(Pentabromophenyl)methyl acrylate	Latex, rubbers		x
TBNPA	Tribromoneopentyl alcohol	Used as a reactive intermediate for high molecular weight flame retardants, particularly in the production of phosphorus and bromine containing FRs		x
TBP	2,4,6-tribromophenol	Reactive flame retardant with a high content of aromatic bromine, mainly used as intermediate in the production of other BFRs. It is also an effective fungicide and wood preservative	1,000-10,000	x
TEBP-Anh	Tetrabromophthalic anhydride	Designed as a reactive intermediate for use in unsaturated or saturated polyesters, polyols, esters and imides	100-1,000	x

Abbreviation	Common name/description	Application	Registered import /production t/y	Manufactured by major manufacturers
-	Halogenated polyetherpolyol B	Particularly well suited for the production of rigid polyurethane foams.	1,000 - 10,000	x
-	Aromatic reactive diol	For rigid polyurethane and polyisocyanurate foams, urethane elastomers and coatings		x
-	Tetrabromophthalic anhydride based diol	Uses include rigid foam, polyurethane RIM, elastomers, coatings, adhesives, and unsaturated polyesters.	1,000 - 10,000	x

*1 See section 5.3.2. N: among the BFRs detected in highest concentration in the Nordic Environment. A: detected in Arctic – marked in bold and underline, suggested as particular relevant for monitoring in the Arctic.

3.3.3 Consumption of BFRs in Denmark

The only detailed survey of the use of BFRs in Denmark dates from 1999 (Lassen *et al.*, 2009). The study consisted of two parts: a substance flow analysis of brominated flame retardants and an assessment of alternatives to brominated flame retardants.

The consumption by end use area and main group of BFRs is shown in Table 22. The total consumption was estimated at 320-660 tonnes broken down to 47% TBBPA and its derivatives, 12% PBDEs, 1% PBBs, 11% HBCDD and 29% other brominated flame retardants. About 44% of the total was used as reactive constituents.

The principal fields of application were:

- Electric and electronic equipment accounting for about 70% of the total
- Building materials accounting for about 15% of the total
- Transportation accounting for about 12% of the total

The use of brominated flame retardants was widespread. Brominated flame retardants were present in almost all products containing electronic components i.e. virtually all electronic products and means of transport and a large portion of electric products. In addition, brominated flame retardants were used in a significant part of plastics in contact with live parts in electric equipment such as switches, plugs, and sockets for lighting. Brominated flame retardants were not produced in Denmark (and are still not). The total import of brominated flame retardants with chemicals, polymer compounds and plastic semi-manufactures for production in Denmark was 260-390 tonnes in 1997. Of this TBBPA accounted for about 54%, while PBBs and PBDEs in total accounted for only about 2%.

At that time, there had been a marked shift from PBDEs to TBBPA (and derivatives) in thermoplastics used in Danish production. The total consumption of decaBDE for manufacture in Denmark was 0.1-0.2 t/y while the consumption of TBBPA and derivatives was 34-42 t/y; of this 99% was used as additive BFR.

This trend was also seen for housings of imported electronics, although PBDEs were still present in many imported products. Assessments on the overall European consumption only indicated a decrease in the consumption of PBDEs in Northern Europe. BFRs other than TBBPA and derivatives appear to be dominating alternatives to the PBDEs today. Due to the RoHS restriction of PBDEs

and PBBs in electrical and electronic equipment (EEE), the presence of these substances in the first 5 use areas in Table 22 must be expected to be significantly lower today and only present in types of EEE still exempt from the RoHS Directive (e.g. medical devices and monitoring and control instruments) or beyond the scope of the directive (e.g. large-scale stationary industrial tools and large-scale fixed installations.)

Brominated polyetherpolyol was used reactively for production of rigid polyurethane foam for insulation in Denmark and HBCDD was used for production of expanded polystyrene for export.

There was at that time a significant difference between the consumption of BFRs in Danish production of plastics parts and the distribution of BFRs in the Western European market. PBDEs in Danish production only accounted for about 2% of the total BFR consumption in 1997 in comparison to approximately 26% and 11% of the W. European market in 1996 and 1998, respectively.

Imported goods accounted for about 90% of consumption with end products and at the same time the majority of the BFRs and BFR-containing raw materials used in Danish production were exported with the produced articles. The use of BFRs with final mixtures and articles in Denmark consequently reflected the general global use of the BFRs rather than the use of BFRs in Danish production.

The survey formed a basis for the development of an action plan for brominated flame retardants which was published in 2001 by the Danish EPA (Danish EPA, 2001).

TABLE 22
CONSUMPTION OF BROMINATED FLAME RETARDANTS IN END PRODUCTS IN DENMARK 1997

End use area	Total consumption of BFRs		Consumption of specific BFRs (t/y)				
	t/y	%	PBDE	TBBPA	PBB	HBCD	Other BFRs
Printed circuit boards	100-180	29	0.3-5.2	100-180			0-2
<i>Epoxy laminates</i>	92-150			92-150			
<i>Paper/phenolic laminates</i>	3-4.8		0.3-1	2.3-3.8			
<i>Electronic component encapsulates</i>	6-22		<2.2	7.4-22			
<i>Other plastic parts</i>	<4		<2	<2			<2
Housing of EE appliances and machines	80-130	21	3-10	56-89			25-49
<i>PC monitors</i>	48-73			34-52			14-21
<i>Notebook computers</i>	3-4			2-3			1-1.4
<i>Other office machines</i>	20-31			17-25			3.7-5.5
<i>TV-sets</i>	3-4		1-3	1-2			2-4
<i>Other consumer electronics</i>	2-6		0.5-2	0.5-2			2-6
<i>Medical and industrial electronics</i>	2-14		1-4	1-4			2-10
<i>Small household appliances</i>	0.5-2		0.5-1	0.5-1			0.5-1
Other parts of EE appliances and machines	20-50	7	5-14	3-8	0-2		16-43
<i>Switches, relay parts etc.</i>	10-25		2-6	2-6			8-20
<i>Moulding fillers</i>	2-5		2-5				2-5
<i>Other plastic parts</i>	6-20		1-3	1-2	0-2		6-18
Lighting	4-14	2	1-7	4-11			1-9

End use area	Total consumption of BFRs		Consumption of specific BFRs (t/y)				
	t/y	%	PBDE	TBBPA	PBB	HBCD	Other BFRs
<i>Sockets in lamps and fluorescent tubes</i>	4-7		1-3	4-7			1-3
<i>Plastic cover parts</i>	<3		<2	<2			<2
<i>Switches, electronic parts etc.</i>	<4		<2	<2			<4
Wiring and power distribution	30-80	11	7-29	4-15	1-5	2-4	20-49
<i>Rubber cables</i>	2-10		1-5		1-5		
<i>Other cables</i>	<5		0-5				0-5
<i>Wiring of houses</i>	11-26		2-7	2-7		2-4	7-14
<i>Contactors, relays, switches etc. for automation and power distribution</i>	15-35		4-12	2-8			13-30
Textiles, carpets and furniture	2-11	1.3	0-5			2-9	0-5
<i>Protective clothing</i>	<0.1		<0.1			<0.1	<0.1
<i>Curtains, carpets and tents</i>	<1		<1			<0.5	<0.5
<i>Furniture, Foam and stuffing</i>	2.2-9.7		<4			2.2-8.7	<4
Building materials	50-100	15	1-5	0-2		13-36	41-66
<i>Expanded polystyrene, EPS</i>	0.5-2.7					0.5-2.7	
<i>Extruded polystyrene foam, XPS</i>	11-29					11-29	
<i>Polyurethane foam</i>	40-60						40-60
<i>Other uses</i>	1-7		1-5	0-2		1-4	1-6
Paint and fillers	0.6-1.7	0.2	0.1-0.5				0.5-1.2
<i>Paint</i>	0.1-0.3		0.1-0.3				
<i>Fillers and wood proofing</i>	0.5-1.4		0-0.2				0.5-1.2
Transportation	30-90	12	13-46	14-52		9.4-30	19-71
<i>Cars, lorries and busses</i>	24-72		13-41	12-37		9.4-29	18-52
<i>Trains</i>	0.3-4		0.04-1.7	0.3-4			0.3-4
<i>Other means of transport</i>	1-15		0-3	1-11		0-1.5	1.5-15
Other uses	<3	0.3	0-2	0-2		0-1	0-2
Total (round)	320-660	99	30-120	180-360	1-7	26-80	120-300

DecaBDE in other products than electronic and electrical equipment

A survey of decaBDE in products other than electronic and electrical equipment from 2007 (Mortensen *et al.*, 2007) detected decaBDE in tents, cars, and heat-shrink tubing. DecaBDE was not detected in upholstered furniture, bedroom articles, cables, furnishing fabrics, glue, nursing articles, baby and children's articles, paints and joint fillers. The information on decaBDE import as part of finished articles was, however, subject to considerable uncertainty.

Updated information of the use of BFRs in Denmark

It has been beyond the scope of the current survey to prepare an updated inventory of the use of BFRs in Denmark. It must be expected that more than 90% of the BFRs in articles placed on the Danish market is still imported, and the presence of BFRs for electrical and electronic equipment, wiring and means of transportation will likely reflect the general EU market for these articles.

For two application areas, the use of BFRs differs significantly among the EU Member States: Insulation materials for buildings and construction and furniture/textiles.

Data from the Danish Product Register

Data on brominated flame retardants registered in the Danish Product Register were retrieved in April 2013 on the basis of the gross lists of brominated flame retardants shown in Table 1 and 2.

The Danish Product Register includes substances and mixtures used occupationally and which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). Of the brominated flame retardants, only a few are classified as dangerous. For the other non-classified substances, the registration will only occur if they are constituents of mixtures which are classified and labelled as dangerous due to the presence of other constituents. Polymer compounds and masterbatches used in the production of plastics are not covered by the notification scheme. The data consequently do not provide a complete picture of the presence of the substances in mixtures placed on the Danish market. As stated above, the amounts registered are for occupational use only. However, for substances used for the manufacture of mixtures in Denmark, the data may still indicate the quantities of the substances in the finished products placed on the market both for professional and consumer applications.

In total 10 substances were registered as present in imported or produced mixtures. The registered substances are listed in Table 23. The data for the 9 of the substances are confidential because mixtures containing each substance were reported by less than three companies or less than three different mixtures with the substance were reported.

TABLE 23
BFRS REGISTERED IN THE DANISH PRODUCT REGISTER MARCH 2013

CAS No	Substance name (as indicated in the Product Register)	Abb.
79-94-7	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol	TBBPA
1163-19-5	Decabromodiphenyl oxide	decaBDE
12124-97-9	Ammonium bromide	-
20566-35-2	2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	HEEHP-TEBP
25637-99-4	1,2,5,6,9,10-Hexabromocyclododecane	HBCDD
26040-51-7	Bis(2-ethylhexyl) tetrabromophthalate	BEH-TEBP
32588-76-4	N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide)	EBTEBPI
52434-90-9	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	TDBP-TAZTO
68441-62-3	2-butyne-1,4-diol, polymer with 2-(chloromethyl)oxirane, brominated, dehydrochlorinated, methoxylated	-
88497-56-7	Benzene, ethenyl-, homopolymer, brominated	-

The only substance registered in significant amounts (production and import of 101 t/y) was halogenated polyetherpolyol B, which is registered in a volume of 1,000-10,000 t/y at EU level. The application of the substances is discussed below.

TABLE 24
BROMINATED FLAME RETARDANTS IN MIXTURES PLACED ON THE DANISH MARKET IN 2011 AS REGISTERED IN THE DANISH PRODUCT REGISTER

CAS No	Chemical name	No of mixtures	Registered tonnage, t/y		
			Production + import	Export	Consumption *1
68441-62-3	2-butyne-1,4-diol, polymer with 2-(chloromethyl)oxirane, brominated, dehydrochlorinated, methoxylated	4	101	89	12
Other BFR	9 CAS No	28	4,9	1,5	3,3
Total		32	106	91	15

*1 Total content of mixtures placed on the Danish market

Use of BFRs in Danish production

Data on the import of brominated flame retardants with polymer raw materials for production in Denmark was in the 1999 survey obtained through a questionnaire in co-operation with the Danish Plastics Federation (Plastindustrien). As part of this survey, a request for updated information was sent to suppliers of raw materials for plastics by the Danish Plastics Federation and to manufacturers of paints and adhesives via the Danish Coatings and Adhesives Association.

Limited information was obtained on BFRs in raw materials for plastics; the answers did not provide a comprehensive view of import of BFRs with plastic materials (compounds and masterbatches).

Besides information on BFRs in raw materials for production of insulation materials described below, it was reported that about 60 t/y octaBDE in polycarbonate was imported for use in the electronics industry. Some of the polycarbonate was fiberglass reinforced. OctaBDE may still be used for applications exempt from the RoHS Directive. The use of octaBDE in Denmark was unexpected, but has been confirmed by a follow up request.

In the 1999 survey, the main additive BFR used in raw materials for the Danish plastics industry was TBBPA and derivatives, but no information on the continued use of these substances was obtained.

None of the Danish manufacturers of paints and coatings use BFRs in production according to the information obtained. Furthermore, no imports of BFRs in paint and adhesives are registered in the Danish Product Registry.

As shown in Table 14, an import in 2011 of 2 tonnes of EBTEBPI and of 1 t/y the previous 5 years was registered by Statistics Denmark. It has not been possible to obtain any information on the use of the substances, but it is likely used for the production of plastic parts for electrical and electronic equipment.

Use of BFRs in insulation materials

Production and import of 101 t/y halogenated polyetherpolyol B and an export of 89 t/y of the substance were registered in the Product Register. The consumption in Denmark by final product can be estimated at 12 t/y. It is not clear from the available data whether the export concerns re-export (without any formulation in Denmark) or represents an export of mixtures formulated in Denmark. According to data from the SPIN Database (based on data from the Danish Product Register), the total annual registered consumption in Denmark varies considerably with 6 t/y in 2010 and 2009, 131 t/y in 2008 and 45 t/y in 2007.

According to information from the manufacturer of the substance, it is particularly suited as a reactive BFR for production of flame retardant rigid polyurethane (PU) foam. According to the survey from 1999, the major use of BFRs in Danish industry was the use of 80-120 t/y brominated polyetherpolyol used for manufacture of rigid PU foam; the consumption with end uses in Denmark was estimated at 40-60 t/y. The flame retardant rigid polyurethane foam was used for various insulation purposes within the construction industry. PUR foam has good insulation characteristics and was widely used within the building sector for cold-storage plants, freezing rooms and cold stores, e.g. at supermarkets, processing rooms in the food industry, and refrigerating holds in ships and in containers. Minor consumption areas were façade insulation, pre-insulated pipes, and joint filler foam. In 1999, these applications were usually flame retarded except for the latter three examples where the use of flame retardants depended on the actual application. This is likely still the situation. In a number of applications of rigid PU foam, flame retardants were not used in 1999 and probably still are not. These were domestic refrigerators and plain district heating pipes (some indoor uses, e.g. in factories, may imply the use of BFRs).

According to information obtained from the Danish Plastics Federation, about 1 t/y of HBCDD was used in Denmark for production of flame retarded EPS in 2011 corresponding to approximately 140 t/y flame retarded EPS if the HBCDD concentration is 0.7%. Compared to the 6-13 t/y HBCDD used in 1999 for production of flame retarded EPS for export, the consumption seems to have decreased significantly. In accordance with the general use of HBCDD in the EU, the majority of the flame retarded EPS was used for building insulation and a small part was used for packaging for electronic equipment. A new application area of flame retarded EPS in Denmark is zero energy houses with walls of EPS covered with plaster (an example of this application in Bozel, 2013).

Flame retarded EPS is used in some walls and sandwich constructions, but is not required by the building fire regulations in Denmark. In any case, the building fire regulations require that the EPS is covered by fire-resistant materials (e.g. plaster). The main driver for the use of flame retardant grades is to avoid fire at the construction site and by mounting the EPS sheets, according to the Danish Plastics Federation.

Approximately 90-95% of the 30,000 t/y EPS used in Denmark (for all applications) is produced in Denmark while the rest is imported from Germany and Poland. Data have not been obtained on the possible content of BFRs in imported EPS sheets. If all of the imported EPS was flame retarded, the total HBCDD content would be approximately 21 t/y.

The major use of HBCDD in articles in 1999 was HBCDD in imported XPS, where the sheets generally contained HBCDD. Total consumption of HBCDD was estimated at 11-29 t/y (Table 22). The sheets are mainly used below ground for basement insulation, below parking decks, patios, artificial turf, etc.; flame retardants are not required for these uses. According to the Danish Plastics Federation today, $\frac{3}{4}$ of the total volume is imported from Scandinavia and does not contain flame retardants, while $\frac{1}{4}$ is imported from Germany and Austria and contains HBCDD. The application areas are the same for sheets imported from Scandinavia and other countries. The total imported volume was not reported.

In the import/export statistics, the EPS and XPS sheets for insulation are included in the commodity group 3921 11 00: "Other plates, sheets, film, foil and strip, of plastics, – Cellular, – – Of polymers of styrene". The commodity group also includes some EPS used for packaging. The total import in 2011 was approximately 2,800 tonnes.

Use of BFRs in furniture and textiles

The 1999 survey estimated that the main use of BFRs in furniture and textiles was in imported upholstered furniture and in foam and stuffing. Flame retardants are not required for upholstered

furniture for the private market in Denmark. In 1999 furniture used for the contract market was normally flame retarded, but not with BFRs. At that time, seemingly no application of BFRs for textiles and furniture took place in Denmark. This conclusion was based on inquiries among the Danish industries and major foreign suppliers of brominated flame retardants for textiles. Inquiries among Danish producers of slap-stock foams also indicated that no brominated flame retardants were used in Danish production of foams. The estimated consumption of 2-11 t/y of BFRs was based on limited evidence, assuming that some furniture imported from countries with more extensive use of BFRs in textiles and furniture such as the U.K. and Ireland must contain BFRs. It has been beyond the limits of this survey to provide an updated view of the possible content of BFRs in furniture and textiles sold on the Danish market.

3.4 Historical trends in use

The historical trend in the global consumption of BFRs during the period from 1994 to 2011 is shown in Table 25. For 2011, the overview is based on information from different sources. For decaBDE the estimates are uncertain as the consumption has probably decreased in recent years, but no updated information has been available. The total use of BFRs has increased considerably from about 150,000 t/y in 1994 to approximately 360,000 t/y in 2011. During the last decade, the global consumption of HBCDD and TBBPA and derivatives has increased while the consumption of decaBDE, in particular during the last 5 years, has decreased. The consumption of other BFRs, estimated as the difference between the total and the estimated consumption of the three main BFRs, has increased significantly during the last decade.

The world market for flame retardants is expected to rise by about 5 % per year the next year in several market research reports, but forecasts specifically for the BFRs have not been found in the public part of the market research reports. The mineral yearbook from the United States Geological Survey states in the outlook section that " Use of BFRs, however, will likely increase at a slower pace than FRs in general because of legislative mandates and customer demand for more environmentally friendly materials." (USGS, 2012)

As a consequence of the inclusion of HBCDD in Annex A to the Stockholm Convention, it must be expected that the consumption of HBCDD will decrease significantly over the next 5 years, though a time-limited exemption has been granted for the use of HBCDD in EPS/XPS for building application. Alternatives to HBCDD have been introduced by all major manufacturers of BFRs, and alternatives are marketed with reference to the Stockholm Convention restriction.

The consumption of decaBDE is expected to decrease significantly due to voluntary phase out of decaBDE by major manufacturers in the USA, cessation of some exemptions under the RoHS Directive, possible requirements for authorisation under REACH and possible inclusion of the substance in Annex A to the Stockholm Convention.

The consumption of TBBPA and derivatives is more likely to increase in the coming 5 years in the absence of drivers for a reduced demand.

The use of other BFRs seems to have increased considerably. The main drivers have been a generally increased demand for flame retardants (in particular in Asia) and the introduction of alternatives to decaBDE, other PBDEs and recently HBCDD. The increasing trend will most probably continue in the coming years.

In the electronics industry, a trend away from the use of BFRs (or at least additive BFRs) has been reported, but it has not been possible to identify market data demonstrating a significant effect of this trend on the total consumption of BFRs.

TABLE 25
HISTORICAL TREND IN THE GLOBAL CONSUMPTION OF BFRS

	1994 *1		2001 *2		2011	
	t/y	% of total	t/y	% of total	t/y	Reference
C-pentaBDE	4,500	3	7,500	2.4	~0	*3
C-octaBDE	6,000	4	3,790	1.1	100-1000	*4
C-decaBDE	30,000	20	56,100	18	25,000-50,000	*5
HBCDD	Included in other	-	16,700	5	31,000	(POPRC, 2011, 2012)
TBBPA and derivatives	49,500	33	119,700	39	120,000-150,000	OSPAR, 2011
PBBs	<2,000	<1.5	106,210	34	0	2011
Other BFRs	~58,000	~39			~130,000-180,000 *6	2011
TOTAL	150,000	100	310,000 *1	100	~360,000	Clariant, 2013

*1 Source: OECD, 1994

*2 Source: BSEF, 2006, as cited by Lassen *et al.*, 2006. Total for 2001 is not available. Total for 2000 from Alae *et al.*, 2003 used as best estimate. Other BFRs estimated as difference between total in 2000 and the reported volumes for 2001.

*3 As of 2007 c-pentaBDE were not manufactured in Europe, Japan, Canada, Australia and the U.S.A., but no information on the status of the production in China was available (POPRC, 2007a)

*4 Since c-octa was no longer produced in the EU, USA and the Pacific Rim, no information was available that indicates it was being produced in developing countries (POPRC, 2007b). In 2013 OctaBDE was still imported to Denmark with polycarbonate raw materials, demonstrating that the substances is still produced in at least one country (details not provided).The indicated range is a rough estimate.

*5 Updated information only available for Europe (see section 3.3.1). In 2006 the market in the production/import volume in the U.S.A. is reported to be in the range of 25,000 – 50,000 t/y (US EPA Inventory Update Reporting as cited by Norway, 2013). The manufactured volume in China in 2005 is reported to be 30,000 t/y (Xia *et al.* 2005, Zou *et al.* 2007 as cited by Norway, 2013). Around 2005/2006 the global demand was in the range of 65,000-90,000 t/y. The volume in the USA and China has most probably decreased in recent years as result of regulatory actions (e.g. the EU ROHS Directive) and a voluntary phase out of the production in the USA. The total global volume in 2011 is roughly estimated at 25,000-50,000 t/y.

*6 Estimated as the difference between the total and the estimated consumption of the three main BFRs.

3.5 Summary and conclusions

Global and EU consumption

The total global production of BFRs has increased from 150,000 t/y in 1994 to approximately 360,000 t/y in 2011. The increase in production and consumption has primarily been in Asia. Historically, the PBDEs and TBBPA (and derivatives) have been the main BFRs accounting for nearly 2/3 of the global production in 1994. On a global scale, the BFRs account for approximately 20% of the consumption of flame retardants. A detailed breakdown by application area is not available. The major use area is electrical and electronic equipment, where the BFRs are also the dominating flame retardants. Other application areas include wiring and power distribution; textiles, carpets and furniture; building materials; means of transportation (vehicles, trains, airplanes, ships, etc.), and paints and fillers.

PBDEs - The global consumption of the PBDEs in 2001 was 56,100 t/y, of which decaBDE accounted for nearly 90%. No updated data for 2011 have been available. The consumption of pentaBDE and octaBDE has more or less ceased, while the consumption of decaBDE more recently has been decreasing due to regulatory action (e.g. the RoHS Directive) and a voluntary phase out of production in North America by the major manufacturers of BFRs. In the EU, the average consumption for the period 2010-2011 was 5,000-7,500 t/y. Approximately 1/3 was used for textiles, while the remaining part was used for plastic parts for means of transport and electrical and electronic equipment exempted from or out of scope of the RoHS Directive. DecaBDE in electrical and electronic equipment has apparently mainly been replaced by DBDPE and to a smaller degree by EBTEBPI, TTBP-TAZ, polymeric BFRs and non-brominated flame retardants (in some with a change in the base resin as well).

HBCDD - The global consumption of HBCDD has increased from 16,700 t/y in 2001 to 31,000 t/y in 2011. In the EU, the average consumption of HBCDD for the period 2010-2011 was 10,000-12,500 t/y and HBCDD is currently the BFR used in the highest quantities in the EU. The main part (90 %) of HBCDD is used as flame retardant in polystyrene in the EU. PS-containing HBCDD, in the form of expanded PS (EPS) or extruded PS (XPS), is mainly used as rigid thermal insulation panels/boards for buildings and for road and railway constructions to prevent frost heaves and provide a lightweight load-spreading construction material. The remaining part is used for the plastic material HIPS and for textiles.

TBBPA - TBBPA is still the main BFR accounting for about 40% of global production and is mainly used as a reactive flame retardant in printed circuit boards of electronic equipment. In the EU, the average consumption of TBBPA in 2010-2011 was 1,000-2,500 t/y; the substance accounts for a smaller part of the use of BFRs in the EU. About 90% of the consumption in the EU is as reactive flame retardants for printed circuit boards. The majority of the amount of TBBPA end-products (where it is present in reacted form) is imported into the EU in finished articles and components, primarily from Asia.

DBDPE and EBTEBPI – DPDPE seems to be a main substitute for decaBDE so far; the data indicated that DBDPE is among the main additive flame retardants in the EU, China and Japan. In the EU the registered production and import is indicated as 1000+ without an upper limit. EBTEBPI is registered in the EU with a production and import in the 100-1,000 t/y tonnage band.

Other BFRs - For the other BFRs, information on global and EU production/consumption is more limited. The global consumption has increased from about 110,000 t/y in 2001 to about 150,000 t/y in 2011 (also including DBDPE and EBTEBPI). For the non-polymeric BFRs, the registrations at ECHA's website indicate total import in tonnage bands (e.g. 100-1,000 t/y), but for the polymeric BFRs, no data are available as the polymers are not subject to registration. The BFRs registered in the highest tonnage (apart from the substances mentioned above) are the reactive halogenated polyetherpolyol B and TBP and the additive BFR TTBP-TAZ, which are all registered in the 1,000-10,000 t/y tonnage band. TBNPA is registered with confidential tonnage. Other additive BFRs registered with an import and production in the 100-1,000 t/y tonnage band are EBTEBPI, TTNPP, PBB-Acr and BEH-TEBP. The overall applications of the different BFRs is known and described in this survey, but detailed breakdowns of the use of each substance by end-application areas are not available.

Denmark

A comprehensive inventory of the use of BFRs in Denmark in 1999 exists. At that time approximately 90% of the consumption of BFRs in end products (mixtures and articles) were due to import of articles, primarily electrical and electronic products. Of the total consumption of 330-660 tonnes of BFRs, more than 70% was in electrical and electronic equipment. This is likely still the situation; the BFRs in articles on the Danish market are a reflection of the general use pattern in the EU and

globally rather than the use pattern of BFRs in Danish industry. A full update of the inventory has been beyond the scope of this survey.

In Danish industry, the main application of BFRs in 1999 and 2012 was in reactive brominated polyols used for production of flame retardant PU foams for insulation. DecaBDE was not used in production in Denmark in significant amounts either in 1999 or 2012, but decaBDE may be present in various imported articles e.g. cars and other means of transport. In 2011, an import of 2 tonnes of EBTEBPI was registered, likely used as a decaBDE alternative in the production of plastic parts for electrical and electronic products. In 2012, about 60 t/y octaBDE in polycarbonate was imported for use in the electronics industry in Denmark. The use of octaBDE is surprising, as the production of the substance has been phased out in most countries and the substance is banned for all uses in Denmark.

HBCDD was used for manufacture of EPS sheets for building applications and packaging for electronics. The total consumption for production in Denmark was about 1 tonne in 2012 as compared to 6-13 tonnes in 1999. In 1999 most of the produced flame retarded EPS was exported. In 1999 the main usage of HBCDD in building/construction materials was in imported flame retarded XPS, accounting for 11-29 tonnes HBCDD, and most likely still is. XPS imported from origins other than the Nordic countries currently contains HBCDD. For applications in buildings and construction in Denmark, flame retarded grades of EPS and XPS are not required, as the materials are combustible and need to be covered by a non-combustible material. Among other applications, flame retarded grades of EPS are to some extent used in in "zero energy" houses of a new construction, where the walls are built of flame retarded EPS sheets covered non-combustible materials.

Flame retardants are not required for upholstered furniture for the private market in Denmark. In 1999, furniture used for the contract market was normally flame retarded, but not containing BFRs. In 1999, the estimated consumption of 2-11 tonnes of BFRs was based on limited evidence, assuming that some furniture imported from countries with more extensive use of BFRs in textiles and furniture such as the U.K. and Ireland contain BFRs. This is probably still the situation.

Data gaps

Detailed data on the use of BFRs other than the PBDEs, HBCDD and TBBPA globally and in the EU are not available in the public literature. The public part of the REACH registrations provide some indication on the production and import in the EU tonnage bands, as mentioned, but the polymeric BFRs are not subject to registration and no information on the market volumes of these substances is available. The consumption of some of the other BFRs is expected to be increasing, but the lack of data constrain an assessment of the trends in the use of the BFRs and the monitoring of the effects of regulatory action. The lack of detailed data on the consumption by application areas furthermore constrains an assessment of the potential releases and exposure of humans and the environment.

4. Waste management

4.1 Waste from manufacture and industrial use of brominated flame retardants

The amounts of BFRs directed to waste from manufacture and industrial use of BFRs are generally not quantified in the EU Risk Assessment reports.

According to the VECAP guidelines of managing emissions of polymer additives through the proactive implementation of good practice, the following potential emissions have to be considered: residual products in the empty packaging; spills and floor sweepings; contaminated products; off specification products; test specimens; dust filters; sludge resulting from waste water treatment; and emissions potentially resulting from the selling of discharged big bags or internal bulk containers, without proper treatment. (VECAP, year not indicated). Potential land emissions, resulting from residual products in empty packaging, are considered to potentially represent the majority of overall potential emissions. As part of the programme, it is recommended that empty packaging should be disposed of using either incineration or a chemically secure landfill; VECAP has developed some guidelines on best available technique for emptying bags containing polymer additives (together with guidelines on a number of other management actions, please consult the guidelines for more information). According to the VECAP 2012 progress report, the total emission to land from all sources decreased from 575 g/t in 2008 to 60 g/t for decaBDE, from 170 g/t to 1 g/t for HBCDD and 175 g/t in 2008 to 0 g/t for TBBPA (Vecap, 2012). The reduced emission is partly a consequence of reduced generation of waste (lower quantities of flame retardant left in the bags) and partly a consequence of the direction of the waste from landfilling to incineration or chemically secure landfill.

With losses to waste in the range of less than 0.1 % of the volumes handled, losses from the manufacture and industrial sources are small compared with the losses to waste from the use and final disposal of mixtures and articles.

4.2 Waste products from the use of brominated flame retardants in mixtures and articles

An overview of the disposal of post-consumer BFR-containing mixtures and articles in Denmark is shown in Table 26 and further discussed in the below table. Aside from the post-consumer products, some solid waste will be generated from production of flame retarded plastic parts and printed circuit boards in Denmark. According to the 1999 survey, this waste fraction accounted for less than 10% of the total BFRs in solid waste (Lassen *et al.*, 1999).

TABLE 26
DISPOSAL OF BFR-CONTAINING POST-CONSUMER WASTE IN DENMARK

Product group	Disposal method in Denmark	Legislation
Electrical and electronic equipment including EEE in vehicles	<p>After a pre-treatment, the majority of the waste electrical and electronic equipment (WEEE) (excl. cables and wires) is exported for processing in other EU countries.</p> <p>A part is dismantled in Denmark. Plastic parts are disposed of to municipal waste incinerators</p> <p>A part of the WEEE is incorrectly disposed of to municipal waste incineration with waste from households and enterprises</p> <p>No overview of the final destination of BFR-containing plastic parts after dismantling abroad is available</p> <p>Some functioning equipment (in fact not WEEE) is exported to countries outside the EU for reuse of the equipment. The final disposal of the BFR-containing parts is not known</p> <p>Some WEEE is illegally exported to countries outside the EU. The final disposal of the BFR-containing parts is not known</p>	<p>According to the recast WEEE Directive (Directive 2012/19/EU) plastic containing brominated flame retardants has to be removed from any separately collected WEEE and shall be disposed of or recovered in compliance with the Waste Directive (Directive 2008/98/EC). The Danish WEEE statutory order (BEK no 1296 of 12/12/2011) states specifically that plastic with bromine content of less than 5 ppm (mg/kg) can be returned for reprocessing and recycling by companies that have been approved under the Environmental Protection Act § 33 or similar legislation abroad. For plastics containing more than 5 ppm BFRs, the Statutory Order indicates that it must be delivered to companies that are authorized to handle brominated waste approved under the Environmental Protection Act § 33 or similar legislation abroad.</p> <p>Note that the scope of the Danish statutory order goes beyond the WEEE Directive e.g. without a transitional period for some types of WEEE</p>
	<p>BFRs in printed wiring boards are probably incinerated in connection with the regeneration of metal parts outside Denmark</p>	<p>The Danish statutory order (BEK no 1296 of 12/12/2011) states that printed circuit boards after dismantling shall be delivered to the facility which is approved for treatment of metallic waste containing BFRs, PCBs and beryllium under the Environmental Protection Act § 33 or similar legislation abroad.</p>
	<p>Electrical and electronic equipment from vehicles is expected to be disposed of as other WEEE</p>	<p>The Danish statutory order on end of life vehicles (BEK no 1312 of 19/12/2012) requires that electrical and electronic equipment is dismantled and disposed of WEEE (requirements beyond the requirements of the End-of-life Vehicles Directive (ELV, Directive 2000/53/EC). The Danish WEEE Statutory order specifies that waste EEE removed from vehicles shall be treated as WEEE (beyond the WEEE Directive):</p>

Product group	Disposal method in Denmark	Legislation
	Wires and cables are to a large extent recovered in Denmark (not covered by the WEEE and BAT statistics). The plastic parts are either recycled, incinerated or disposed of to controlled landfill	
Vehicles (textiles and stuffing in seats, interior parts, etc.) excl. electrical and electronic parts	Mainly disposed of with shredder waste to controlled landfill	The statutory order on end of life vehicles (BEK no 1312 of 19/12/2012) does not have any specific requirements for treatment of other parts with BFRs in vehicles.
Textiles, carpets and furniture	Disposed of to municipal waste incinerators	No specific legislation
Building materials (EPS/XPS and PU foam insulation, sheets, etc.)	Disposed of to municipal waste incinerators	No specific legislation
Paint, fillers and wood proofing	Fireproof wood is expected to be disposed of to municipal waste incinerators. Paints mainly disposed of metal recycling as fire-proof paints are mainly used on metal parts	No specific legislation

The main issues with regard to the disposal of BFRs with solid waste are:

- Standards for treatment of plastics containing BFRs
- Uncontrolled final disposal due to export of WEEE and second hand electronic products to countries with management of WEEE not meeting the requirements of EU legislation;
- Particular requirements to BFRs considered POPs and covered by the EU POPs Regulation;
- Fate of the BFRs by municipal solid waste incineration and uncontrolled burning – destruction efficiencies and formation of dioxins and furans (section 4.2), and
- Releases of BFRs from landfills (section 4.2).

Alongside these issues, section 4.2 discusses the potential releases from the application of sewage sludge containing BFRs.

4.2.1 Standards for treatment of plastics containing BFRs

The European Commission has on 4 February 2013 requested the European Standardization Organizations to develop European standards for the treatment of WEEE. It is likely that also standards for the treatment of brominated flame retardants will be developed.

As part of the EU funded WEEELABEX project, the WEEE Forum, jointly with stakeholders from the community of WEEE processors and producers of electrical and electronic equipment, has developed normative technical requirements for WEEE treatment (WEEELABEX, 2011). The WEEE Forum is the European Association of Electrical and Electronic Waste Take Back System. Among the developed requirements are requirements for treatment of Plastics containing certain types of brominated flame retardants. It is by the Danish EPA considered likely that future standards will build on the normative standards developed by the WEEE Forum.

4.2.2 Uncontrolled final disposal of WEEE

Total treated WEEE quantity collected in Denmark in 2011 was 82,917 tonnes (DPA, 2011). According to the statistics on WEEE and BAT from the DPA system (DPA, 2011), which administers Danish producer responsibilities, in 2010, around 70% of the waste received primary treatment in Denmark. However, this seems to refer primarily to a pre-treatment, whereas actual dismantling and reprocessing of most of the waste takes place abroad (Danish EPA, 2012). The Danish Statutory Order states that BFR-containing plastics in WEEE must be separated and delivered to companies that are authorized to handle brominated waste approved under the Environmental Protection Act § 33 or similar legislation abroad. The WEEE Directive requires that the BFR-containing plastics should be separated, but has no specific clause on the final treatment of the plastics and permit requirements. It has not been assessed to what extent authorisation schemes for handling brominated waste is in place in all EU Member States.

The fate of WEEE in Denmark and the EU and the possible illegal export of WEEE to developing countries are not described in detail.

A Dutch review of the WEEE flows in The Netherlands (Huisman *et al.*, 2012), concludes that in 2011 a maximum potential of 8,000-14,000 t/y, of a total WEEE + used EEE of 392,000 t/y, was illegally exported.

Illegal shipment of 10-15% of the WEEE has been reported from several other Member States as cited in a review of the WEEE Directive for the European Commission (Huisman *et al.*, 2007). The review also concluded that more than half of the collected WEEE in the EU was potentially the object of improper treatment and illegal exports.

Export of second hand, still functioning EEE in good working condition for reuse abroad is legal as the equipment is not considered waste. It is, however, very difficult to enforce, as the equipment may be outdated, but still functional. One of the objectives of the recast WEEE Directive is to give the EU Member States the tools to fight illegal export of waste more effectively, according to the European Commission.

A report from 2006 investigated the fate of second hand electronic equipment exported for reuse abroad (Planmiljø, 2006). At that time, about 2,500 tonnes in second hand EEE was exported for reuse; of this, half was exported by Danida supported aid organisations. The report did not assess to what extent the exported equipment was actually reused. It notes that export to Africa, for the purpose of scrapping the equipment in Africa, is not very likely, as the cost of shipment to Africa is many times the cost of shipment to China or India. DanWatch (2011) concludes that if just 25 computers in a container with 300 are functioning, it may cover the shipment costs to Ghana. Newer assessments of the total export have not been identified. The assessment of the Dutch WEEE flows concluded that more than 10% of the generated WEEE+ used EEE in The Netherlands, corresponding to 44,000 tonnes in 2011, was exported (Huisman *et al.*, 2012).

Whether the equipment is reused or not before disposal, the final disposal will most likely not meet the EU requirements. The flame retarded plastics may be recycled one or more times (for different purposes - not necessarily purposes requiring flame retardants (UNEP, 2012b)), but the ultimate disposal of the flame retarded plastics is most likely uncontrolled burning or waste dumping. It should be noted that the same would be in fact be the situation for flame retarded plastics in new EEE exported from EU countries to developing countries.

4.2.3 POPs BFRs in waste in the EU and Denmark

HexaBB and four of the PBDEs (corresponding to the commercial c-pentaBDE and c-octaBDE) are covered by the EU POPs regulation (here collectively referred to as POPs BFRs), and in the near future HBCDD will be added to the list. Particular provisions for waste containing POPs are stipu-

lated in Commission Regulation (EU) No 756/2010 amending the POPs Regulation. For hexabromophenyl, a limit value for disposal provisions of 50 mg/kg is established, but no concentration limits have been established yet for the PBDEs. In order to assess the potential impact on establishing different limit values for new POPs, the ESWI consortium, on behalf of the European Commission, DG Environment undertook a “Study on waste related issues of newly listed POPs and candidate POPs” (ESWI, 2011). Dependent on the actual values established, it may be necessary to separately collect and destroy plastic with the POPs BFRs.

As part of the updated implementation plan for the Stockholm Convention, the presence of the POPs BFRs in articles in used in Denmark was assessed. The following is based on the implementation plan. In the survey of brominated flame retardants from 1999 (Lassen *et al.*, 1999), the total Danish consumption of PBDEs was estimated at 30-120 tonnes. Most of the PBDEs were imported in articles. The report does not include individual estimates for the three types of technical PBDE. Since no specific inventories are available of the historical consumption of the POPs BFRs in Denmark, reference was made to the ESWI (2011) report. The results of this study are summarised in Table 27.

According to the ESWI (2011) report, the total consumption of technical pentaBDE in the EU, including imports of articles decreased from around 1,100 tonnes in 1994 to 200-250 tonnes in 2000, and subsequently ceased altogether in 2004. Around 95% of the technical pentaBDE was used in the EU in polyurethane foam in mattresses and upholstered furniture. Around half was used in vehicles: in the seats, dashboard, steering wheel, roofs, sound insulation and door panels. Concentrations in polyurethane foam varied from 2-18%. The remaining 5% was used in other plastics (in electronics in particular), and in rubber, paints and varnish, textiles, and hydraulic oils. With regard to the portion of the consumption linked to vehicles, there is no basis for assuming that Danish consumption figures vary significantly from those of the other EU countries. The accumulated consumption of technical pentaBDE in the EU is estimated at around 15,000 tonnes. Of these, around 8% or around 320 tonnes, was estimated still to be in use in 2010. If consumption and disposal patterns for technical pentaBDE in Denmark correspond to the European average, there should be around 3 tonnes of technical pentaBDE left in articles that have been used in Denmark. Around three-quarters of these are in vehicles produced before 2004, and around one-quarter are in polyurethane foam which was previously used in mattresses and upholstered furniture. Although this is an uncertain estimate, it gives us an idea of the order of magnitude of quantities. The study carried out for the European Commission concluded that more or less all of the technical pentaBDE in vehicles in the EU will be disposed of by 2016. Since cars are used for relatively longer periods of time in Denmark, it will probably take somewhat longer before all technical pentaBDE has been disposed of in Denmark.

According to the ESWI study from 1970 to 2005, the accumulated consumption of octaBDE in the EU was around 17,000 tonnes, of which an unknown quantity was exported. Globally, around 95% of technical octaBDE were used in ABS plastics, which are typically used in enclosures for electrical and electronic equipment. The remaining 5% are used in other types of plastic, as well as in electrical and electronic equipment. Technical octaBDE was typically used in concentrations of 10-18%. As the articles in which octaBDE has been used have a relatively short lifetime, it is assumed that the majority of the quantity in circulation has been disposed of at present. At EU level, in 2010, it was estimated that around 128 tonnes of octaBDE in waste electrical and electronic equipment (WEEE) was disposed of, and that most materials containing this substance will have been disposed of by 2012. Since the technical octaBDE present in Denmark is primarily in imported electrical and electronic equipment, there is no basis for assuming that consumption in Denmark has been considerably different from consumption in the EU. It will therefore have to be assumed that all octaBDE is already disposed of, while a few tonnes of the remaining technical octaBDE will be disposed of over the next couple of years.

TABLE 27
COMMERCIAL PENTA- AND OCTABDE IN ARTICLES IN USE AND IN WASTE IN THE EU (ESWI, 2011 AS SUMMARISED BY DANISH EPA, 2012)

Articles	Amounts used in the EU	Lifetime	Amounts in articles in use in the EU in 2012	Penta- and octaBDE concentration in waste	Penta- and octaBDE amounts in waste in the EU in 2012
Polyurethane foam	Total consumption of pentaBDE in the EU in the period 1970-2000: about 15,000 tonnes. Of these, 95% for polyurethane foam. Of this, around 60% is incorporated in upholstered furniture and mattresses, 36% in vehicles, and 4% for other uses. Polyurethane foam typically contains 2-18% pentaBDE.	Vehicles: 12 years Upholstered furniture 10 years	Car interiors: in 2012 around 97.4 tonnes accumulated pentaBDE, decreasing to zero tonnes in 2016. Upholstered furniture: in 2012 around 112 tonnes accumulated pentaBDE, decreasing to zero tonnes in 2014.	2-18% pentaBDE in polyurethane foam. Calculations are based on an average of 4% for car interiors and 3.8% for upholstered furniture. The maximum content per vehicle is stated at 150 g pentaBDE.	Car interiors: around 12 tonnes pentaBDE in 2012. Upholstered furniture: around 75 tonnes pentaBDE in 2012.
Electrical and electronic equipment	Around 4% of the 15,000 tonnes of total consumption of pentaBDE in the period 1970-2000. The uses shown include printed circuit boards.	9-15 years	Not stated.	Not stated.	Not stated.
Electrical and electronic equipment	Total accumulated consumption in the EU in the period 1970-2005: 16,590 tonnes octaBDE. Around 95% of octaBDE was used in ABS plastics in concentrations of 10-18%. The remaining 5% was used in other plastic types. More or less all plastics containing octaBDE were used in electrical and electronic equipment.	9 years	Around 128 accumulated tonnes octaBDE in 2012. It is assumed that all will be disposed of by 2012.	10-18% in plastic components containing octaBDE.	128 tonnes octaBDE in 2010; zero tonnes in 2012 (it is assumed that all octaBDE will be disposed of by 2012).

According to the 1999 survey of BFRs, the only polybrominated biphenyl (PBB) used with certainty was technical decaBB (with ten bromine atoms). According to data from the OECD, the technical decaBB did not contain hexaBB. Considering that hexaBB has not been used since the 1970s, it is likely that only an insignificant number of articles containing hexaBB remain.

4.1 Recycling

According to the WEEE Directive (Directive 2012/19/EU), plastic containing brominated flame retardants have to be removed from any separately collected WEEE and be disposed of or recovered in compliance with the Waste Directive (Directive 2008/98/EC). Recycling is one of the recovery operations, which means that BFR-containing plastics in accordance with the WEEE Directive can be recycled if the plastics do not contain restricted BFRs. The Danish statutory order on waste electrical and electronic equipment states specifically that plastic with bromine content of less than 5 ppm (mg/kg) can be returned for reprocessing and recycling by companies that have been approved under the Environmental Protection Act § 33 or similar legislation abroad. For plastics containing more than 5 ppm BFRs the Statutory Order indicates that it must be delivered to companies that are authorized to handle brominated waste approved under the Environmental Protection Act § 33 or similar legislation abroad. It is not specifically stated that the waste cannot be recycled.

According to the POPs Regulation, articles and preparations containing concentrations below 0.1 % by weight of each of the four covered PBDEs may be placed on the market if they are produced partially or fully from recycled materials or materials from waste prepared for re-use. As the limit concerns the individual PBDEs, the limit for the commercial octaBDE (of which heptaBDE accounts for less than 50%) would be at least double. The POPs Regulation has a derogation for EEE which fall within the scope of the RoHS Directive. According to the RoHS Directive materials should not contain more than 0.1% total PBDEs, recycled or not. The restrictions on recycled material are consequently generally stricter for EEE than for other applications, while for some EEE exempt from the RoHS Directive (but still in the scope of the Directive), no restriction applies. Plastics containing decaBDE may not be recycled for use in EEE (if the concentration is >0.1 %), but may be recycled for other purposes. Plastics containing other BFRs can be recycled without any restriction.

No data on the actual recycling of BFR-containing waste in Denmark or the EU have been identified.

The draft guidance on best available techniques and best environmental practices for the recycling and disposal of articles containing PBDEs listed under the Stockholm Convention includes a detailed description of recycling activities (UNEP, 2012b). According to the guidance, PUR foams in furniture, transport, end-of-life vehicles and mattresses are partially recycled into new articles by processes such as carpet rebond and regrinding (no quantitative data provided). It further reports that recent studies have shown that plastics containing POP-PBDEs and other BFRs have been recycled in the production of articles for which no flame retardancy is required, including children's toys, household goods and video tapes.

4.2 Release of brominated flame retardants and degradation products from waste disposal

4.2.1 Municipal solid waste incineration and uncontrolled combustion

According to the statistics on WEEE and BAT from the DPA system (DPA, 2011), in 2011, 7,272 tonnes of waste from treatment of WEEE was incinerated in Denmark in municipal waste incinerators, corresponding to less than 10% of the total weight of the collected WEEE. In addition, incineration of approximately 3 % of the generated quantity of WEEE as discussed above should be included.

The quantity directed to municipal waste incineration in 1999 was estimated at 170-360 t/y (Lassen *et al.*, 1999); of this WEEE accounted for approximately 85%. Using data from the 1999 survey the total amount of BFRs incinerated with EEE waste can be estimated at 70-100 t/y, assuming that plastics flame retardant with 10-15% BFRs on average accounted for approximately 10% of all plastics.

One of the main concerns about the incineration of BFR-containing plastics has been the risk of formation of brominated dibenzo-p-dioxins and brominated dibenzo furans (PBDD/F) and mixed polybrominated and polychlorinated dioxins and furans (PXDD/F). In the Danish action plan for BFRs from 2001, it was stated that the formation of dioxins and furans by incinerations was of concern, and the European Commission considered requiring that all BFR-containing plastics from WEEE should be disposed of in hazardous waste incinerators. Brominated dioxins and furans have been shown to have toxicities similar to, and in some cases greater than, their chlorinated counterparts in human cell lines and mammalian species and assay tests (UNEP, 2010), but dioxins' toxicity equivalency factors do not exist for the (PBDD/F) and (PXDD/F).

Some of the BFRs, in particular the PBBs and PBDEs, are highly similar to the brominated dioxins and furans and can serve as precursors (building blocks) for the formation of the dioxins and furans if the substances are not decomposed during incineration. In addition, all BFRs serve as bromine donors for the so-called "*de-novo*" synthesis of the dioxins and furans in the post-combustion zone of the incinerator. According to the EU Risk Assessments for decaBDE, the relative proportions of bromine to chlorine in most waste prior to incineration indicates that the major dibenzo-p-dioxins and furans formed will contain chlorine only, with mixed bromine/chlorine containing species (most likely containing 1 bromine) making only a very minor contribution (ECB, 2002). In addition to this, European Regulations exist on the design of municipal incinerators in order to minimise the formation of chlorinated dioxins and furans during incineration. Proper incinerator design should also reduce the potential for release to the environment of the brominated dioxins and furans. The EU Risk Assessment concludes that it is expected that emissions from controlled incineration processes will be near zero, although the question of formation of brominated dioxins and furans has been raised as a potential problem. The EU Risk Assessment for octaBDE (ECB, 2003) concludes that overall, for disposal by incineration and landfill, metal recycling and accidental fires, the polybrominated diphenyl ethers, as a source of bromine, can contribute to the formation of halogenated dioxins and furans generated during such processes but it is not possible to quantify the amounts or assess the environmental significance of these products. Furthermore, it is noted that halogenated dioxin and furan formation from some of these processes is well known and emission control technology is available for incinerators and metal recycling that can be used to reduce the amounts of these substances formed in the process to acceptable levels.

Vikelsøe (2003, 2004) measured the concentration of PBDD/F and PBCDD/F in flue gas from two incinerators in Denmark and in soil around the incinerators in 2003 and 2004. Elevated levels of PBDD/F were found in the vicinity of the two incinerators as compared to a remote area, demonstrating the significance of the incinerators as sources of PBDD/F in their surroundings. Incinerators in Denmark have since been equipped with better flue gas controls.

In a Nordic study from 2005 of emission during incineration of waste containing bromine, incineration tests and measurements of brominated, chlorinated and mixed brominated/chlorinated dioxins and furans were performed in three full-scale incineration plants in Norway (Borgnes and Rikheim, 2005). All plants were equipped with advanced flue gas treatment systems. Measurements were performed during incineration of waste from households and the commercial sector (waste with low BFR content), and the results showed very low levels for all analysed dioxins. The main goal of the incineration tests was to establish the flue gas concentration of halogenated dioxins and furans before and after flue gas cleaning, with different proportions of plastic waste containing BFRs. The measured results confirmed that BFRs decompose in the incineration process. The

amount of BFRs in output flows is less than 0,001 % by weight of the total amount of BFRs in the waste mix (i.e. a destruction efficiency of better than 99.999%). Emissions of chlorinated, brominated and chlorinated/brominated dioxins were measured without any addition of brominated waste, and with the addition of 5 % by weight, 10 % by weight and 20 % by weight bromine-containing waste. Increasing the content of BFRs in the waste gave no significant increase in the emissions of either chlorinated dioxins, or brominated or chlorinated/brominated dioxins. The emission measurement results indicate that the incineration efficiency and the operating conditions of the flue gas treatment systems are of greater importance to the resulting emission levels of dioxins and furans, rather than the bromine content level. Measurements of halogenated dioxins and furans in the flue gas before and after flue gas cleaning were carried out with addition of 10 % by weight bromine-containing waste at the Klemetsrud Plant (Oslo). The concentration of chlorinated/brominated dioxins before cleaning was approximately three times the concentration of chlorinated dioxins. The removal efficiency for chlorinated/brominated dioxins was >99%, while it was approximately 93% for chlorinated dioxins/furans.

In Denmark, BFR-containing plastics are currently incinerated in municipal solid waste incinerators equipped with filters for control of emissions of PCDD/F (chlorinated dioxins and furans). To what extent the destruction efficiency of the POPs BFRs in these incinerators is sufficient to meet the requirements of the Stockholm Convention is not totally clear, but the available information as described above indicates a destruction efficiency of better than 99.999%. One of the actions of the updated national implementation plan for the Stockholm Convention is to encourage the European Commission to prepare a study to validate whether technical pentaBDE is sufficiently destroyed in ordinary waste incinerators. In an e-mail to the Danish EPA of 21 June 2013, the European Commission states that according to the experts the European Commission have consulted, it would seem that PBDEs could be incinerated in municipal solid waste incinerators, taking necessary measures to secure that the bromine concentration is not excessive.

Dioxin toxicity equivalency factors have not been established for brominated and mixed brominated/chlorinated dioxins and furans; these substances are not included when estimating the total dioxin toxicity equivalency of e.g. flue gas emissions or dioxins and furans in food (limit values are expressed in dioxin toxicity equivalency rather than total content of the substances).

Whilst the emission from well-equipped incinerators may be of no concern, much literature indicated that the emissions of dioxins and furans from fires (including incidental landfill fires) and uncontrolled burning of BFR-containing plastics may be significant (Weber and Kuch, 2003; Desmet *et al.*, 2005; Lai *et al.*, 2007; Yu *et al.*, 2008). Uncontrolled burning of waste is illegal in the EU, but some BFR-containing plastics will be destroyed in fires in buildings and vehicles and by accidental landfill fires.

The possible formation of hazardous substances by thermal decomposition is one of the main arguments against the use of BFRs e.g. by environmental NGOs, manufacturers of alternative FRs and parts of the scientific community.

Weber and Kuch (2003) have studied the effect of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. According to the results, under insufficient combustion conditions, e.g. accidental fires and uncontrolled burning as well as gasification/pyrolysis processes, considerable amounts of PBDDs/PBDFs (brominated dioxins and furans) can be formed from BFRs, primarily via the precursor pathway. The precursor pathway is relevant for BFRs which may act as precursors, in particular the PBDEs and PBBs, but possibly other BFRs as well.

A technical review of the implications of recycling *c*-pentaBDE ether and *c*-octaBDE for the POPs Review Committee under the Stockholm Convention has been undertaken on the subject (UNEP,

2010). PBDD/F are present as impurity of technical PBDEs (which was the background for the phase out in Germany in the 1990s) and can be formed in different life-cycle steps. According to the review, compelling evidence has accumulated over the past twenty years or so that BFRs, and especially PBDE, are a major source of toxic tri- to octa-brominated dioxin and furan contamination. The peer-reviewed and grey literature clearly shows that the generation, emissions and impacts of PBDD/DF are relevant considerations in relation to the manufacture/processing, recycling and disposal of products containing, or contaminated with, PBDE and related compounds. The total generation of PBDD/DF from all types of PBDE are at a scale of tons per year (Zennegg, 2009 as cited by UNEP, 2010) and therefore of the same order or even larger than the total inventory of PCDD/F.

The draft guidance on best available techniques and best environmental practices for the recycling and disposal of articles containing PBDEs listed under the Stockholm Convention includes detailed information on the possible generation of PBDD/F from different recycling activities, in particular thermal recycling activities (UNEP, 2012b).

Gouteux *et al.* (2013) has recently demonstrated that upon application of thermal stress to samples of polymeric BFRs with brominated aromatic moieties, a drastic increase of the release of brominated compounds was observed. A variety of substituted alkyl benzenes or phenols with two to six bromine atoms were formed. The paper deals with the potential environmental effects of the formed substances, and does not discuss the significance of the releases of the substances on the potential formation of hazardous PBDD/F by combustion of the products.

4.2.2 BFRs emission from landfills

A limited amount of BFR-containing plastics in Denmark would end up in landfills as the general policy is to incinerate combustible waste for energy recovery. In other EU Members States, a larger part (up to 100%) of the combustible waste is landfilled.

When additive BFRs in plastics are disposed of to landfill, in theory they could leach out of the plastic and into groundwater or volatilise to the atmosphere.

According to the EU Risk Assessment for decaBDE (ECB, 2002), however, several experiments have shown that leaching of decaBDE from polymers is minimal (see below) and it would not be expected to leach to a significant extent from polymers in landfill, unless the polymer itself undergoes some form of degradation, thus releasing the decaBDE. Any released decaBDE is likely to adsorb strongly onto soil, thus minimising the possibility of reaching groundwater (see also Section 3.1.1.6.2). Similarly, the low vapour pressure of the substance would limit its volatility to the atmosphere. Although the available information indicates that leaching of decaBDE from landfills will be minimal, movement of polymer particles containing decaBDE within the landfill could provide a transport mechanism leading to entry into leachate water or groundwater. However, it is not currently possible to assess the significance of this type of process. Well-designed landfills already include measures to minimise leaching in general terms, and these measures would also be effective in minimising the leaching of any decaBDE present. (ECB, 2002).

4.2.3 BFRs in sewage sludge

The Danish Statutory order in sludge ("Slambekendtgørelsen") does not include any limit values for PBDE or any other BFR; furthermore, BFRs levels in sludge are not regulated at EU level. The Danish action plan for BFRs (Danish EPA, 2001) considered that the levels of BFRs found in sludge did not call for establishing limit values, as no environmental and health risk from the application of sewage sludge to agricultural soils was anticipated. General limit values for the PBDEs covered by the EU POPs regulation are still not established. The established limit value for hexaBB is 50 mg/kg and if similar values are established for the PBDEs, these will not have any impact on the disposal of sewage sludge.

PBDEs - Data on PBDEs in sewage sludge in Denmark is summarised in Table 28. In the only study which included BDE-209 (decaBDE) this congener was higher than the concentration of Σ tri-heptaBDEs (Christensen *et al.*, 2003). No data for other BFRs in sludge from Danish waste water treatment plants have been identified.

TABLE 28
BFRS IN SEWAGE SLUDGE FROM DANISH MUNICIPAL SEWAGE TREATMENT PLANTS

	Concentration, $\mu\text{g}/\text{kg d.w.}$ Average	Number of mu- nicipal sewage plants	Source
BDE-17	3.0	1	Christensen <i>et al.</i> (2003) – NCL analysis shown – nearly similar results obtained with HREI analy- sis
BDE-28	1.9	1	
BDE-47	96.8		
BDE-49	10.7		
BDE-66	1.7		
BDE-85	3.1		
BDE-99	86.2		
BDE-100	19.1		
BDE-153	7.8		
BDE-154	6.1		
BDE-183	2.0		
Σtri-heptaBDEs	238		
BDE-209	248		
BDE-47	70	1	Vikelsøe <i>et al.</i> , 2002
BDE-99	90		
BDE-100	14		
BDE-153	< detection limit		
ΣPBDEs	51-92 (average not reported)	2	Videncenter for Jord- forurening (2011)
BDE-47	25	2	Aarhus Amt, 2005 as cited by Jensen <i>et al.</i> , 2011
BDE-99	37		
BDE-100	6		
BDE-153	4		

Some data on PBDEs in sewage sludge from other European countries have been summarised by Jensen *et al.* (2011). Consistently, BDE-209 (decaBDE) accounts for more than 50% of the total PBDE concentration. The concentrations of decaBDE in sludge from different countries were (year of sampling): Germany 2002/3 (mean = 429 $\mu\text{g}/\text{kg w.w.}$), Sweden 2002 (mean = 11 $\mu\text{g}/\text{kg d.w.}$), Sweden 2007/8 (mean = 383 $\mu\text{g}/\text{kg w.w.}$), Sweden (2007 (mean = 291 $\mu\text{g}/\text{kg}$), Sweden (2008 (mean = 292 $\mu\text{g}/\text{kg}$), and Switzerland 2003-5 (mean = 310 $\mu\text{g}/\text{kg}$).

As a result of the risk assessment of decaBDE, a ten-year monitoring programme (known as the conclusion (i) monitoring programme) was requested by the EU Member States to investigate the long-term trends in the levels of decaBDE in sewage sludge, sediment, air and birds' eggs (Environment Agency, 2009). Under this programme, financed by BSEF, sewage sludge samples from a total of twelve sites in the EU are being analysed with three samples being collected at each site over a one week period in each sampling year. Of the 11 sites, 7 are sewage treatment plants (STPs) with mainly domestic waste water input. The levels of decaBDE in the sludge from these STPs in 2007 differed significantly between the countries with $3,810 \pm 2,580$ $\mu\text{g}/\text{kg}$ d.w. and $5,490 \pm 2,890$ $\mu\text{g}/\text{kg}$ d.w. in sewage from two STPs in UK, $5,170 \pm 989$ $\mu\text{g}/\text{kg}$ d.w. in one STP in Ireland and 248 ± 145 $\mu\text{g}/\text{kg}$ d.w., 208 ± 29 $\mu\text{g}/\text{kg}$ d.w., 353 ± 28 $\mu\text{g}/\text{kg}$ d.w. and 463 ± 35 $\mu\text{g}/\text{kg}$ d.w. in four STPs in The Netherlands. Similar results were obtained in 2006 (Environment Agency, 2009).

Compared to the levels found in the STPs in The Netherlands and other European countries, the levels in Ireland and the UK were a factor of ten higher. A similar pattern is found for HBCDD as described below.

HBCDD - According to the EU Risk Assessment for HBCDD, in general, the concentrations of HBCDD in sludge observed in Ireland (median = 1439 $\mu\text{g}/\text{kg}$ d.w.) and UK (median = $1,256$ $\mu\text{g}/\text{kg}$ d.w.) are more than one order of magnitude higher than those observed in The Netherlands (median = 21 $\mu\text{g}/\text{kg}$ d.w.), Norway (median = 35 $\mu\text{g}/\text{kg}$ d.w.) and Sweden (median = 24 $\mu\text{g}/\text{kg}$ d.w.) (ECB, 2008). In a Swiss study from 2008, mean concentration of HBCDD (n=16 wastewater treatment plants) was 149 ($39 - 597$) $\mu\text{g}/\text{kg}$ d.w. (Kupper *et al.*, 2008).

The higher concentrations of HBCDD and decaBDE in sludge from Ireland and the UK may quite well be a consequence of a higher consumption of HBCDD and decaBDE in textiles and furniture in these countries, as washing of textiles is one of the main sources of decaBDE and HBCDD to waste water.

TBBPA - Compared to decaBDE and HBCDD, the concentration of TBBPA in sludge is generally lower. The EU Risk Assessment reports (ECB, 2007) on concentrations of TBBPA in sewage samples from a range of European countries (year of publication indicated): Finland 2002 (all < 0.2 $\mu\text{g}/\text{kg}$ d.w.), Sweden 2002 (median = 2.0 $\mu\text{g}/\text{kg}$ w.w.), Germany 2003 (median = 16 $\mu\text{g}/\text{kg}$), Germany 2001 (range = $5.2-34.5$ $\mu\text{g}/\text{kg}$; dimethyl derivative range = $0.39-11.0$ $\mu\text{g}/\text{kg}$ d.w.), Ireland 2004 (mean = 95 $\mu\text{g}/\text{kg}$ dry weight), U.K 2004 (mean = 59 $\mu\text{g}/\text{kg}$) and The Netherlands (mean = 79 $\mu\text{g}/\text{kg}$ d.w.)

Other BFRs – The Nordic screening report (Schlabach *et al.*, 2011) analysed 16 "new" BFRs in sludge from the Nordic countries and 16 PBDE congeners for reference. The BFRs were present in sludge from WWTPs, storm water sludge, and sludge from landfills. The frequent occurrence in the different sludge samples indicates a widespread use of these substances in the Nordic countries. Results for the BFRs found in the highest concentration in the sludges are shown in the figure below. The highest concentrations were found for DBDPE (range = $4.5-160$ $\mu\text{g}/\text{kg}$ d.w.), PBT (range = $0.027-5.2$ $\mu\text{g}/\text{kg}$ d.w.) and DBE-DBCH (range = $< 0.27-9.0$ $\mu\text{g}/\text{kg}$ d.w.). The concentration of DBDPE is in the same range as reported for decaBDE and HBCDD, whereas the concentrations of the other analysed BFRs were considerably lower.

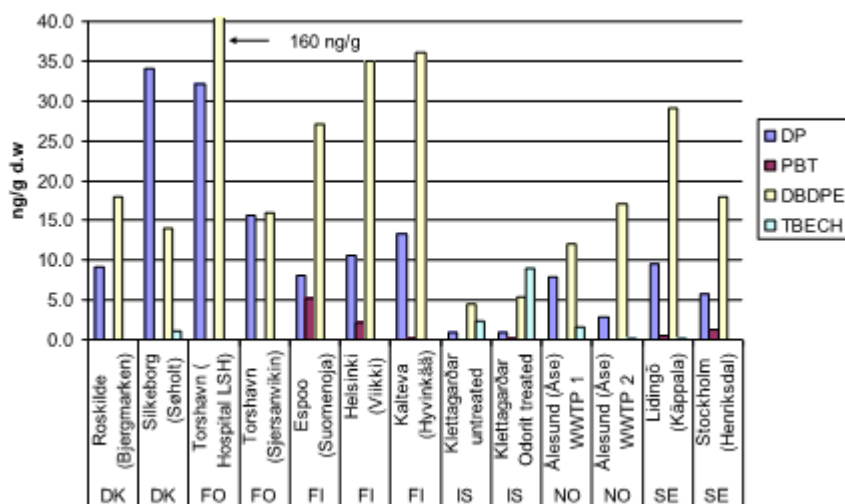


FIGURE 2 CONCENTRATIONS OF THE MOST SIGNIFICANT ANALYSED FLAME RETARDANTS IN SLUDGE SAMPLES (SCHLABACH ET AL., 2011). DP IS THE NON-BROMINATED DICHLORANE PLUS. TBECH = DBE-DBCH.

Total releases to land from sewage sludge

The emissions of PBDEs to environmental compartments within the Baltic Sea region as estimated in the COHIBA Project tend to originate mainly from the application of contaminated sewage sludge, followed by emissions during the service life of flame retardant products in the form of release from the indoor environment. The releases from the indoor environment are, however, noted to be highly uncertain and possibly underestimated. The total releases to land in the Baltic Area from application of sewage sludge is estimated at 0.2-0.4 t/y for the total PBDEs and 0.03-0.06 t/y for HBCDD.

An inventory and assessment of options for reducing emissions of PBDEs as part of the source control of priority substances in Europe (Socopse) estimates the total release to land from sewage sludge applications in the EU at 0.4-1.5 t/y for pentaBDE and 0.9-1.5 t/y for decaBDE (Socopse, 2009).

Risk evaluation of application of BFRs in sludge to agricultural land in Denmark

A risk evaluation of BFRs and four other groups of persistent organic contaminants in sewage sludge in Denmark has recently been published (Jensen *et al.*, 2012). Due to lack of data, a risk evaluation was done for BDE-209 (decaBDE) and TBBPA only. For the risk evaluation Jensen *et al.* (2012) used a concentration of BDE-209 of 750 µg/kg d.w. and, for TBBPA, the highest reported sludge concentration of 220 µg/kg d.w. Based on the exposure model the following steady-state soil concentrations (PECss) were predicted after multiple sludge applications: PECss (BDE-209) = 0.011 mg/kg; PECss (TBBPA) = 0.001 mg/kg. These predicted concentrations are at the lower end of the observed concentrations reported for agricultural fields amended with very large amounts of sewage sludge for multiple years. According to the authors, such scenarios are, however, no longer valid for a typical situation in Denmark, where sludge amendment of agricultural land is strongly regulated. An additional margin of safety may, however, be needed in order to encompass the possibility of higher soil concentrations in areas that are not in compliance with e.g. the Danish sludge regulations, or areas receiving sludge from sewage treatment plants treating waste water specifically from industries producing or making use of BFR. (Jensen *et al.*, 2012)

Based on a comparison between the lowest test concentration, where no significant effects were observed (NOEL), and the predicted concentrations in soils after multiple sewage sludge amendment, a margin of safety (MoS) was estimated at 9091 for BDE-209 and 260 for TBBPA. On this basis, it was concluded that it was unlikely that the levels found in Danish sludge should pose a

significant risk to soil dwelling organisms and soil quality in general, if the current application guidelines of sewage sludge are followed. (Jensen *et al.*, 2012)

Transformation in sewage sludge

One of the issues regarding decaBDE in sewage sludge is the transformation of decaBDE to lower brominated PBDEs (UK, 2012). The available studies on the transformation have been reviewed as part of the Annex XV dossier for decaBDE. According to the dossier, overall, these studies provide good evidence that decaBDE can be transformed to at least octaBDE congeners by sewage sludge micro-organisms over a period of about eight months. The amounts appear to be below 10% over this timescale, and the rate of reaction appears to depend on the presence of other substances. Whilst these findings do not suggest that tetra- to heptaBDE congeners would be formed in significant amounts during wastewater treatment processes (since sludge residence times are usually too short, at around 20 days), they do provide some supporting evidence that the reaction might occur over longer time scales in the environment under appropriate conditions. (UK, 2012)

4.3 Summary and conclusions

Disposal of BFR-containing waste – Waste electrical and electronic equipment represent the majority of BFRs in solid waste. Other major waste fractions are building insulation materials (EPS/XPS and PU foam) and waste from shredding of vehicles while BFRs in textiles, furniture, paints, etc. take up a small part. The WEEE Directive requires that plastics containing BFRs should be removed from the collected equipment for selective treatment. The Danish statutory order further requires the removed BFR-containing plastics should be disposed of to enterprises with a permit for handling of bromine-containing equipment. In Denmark, the BFR-containing plastics from WEEE are disposed of to municipal solid waste incineration with a permit for incineration of BFRs. The same is the situation for BFR-containing plastics from the building sector and textiles and furniture. Plastics from shredding of vehicles are disposed of to controlled landfill.

A part of flame retarded plastics in WEEE in the some EU Member States still appears to end up in uncontrolled waste handling in countries outside the EU, either by illegal shipment of the EEE or exported as second- hand equipment for reuse in developing countries. The ultimate disposal of the BFR-containing plastics (possibly after recycling) in any case is expected to be uncontrolled burning or landfilling.

POP BFRs - HexaBB and four of the PBDEs (corresponding to the commercial c-pentaBDE and c-octaBDE) are covered by the EU POPs regulation, and in the near future HBCDD will be added to the list. Particular provisions for waste containing POPs are stipulated in Commission Regulation (EU) No 756/2010 amending the POPs Regulation. For hexabromophenyl a limit value for disposal provisions of 50 mg/kg is established, but it has no practical implications for Denmark, as hexabromophenyl is not likely present in the waste. No concentration limits have been established as yet for the PBDEs. Depending on the limits to be established by the European Commission, separate collection and treatment of some waste fractions may be necessary.

Incineration and uncontrolled burning - One of the main concerns about the incineration of BFR-containing plastics has been the risk of formation of brominated and mixed brominated/chlorinated dioxins and furans. The available data indicates that the destruction efficiency for BFRs is better than 99,999%, that the incineration of BFRs may contribute a less significant part to the total generated dioxins and furans, and that the filters for control of emissions of dioxins and furans are also efficient in capturing the brominated and mixed brominated/chlorinated dioxins and furans.

Whilst the emission from well-equipped incinerators may be of no concern, much literature indicates that the emissions of dioxins and furans from fires (including incidental landfill fires) and uncontrolled burning of BFR-containing plastics may be significant.

Application of sludge on agricultural soils –The majority of the BFRs in sewage water ends up in the sludge fraction in sewage treatment plants. DecaBDE, HBCDD and DBDPE are the dominant BFRs in municipal sewage sludge. The available data indicates that the levels of decaBDE and HBCDD levels in sewage sludge in the UK and Ireland is approximately a factor of 10 higher than in other EU Member States, indicating a link to the widespread use of these substances in textiles and furniture in the two countries. Recent analyses of 16 "new" BFRs in sewage sludge show that the concentration of DBDPE is of the same magnitude as for decaBDE and HBCDD in other studies, whereas the concentrations for the remaining 15 BFRs is considerably lower. The results confirm that DBDPE to a large extent has substituted for decaBDE in applications that may lead to releases to waste water.

A risk evaluation from 2012 of the application of BFR-containing sludge to agricultural land in Denmark, which included a detailed assessment of decaBDE and TBBPA, concluded that it was highly unlikely that the levels of BFRs found in Danish sludge should pose a significant risk to soil dwelling organisms and soil quality in general, if the current application guidelines of sewage sludge are followed.

Main data gaps

Information on the actual fate of WEEE exported for waste management outside Denmark.

The significance of the different BFRs on the formation of brominated and mixed brominated/chlorinated dioxins and furans by different types of thermal processes is not known for most BFRs. In solid waste incinerators equipped with filters for dioxins and furans control, the dioxins and furans formed in the process will end up in the flue gas cleaning products.

5. Environmental hazards and exposure

5.1 Environmental hazard

5.1.1 Classification

Three of the BFRs have a harmonised classification according to the CLP Regulation (see Table 6 in section o). TBBPA and penta BDE are assigned the Hazard Class and Category Codes “Aquatic Acute 1” and “Aquatic Chronic 1”, whereas octaBDE is not assigned any environmental Hazard Class and Category Codes. The proposed harmonised classification for HBCDD (see section 2.1.2) does not include environmental Hazard Class and Category Codes, whilst almost all notifiers in the C&L Inventory have been assigned Aquatic Chronic 1.

The following table lists the harmonised classification and the environmental Hazard Class and Category Code(s) and Hazard Statement Codes assigned to the substances by more than 25% of the notifiers in the C&L Inventory ECHA (2013d). The self-classification of the substances in the C&L Inventory database is shown in Appendix 6.

TABLE 29
BFRS ASSIGNED ENVIRONMENTAL HAZARD CLASS AND CATEGORY CODE(S) ACCORDING TO THE CLP REGULATION AND THE C&L INVENTORY

CAS No	Substance name	Abbr.	Hazard Class and Category Code(s) *1	Hazard Statement Codes *1
118-79-6	2,4,6-Tribromophenol	TBP	Aquatic Acute 1	H400
126-72-7	Tris(2,3-dibromopropyl) phosphate	TDBPP	Aquatic Acute 1 Aquatic Chronic 1	H400 H410
20566-35-2	2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	HEEHP-TEBP	Aquatic Chronic 3	H412
25327-89-3	1,1'-Isopropylidenebis[4-(allyloxy)-3,5-dibromobenzene]	TBBPA-bAE	Aquatic Chronic 4	H413
25637-99-4	Hexabromocyclododecane	HBCDD	Aquatic Chronic 1	H410
32534-81-9	Diphenyl ether, pentabromo derivative	pentaBDE	Aquatic Acute 1 * Aquatic Chronic 1 *	H400 * H410 *
3296-90-0	2,2-bis(bromomethyl)propane-1,3-diol	DBNPG	Aquatic Chronic 4	H413
3555-11-1	Allyl pentabromophenyl ether)	PBPAE	Aquatic Chronic 4	H413
36483-57-5	2,2-dimethylpropan-1-ol, tribromo derivative	TBNPA	Aquatic Chronic 3	H412
52434-90-9	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	TDBP-TAZTO	Aquatic Chronic 4	H413
59447-55-1	(Pentabromophenyl)methyl acrylate	PBB-Acr	Aquatic Chronic 4	H413
608-71-9	Pentabromophenol	PBP	Aquatic Acute 1	H400
79-94-7*	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol	TBBPA	Aquatic Acute 1 * Aquatic Chronic 1 *	H400 * H410 *
84852-53-9	1,1'-(Ethane-1,2-diyl)bis[pentabromobenzene]	DBDPE	Aquatic Chronic 4	H413

*1 Harmonised classification marked by *. Only codes assigned by more than 25% of the notifiers in C&C inventory are included in the table.

H400: Very toxic to aquatic life

H410: Very toxic to aquatic life with long lasting effects

H412: Harmful to aquatic life with long lasting effects

H413: May cause long lasting harmful effects to aquatic life

5.1.2 PBDEs

The risk assessments carried out under the EU Existing Substances Regulation summarise the available ecotoxicity data obtained in standard test systems for decaBDE (ECB, 2002), octaBDE (ECB, 2003) and pentaBDE (ECB, 2001). The data are summarised in Table 30. In some of the aquatic studies no effects were seen and the results are reported as “greater than” values, reflecting the highest concentration tested (which in some cases is above the water solubility of the substance tested; water solubility is approximately 13 µg/l for pentaBDE, 0.5 µg/l for octaBDE and <0.1 µg/l for decaBDE). These results are best interpreted as the substance showing little or no toxicity at the solubility limit of the substance in the test media. The available data show that pentaBDE is generally more toxic than octaBDE and decaBDE to sediment organisms and terrestrial plants. The gen-

eral lack of effects seen with octaBDE and decaBDE means that it is not possible to draw further conclusions from the available data on the relative toxicity of these two substances; however, as these two substances have high molecular weights (>700 g/mole) the lower toxicity of octaBDE and decaBDE compared with that seen for pentaBDE may reflect a low bioavailability of octaBDE and decaBDE compared to pentaBDE.

The PNECs derived from the available data in ECB (2001, 2002 and 2003) are summarised in Table 31.

TABLE 30
SUMMARY OF ECOTOXICITY DATA FOR PBDES

Trophic level	Species	Substance	Endpoint	Concentration	Reference ¹
Water					
Freshwater fish	<i>Oncorhynchus mykiss</i>	PentaBDE	96h-LC ₅₀	>0.021 mg/l ²	Palmer <i>et al.</i> , 1997c (from ECB, 2001)
		PentaBDE	87 day NOEC	0.0089 mg/l	Wildlife International, 2000a (from ECB, 2001)
	<i>Oryzias latipes</i>	DecaBDE	48h-LC ₅₀	>500 mg/l ²	CITI, 1992 (from ECB, 2002)
		OctaBDE	48h-LC ₅₀	>500 mg/l ²	CITI, 1992 (from ECB, 2003)
		PentaBDE	48h-LC ₅₀	>500 mg/l ²	CITI, 1982 (from ECB, 2001)
Freshwater invertebrates	<i>Daphnia magna</i>	OctaBDE	21 day NOEC	>0.0017 mg/l ²	Graves <i>et al.</i> , 1997 (from ECB, 2003)
		PentaBDE	48h-EC ₅₀	0.014 mg/l	Palmer <i>et al.</i> 1997b (from ECB, 2001)
		PentaBDE	21 day NOEC	0.0053 mg/l	Drottar and Krueger, 1998 (from ECB, 2001)
Freshwater algae	<i>Pseudokirchneriella subcapitata</i> (formerly <i>Selenastrum capricornutum</i>)	PentaBDE	96h-EC ₅₀	>0.026 mg/l ²	Palmer <i>et al.</i> , 1997a (from ECB, 2001)
Saltwater algae	<i>Skeletonema costatum</i> and <i>Thalassiosira pseudonana</i>	DecaBDE	72h-EC ₅₀	>1 mg/l ²	Walsh <i>et al.</i> , 1987 (from ECB, 2002)
	<i>Chlorella sp.</i>	DecaBDE	96h-EC ₅₀	>1 mg/l ²	Walsh <i>et al.</i> (1987) (from ECB, 2002)
Sediment					
Freshwater sediment invertebrates	<i>Chironomus riparius</i>	PentaBDE	28 day NOEC	16 mg/kg dry sediment	Wildlife International, 2000d (from ECB, 2001)
	<i>Hyalella azteca</i>	PentaBDE	28 day NOEC	6.3 mg/kg dry sediment	Wildlife International, 2000c (from ECB, 2001)
	<i>Lumbriculus variegatus</i>	DecaBDE	28 day NOEC	≥3,841 mg/kg dry sediment	Krueger <i>et al.</i> , 2001b (from ECB, 2002)
		OctaBDE	28 day NOEC	≥1,272 mg/kg	Krueger <i>et al.</i> , 2001a (from ECB,

Trophic level	Species	Substance	Endpoint	Concentration	Reference ¹
				dry sediment	2003)
		PentaBDE	28 day NOEC	3.1 mg/kg dry sediment	Wildlife International, 2000e (from ECB, 2001)
Soil and terrestrial environment					
Terrestrial invertebrates	<i>Eisenia fetida</i>	DecaBDE	56 day NOEC	≥4,910 mg/kg dry soil	ABC, 2001 (from ECB, 2002)
		OctaBDE	56 day NOEC	≥1,470 mg/kg dry soil	ABC, 2001 (from ECB, 2003)
		PentaBDE	14 day NOEC	≥500 mg/kg dry soil	Wildlife International, 2000f (from ECB, 2001)
Soil microorganisms	Nitrogen transformation activity	PentaBDE	28 day NOEC	> 1 mg/kg dry soil	Inveresk, 1999 (from ECB, 2001)
Terrestrial plants	<i>Allium cepa</i> , <i>Cucumis sativa</i> , <i>Glycine max</i> , <i>Lolium perenne</i> , <i>Lycopersicon esculentum</i> and <i>Zea mays</i>	DecaBDE	21 day NOEC	≥5,349 mg/kg dry soil	Porch and Krueger, 2001 (from ECB, 2002)
		OctaBDE	21 day NOEC	≥1,190 mg/kg dry soil	Porch and Krueger, 2001 (from ECB, 2003)
		PentaBDE	21 day EC ₅	16 mg/kg dry soil (lowest value, for <i>Zea mays</i>)	Wildlife International, 2000g (from ECB, 2001)

*1 See ECB (2001, 2002 and 2003) for full reference.

*2 Value above the water solubility of the substance. The data are best interpreted as showing no effects at the solubility limit of the substance.

TABLE 31
SUMMARY OF PNECS DERIVED FOR PBDES

Substance	PNEC		
	Freshwater	Sediment	Soil
PentaBDE	0.53 µg/l	1.55 mg/kg dry sediment (normalised to 5% organic carbon content)	0.38 mg/kg dry soil (normalised to 3.4% organic matter content)
OctaBDE	>0.2 µg/l	≥127 mg/kg dry sediment	≥23.8 mg/kg dry soil
DecaBDE	No PNEC could be derived	≥384 mg/kg dry sediment	≥98 mg/kg dry soil

5.1.3 HBCDD

HBCDD has been shown to cause adverse effects to aquatic invertebrates in long-term exposures; a 21d-NOEC of 3.1 µg/l has been determined for *Daphnia magna* (ECB, 2008a; Table 32). Based on this value, ECB (2008a) estimated a PNEC of 0.31 µg/l for freshwater and 0.031 µg/l for marine water. In some of the studies, no effects were seen and the results are reported as “greater than” values which reflect the highest concentrations tested. In these cases where the concentration is above the water solubility (approximately 66 µg/l) the results are best interpreted as the substance showing little or no toxicity at the solubility limit of the substance in the test media.

For sediment organisms, the lowest long term NOEC was obtained with *Lumbriculus variegatus* and the PNEC for sediment was estimated by ECB (2008a) to be 0.86 mg/kg dry weight (normal-

ised to a 5% organic carbon content) for freshwater sediment and 0.17 mg/kg dry weight (normalised to a 5% organic carbon content) for marine sediment from these data.

For soil organisms *Eisenia fetida* was found to be the most sensitive species; a PNEC of 5.9 mg/kg dry weight (normalised to a 3.4% organic matter content) was estimated from these data in ECB (2008a).

TABLE 32
SUMMARY OF ECOTOXICITY DATA FOR HBCDD

Trophic level	Species	Endpoint	Concentration	Reference ¹
Water				
Freshwater fish	<i>Lepomis macrochirus</i>	96h-LC ₅₀	>100 mg/l ²	Calmbacher, 1978 (from ECB, 2008a)
	<i>Leuciscus idus L.,</i>	96h-LC ₅₀	>10000 mg/l ²	Kirsch and Munk, 1988 (from ECB, 2008a)
	<i>Oncorhynchus mykiss</i>	96h-LC ₅₀	>0.0025 mg/l	Graves and Swigert, 1997b (from ECB, 2008a)
		88 day NOEC	≥0.0037 mg/l.	Drottar <i>et al.</i> , 2001 (from ECB, 2008a)
Freshwater invertebrates	<i>Daphnia magna</i>	48h-EC ₅₀	>0.0032 mg/l	Graves and Swigert, 1997a (from ECB, 2008a).
		21 day NOEC	0.0031 mg/l	Drottar and Krueger, 1998 (from ECB, 2008a)
Freshwater algae	<i>Scenedesmus subspicatus</i>	96h-EC ₅₀	>500 mg/l ²	Siebel-Sauer and Bias, 1987 (from ECB, 2008a)
	<i>Pseudokirchneriella subcapitata</i> (formerly <i>Sele-nastrum capricornutum</i>)	72-hour EC ₅₀	>0.0025 µg/l	Roberts and Swigert, 1997 (from ECB, 2008a)
Saltwater algae	<i>Chlorella</i> sp.	96h-EC ₅₀	>1.5 mg/l ²	Walsh <i>et al.</i> , 1987 (from ECB, 2008a)
	<i>Skeletonema costatum</i>	72h-EC ₅₀	0.052 mg/l	Desjardins <i>et al.</i> , 2005 (from ECB, 2008a)
	<i>Thalassiosira pseudonana</i>	72h-EC ₅₀	0.040-0.38 mg/l	Walsh <i>et al.</i> , 1987 (from ECB, 2008a)
Sediment				
Freshwater sediment invertebrates	<i>Chironomus riparius</i>	28 day NOEC	NOEC is 13.6 mg/kg dry sediment	Oetken <i>et al.</i> , 2001 (from ECB, 2008a)
	<i>Hyalella azteca</i>	28 day NOEC	≥1,000 mg/kg dry sediment	Thomas <i>et al.</i> , 2003a,b (from ECB, 2008a)
	<i>Lumbriculus variegatus</i>	28 day NOEC	3.1 mg/kg dry sediment	Oetken <i>et al.</i> , 2001 (from ECB, 2008a)
Soil and terrestrial environment				
Terrestrial invertebrates	<i>Eisenia fetida</i>	56 day NOEC	128 mg/kg dry soil	Aufderheide <i>et al.</i> , 2003 (from ECB, 2008a)
Soil microorganisms	Nitrogen transformation activity	28 day NOEC	≥750 mg/kg dry soil	Förster, 2007 (from ECB, 2008a)

Terrestrial plants	<i>Allium cepa</i> , <i>Cucumis sativa</i> , <i>Glycine max</i> , <i>Lolium perenne</i> , <i>Lycopersicon esculentum</i> and <i>Zea mays</i> .	21 day NOEC	≥5,000 mg/kg dry soil	Porch <i>et al.</i> , 2002 (from ECB, 2008a)
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*1 See ECB (2008a) for full reference

*2 Value above the water solubility of the substance (around 66 µg/l). The data are best interpreted as showing no effects at the solubility limit of the substance.

5.1.4 TBBPA and derivatives

The ecotoxicity data for TBBPA have been reviewed in detail in ECB (2008b). The data are summarised in Table 33. The lowest long-term NOEC/EC₁₀ is the 5 day EC₁₀ for the marine copepod *Acartia tonsa* of 13 µg/l, which is similar to a NOEC of 17 µg/l determined in a long-term study with *Mytilus edulis*. PNECs for TBBPA have been estimated as 1.3 µg/l for freshwater, 0.25 µg/l for marine water, 12.5 mg/kg dry weight (normalised to 5% organic carbon) for freshwater sediment, 2.5 mg/kg dry weight (normalised to 5% organic carbon) for marine sediment and 0.012 mg/kg wet weight (normalised to 3.4% organic matter) for soil.

Environment Canada/Health Canada (2012) reported that there is some recent evidence to suggest that TBBPA may be capable of disrupting normal functioning of the thyroid system in amphibians and fish, and enhancing immune system activity in marine bivalves.

Little information is currently available on the environmental hazard from derivatives of TBBPA. Environment Canada/Health Canada (2012) used a modelling approach to predict that the toxicity of TBBPA bis(2-hydroxyethyl ether) (TBBPA-BHEE) may be similar to that of TBBPA. Similar predictions for TBBPA bis(allyl ether) (TBBPA-BAE) suggested that the substance would generally not show any toxicity to aquatic organisms up to its solubility limit; however, the predictions of chronic toxicity values were of an order similar to the solubility limit of the substance.

TABLE 33
SUMMARY OF ECOTOXICITY DATA FOR TBBPA

Trophic level	Species	Endpoint	Concentration	Reference ¹
Water				
Freshwater fish	<i>Brachydanio rerio</i>	96h-LC ₅₀	~3.0 mg/l	Lee <i>et al.</i> , 1993 (from ECB, 2008b)
	<i>Oncorhynchus mykiss</i>	45% mortality after 96 hours	1.1 mg/l	Wildlife International, 2003a (from ECB, 2008b)
	<i>Oryzias latipes</i>	48h-LC ₅₀	8.2 mg/l	CITI, 1992 (from ECB, 2008b)
	<i>Pimephales promelas</i>	96h-LC ₅₀	0.54 mg/l	Springborn Life Sciences, 1988b (from ECB, 2008b)
		35d-NOEC	0.16 mg/l	Springborn Laboratories, 1989b (from ECB, 2008b)
Freshwater invertebrates	<i>Daphnia magna</i>	48h-LC ₅₀	0.96 mg/l	Union Carbide Corporation, 1978a (from ECB, 2008b)
		21d-NOEC	0.30 mg/l	Springborn Laboratories, 1989a (from ECB, 2008b)
	<i>Chironomus tentans</i>	Effects on growth over 14 days	0.066 mg/l	Springborn Laboratories, 1989c (from ECB, 2008b)
Saltwater invertebrates	<i>Acartia tonsa</i>	48h-LC ₅₀	0.40 mg/l	Breitholtz <i>et al.</i> , 2001 (from ECB, 2008b)
		5 day EC ₁₀ (for larval development rate)	0.0127 mg/l	Wollenberger <i>et al.</i> , 2005 (from ECB, 2008b)

Trophic level	Species	Endpoint	Concentration	Reference ¹
	<i>Crassostrea virginica</i>	96h-EC ₅₀ (shell deposition)	0.098 mg/l	Springborn Life Sciences, 1989b (from ECB, 2008b)
	<i>Mysidopsis bahia</i>	96h-LC ₅₀	0.86 mg/l	Goodman <i>et al.</i> , 1988 (from ECB, 2008b)
	<i>Mytilus edulis</i>	70 day NOEC	0.017 mg/l	Brown <i>et al.</i> , 2005 (from ECB, 2008b)
	<i>Nitocra spinipes</i>	96h-LC ₅₀	0.35 mg/l	Breitholtz <i>et al.</i> , 2001 (from ECB, 2008b)
		18 day NOEC	≥0.035 mg/l	Breitholtz <i>et al.</i> , 2001
Freshwater algae	<i>Pseudokirchneriella subcapitata</i> (formerly <i>Sele-nastrum capricornutum</i>)	72h-NOEC	≥5.6 mg/l	Springborn Life Sciences, 1988a (from ECB, 2008b)
Saltwater algae	<i>Chlorella</i> sp.	96h-EC ₅₀	>1.5 mg/l	Walsh <i>et al.</i> , 1987 (from ECB, 2008b)
	<i>Skeletonema costatum</i>	72h-EC ₅₀	0.09-0.89 mg/l	Walsh <i>et al.</i> , 1987 (from ECB, 2008b)
	<i>Thalassiosira pseudonana</i>	72h-EC ₅₀	0.13-1.0 mg/l	Walsh <i>et al.</i> , 1987 (from ECB, 2008b)
Sediment				
Freshwater sediment invertebrates	<i>Chironomus riparius</i>	28d-NOEC	125 mg/kg dry sediment	Wildlife International, 2005a (from ECB, 2008b)
	<i>Hyalella azteca</i>	28d-NOEC	250 mg/kg dry sediment	Wildlife International, 2006d (from ECB, 2008b)
	<i>Lumbriculus variegatus</i>	28d-NOEC	90 mg/kg dry sediment	Wildlife International, 2002d (from ECB, 2008b)
Soil and terrestrial environment				
Terrestrial invertebrates	<i>Eisenia fetida</i>	56 day NOEC	0.29 mg/kg dry soil	ABC Laboratories, 2005 (from ECB, 2008b)
	<i>Enchytraeus crypticus</i>	21 day EC ₁₀	2.7 mg/kg dry weight	Sverdrup <i>et al.</i> , 2006 (from ECB, 2008b)
Soil microorganisms	Nitrogen transformation activity	28 day EC ₁₀	>1,000 mg/kg dry weight	Wildlife International, 2005c (from ECB, 2008b)
		NOEC	300 mg/kg dry weight	Sverdrup <i>et al.</i> , 2006 (from ECB, 2008b)
Terrestrial plants	<i>Allium cepa</i> , <i>Cucumis sativa</i> , <i>Glycine max</i> , <i>Lolium perenne</i> , <i>Lycopersicon esculentum</i> and <i>Zea mays</i>	21 day NOEC	16 mg/kg dry weight (lowest value, for <i>Cucumis sativa</i>)	Wildlife international, 2002a (from ECB, 2008b)
	<i>Trifolium pratense</i>	21 day NOEC	≥1,000 mg/kg	Sverdrup <i>et al.</i> , 2006 (from ECB, 2008b)

*1 See ECB (2008b) for full reference

5.1.5 DBDPE and EBTEBPI

DBDPE - Acute toxicity results for decabromodiphenyl ethane (DBDPE) for fish, invertebrates and algae have been reviewed by the Environment Agency (2007) and the available data are summarised in Table 34 below. Environment Agency (2007) concluded that it was not possible to derive a meaningful PNEC for DBDPE for surface water from these data as no toxic effects were seen in any of the tests with DBDPE, indicating that the substance is not acutely toxic at concentrations up to its water solubility limit in these species. However, a more recent study by Nakari and Huhtala (2010) suggests that DBDPE may be acutely toxic to *Daphnia magna* (48h-EC₅₀ of 0.019 mg/l) and may affect reproduction in fish at relatively low concentrations, although it should be noted that these

results are based on nominal concentrations and the actual water solubility of DBDPE may be lower than these values.

The results of long-term toxicity tests using DBDPE with freshwater sediment-dwelling organisms (*Chironomus riparius* and *Lumbriculus variegatus*) are available (Table 34). No statistically significant effects were observed with either species at concentrations up to 5,000 mg/kg dry weight. Environment Agency (2007) derived a PNEC_{sediment} (normalised to a standard organic carbon content of 5%) of ≥60 mg/kg wet weight for freshwater sediment organisms and ≥6 mg/kg wet weight for marine sediment organisms, based on these data.

Tests using DBDPE with terrestrial organisms (Table 34) give indications of toxic effects in both plants and earthworms at relatively high concentrations. The lowest NOEC with plant species is 1,563 mg/kg dry weight with *Allium cepa* and the NOEC for *Eisenia fetida* is 1,970 mg/kg dry weight. Environment Agency (2007) estimate the PNEC_{soil} to be 26 mg/kg wet weight (normalised to a standard organic matter content of 3.4%).

TABLE 34
SUMMARY OF ECOTOXICITY DATA FOR DBDPE

Trophic level	Species	Substance	Endpoint	Concentration	Reference *1
Water					
Freshwater fish	<i>Danio rerio</i>	DBDPE	Effects on hatching and larval survival	0.010-0.020 mg/l	Nakari and Huhtala (2010)
	<i>Oncorhynchus mykiss</i>	DBDPE	96h-LC ₅₀	>110 mg/l *2	Blankinship and Krueger, 2003a (from Environment Agency, 2007)
	<i>Oryzias latipes</i>	DBDPE	48h-LC ₅₀	>50 mg/l *3	CITI, 1991 (from Environment Agency, 2007)
Freshwater invertebrates	<i>Daphnia magna</i>	DBDPE	48h-EC ₅₀	>110 mg/l *2	Blankinship and Krueger, 2003b (from Environment Agency, 2007)
			48h-EC ₅₀	0.019 mg/l	Nakari and Huhtala (2010)
Freshwater algae	<i>Pseudokirchneriella subcapitata</i> (formerly <i>Selenastrum capricornutum</i>)	DBDPE	96h-EC ₅₀	>110 mg/l *2	Desjardins and Krueger, 2003 (from Environment Agency, 2007)
Sediment					
Freshwater sediment invertebrates	<i>Chironomus riparius</i>	DBDPE	28 day NOEC	≥NOEC of 5,000 mg/kg dry weight	Krueger <i>et al.</i> , 2003a (from Environment Agency, 2007)
	<i>Lumbriculus variegatus</i>	DBDPE	28 day NOEC	≥NOEC of 5,000 mg/kg dry weight	Krueger <i>et al.</i> , 2003b (from Environment Agency, 2007)
Soil and terrestrial environment					
Terrestrial invertebrates	<i>Eisenia fetida</i>	DBDPE	56 day NOEC	1,970 mg/kg dry weight	Aufderheide, 2003 from Environment Agency, 2007)
Terrestrial plants	<i>Allium cepa</i> , <i>Cucumis sativa</i> , <i>Glycine max</i> ,	DBDPE	21 day NOEC	1,563 mg/kg dry soil (for <i>Allium cepa</i>)	Porch and Krueger, 2005 (from Environment Agency, 2007)

Trophic level	Species	Substance	Endpoint	Concentration	Reference ^{*1}
	<i>Lolium perenne</i> , <i>Lycopersicon esculentum</i> and <i>Zea mays</i>				

*1 See Environment Agency (2007) for full reference

*2 Substance tested as a Water Accomodation Fraction (WAF); the result is based on the loading rate. The data are best interpreted as showing no effects at the solubility limit of the substance.

*3 Value above the water solubility of the substance. The data are best interpreted as showing no effects at the solubility limit of the substance.

EBTEBPI - In contrast to DBDPE, few experimental data appear to be available on the ecotoxicity of ethylenebis(tetrabromophthalimide) (EBTEBPI). The substance is listed in the ECHA C&L database, but no environmental classification is given (data lacking).

5.1.6 Other BFRs

Although the BFRs covered in the previous sections are historically the most commonly used, there are numerous other BFRs currently commercially available, or becoming available. Only limited information is generally available for many of these BFRs. The toxicity and fate of these substances are described together in section 5.2.5.

5.2 Environmental fate

5.2.1 PBDEs

Much of the recent work on the environmental fate of PBDEs has focused on decaBDE, particularly whether or not it can degraded, metabolised, or otherwise broken down to form environmentally relevant amounts of PBDEs with lower amounts of bromine, or other hazardous substances. Certain lower brominated PBDEs are more toxic (see above) and more accumulative (see below) than decaBDE itself. For example, tetra- and pentaBDEs (commercial pentaBDEs) and hexa- and heptaBDEs (commercial octaBDEs) are listed as persistent organic pollutants (POPs) in Annex A of the Stockholm Convention. In addition, a recent proposal has been put forward by Norway to identify decaBDE itself as a possible POP under the Stockholm Convention (Norway, 2013). Several recent authoritative reviews and evaluations of the environmental fate of decaBDE have been undertaken (for example ACHS (2010), ECHA (2012b), ECB (2002), ECB (2004), Environment Agency (2009)); this Section is based mainly on the discussions and findings in these evaluations.

Abiotic degradation of decaBDE has been shown to occur in laboratory test systems. A degradation half-life for decaBDE of 51 days on the surface of high impact polystyrene (HIPS) samples, and a degradation half-life of around 12.5 days for decaBDE adsorbed to the surface of natural dusts, have been estimated (ACHS, 2010)⁶. The degradation is thought to proceed by a photolytic reductive debromination mechanism. Abiotic degradation of decaBDE to lower brominated products (e.g. PBDEs with fewer bromine atoms) has also been demonstrated in laboratory studies using test systems containing zero valent iron, iron sulphides or manganese oxides; however, the concentrations of these species used were much higher than typically found in natural soil systems. Consequently, the interpretation of the results in terms of degradation in natural soil systems is unclear (ACHS, 2010).

⁶ Degradation half-life: The time taken for 50% of substance to disappear/dissipate from a compartment following single first-order kinetics.

Laboratory studies using aerobic and anaerobic soils and sediment have generally shown that decaBDE has a long degradation half-life in such systems (typically > 1year). For example, little or no degradation of decaBDE was seen in anaerobic freshwater sediment after 32 weeks in the dark at 22°C. Similarly, only limited degradation of decaBDE was found over a 40 week period in a sediment microcosm study at 22°C in the dark; as well, little or no degradation of decaBDE occurred in aerobic and anaerobic soils with digested or activated sludge (ACHS, 2010).

Even though the degradation of decaBDE in these systems is slow, there is some evidence that debromination to lower brominated PBDEs can occur, albeit at a slow rate. Microflora from sewage sludge have been shown to be capable of debrominating decaBDE to form nona- and octaBDE. The estimated half-life for the degradation was of the order of 700 days when brominated primers (for example 4-bromobenzoic acid or a range of brominated aromatic compounds) were present. The half-life for the degradation was longer in the absence of primers (ACHS, 2010). Similarly it has been shown that decaBDE and octaBDE can be debrominated under anaerobic conditions using cultures of *S. multivorans* derived from activated sludge. Preliminary results from an unpublished mesocosm study carried out under semi-natural conditions in a Canadian lake are also suggestive of debromination of decaBDE to form nona- and octaBDEs in the environment (ACHS, 2010).

As well as for microorganisms, there is evidence that some fungi, e.g. white rot fungus may be capable of degrading decaBDE (ACHS, 2010).

An important recent study has investigated the degradation of decaBDE in a soil-plant system (ACHS, 2010). In this study, little or no degradation of decaBDE was evident over 60 days in a loamy soil without plants. However, in tests using the same soil but also containing plants (the species tested included radish, alfalfa, squash, pumpkin, maize and ryegrass), significant degradation of decaBDE to lower brominated PBDEs (nona-, octa-, hepta- and hexaBDEs) was evident. The degradation products were generally present in both the soil and the plants, so it is possible that metabolism in the plants could have been occurring as well as/instead of degradation in the soil.

Overall it can be concluded that degradation of decaBDE in the environment has the potential to lead to the formation of environmentally relevant amounts of more toxic and accumulative lower brominated PBDEs. The strongest evidence shows that such products include nona-, octa and heptaBDEs, but it is thought that hexa- and pentaBDEs may also be formed. Mechanisms by which this degradation could occur include photodegradation of decaBDE adsorbed to particulates (e.g. dusts) or surfaces, abiotic degradation in soils containing high concentrations of zero valent iron, iron sulphides or manganese oxides or certain aerobic and anaerobic organisms. Debromination of decaBDE could also occur via metabolism in some fish species (ACHS (2010) and ECHA (2012)). PBDEs as a group have high log Kow values (log Kow = 6.57 for pentaBDE (ECB, 2001), a minimum of 6.29 for octaBDE (values up to around 8.35-8.90 have been reported (ECB, 2003)) and a minimum of 6.27 for decaBDE (values up to around 9.97 have been reported (ECB, 2002 and 2004)). Consequently, the substances have high organic carbon-water partition coefficients (Koc is around 555,680 l/kg for pentaBDE (ECB, 2001), 1.36×10^6 l/kg for octaBDE (ECB, 2003) and 1.59×10^6 for decaBDE (ECB, 2002) and are expected to partition mainly to the sediment and soil phases in the environment.

Laboratory bioaccumulation studies with decaBDE have generally shown only limited accumulation of the substance (ECB, 2002). However, decaBDE is widely found in biota in the environment, including top predators and species from more remote regions, albeit at relatively low concentrations. The bioaccumulation potential of PBDEs is known to increase with decreasing bromine content (octaBDE and decaBDE have molecular weights >700 g/mole and their bioaccumulation potential may be limited by reduced bioavailability owing to the large molecular size) and a fish BCF value of around 14,350 l/kg has been determined for a commercial pentaBDE product (BCF values

for individual components within this product were found to be high, up to around 66,700 l/kg for tetraBDE, 17,700 l/kg for pentaBDE and 5,600 l/kg for hexaBDE; ECB, 2001).

5.2.2 HBCDD

The environmental fate of HBCDD has been reviewed in detail in ECB (2008a) and has been considered by European Chemicals Agency (ECHA, 2008).

ECB (2008a) considered that, although abiotic degradation of HBCDD is theoretically possible, it will likely be of limited importance for the environmental fate of HBCDD with the possible exception of anaerobic, reducing sediments.

HBCDD is not readily biodegradable in standard test systems (ECB, 2008a). Simulation studies in soil have shown that HBCDD has a relatively long biodegradation half-life in soil. In one study the biodegradation half-life of γ -HBCDD was determined to be 119 days (recalculated to 12°C) and, in a second study, no biodegradation of HBCDD was seen over 112 days' incubation. Similarly, in simulation studies in sediment, a DT₅₀ (time to 50% degradation) of around 210 days was determined for α -HBCDD under aerobic conditions and under anaerobic conditions (all data are recalculated to 12°C). The data for γ -HBCDD in sediment simulation studies is dependent to some extent on the concentration tested. At very low concentrations, primary degradation half-lives (for disappearance of the parent compound) of 21 and 61 days (both recalculated to 12°C) were obtained in two different sediments, whereas in a study using a concentration corresponding to that in more highly polluted areas, the DT₅₀ for γ -HBCDD was 197 days in aerobic sediment. In addition, data from sediment cores are suggestive of slow degradation rates of HBCDD in the environment (ECHA, 2008; ECB, 2008a). In contrast to this, rapid degradation of γ -HBCDD in anaerobic sediments (half-lives around 2-3 days or less, recalculated to 12°C) and anaerobic soil (half-life ~13 days, recalculated to 12°C) has been seen, possibly by an abiotic debromination process.

The initial degradation products from HBCDD are thought to include 1,5,9-cyclododecatriene (formed by a stepwise debromination reaction), which itself is not readily biodegradable but is mineralised in standard ready biodegradation test systems over extended timescales (e.g. 70% CO₂ formation was seen from 1,5,9-cyclododecatriene after 77 days' incubation using the OECD 301F Guideline test system) (ECB, 2008a).

HBCDD has a high potential for bioaccumulation. The BCF of HBCDD in fish has been determined to be 18,100 l/kg and there is large body of field measurements in biota that are consistent with biomagnification of HBCDD in the environment (ECHA, 2008; ECB, 2008a). ECHA (2008) notes that there are no diastereomer-specific BCFs available. However, it should be noted that the γ -HBCDD generally dominates in abiotic samples, whereas α -HBCDD generally dominates in biological samples despite it being present in commercial HBCDD in a relatively low concentration. It was hypothesised that the reasons for this phenomenon may be differences in bioavailability/uptake, differences in metabolism and/or bioisomerization of the different diastereomers (ECB, 2008a).

HBCDD is expected to adsorb strongly to sediment and soil. The log K_{ow} value for HBCDD is 5.62 and the K_{oc} value is estimated to be around 45,700 l/kg (ECB, 2008a). HBCDD also has potential for long-range transport (ECHA, 2008); the estimated distance for HBCDD to be transported was around 2,550 km in air and 2,600 km in water (ECB, 2008a). The atmospheric half-life is >2 days and the substance has commonly been found in abiotic samples (e.g. air, deposition and sediment) and biota samples (e.g. polar bears, birds' eggs, seals) from remote areas (ECHA, 2008). HBCDD is currently being considered for listing as a POP in Annex A of the Stockholm Convention.

5.2.3 TBBPA

An in-depth evaluation of the environmental fate of TBBPA has been carried out previously by ECB (2008b).

TBBPA is expected to degrade in the atmosphere by reaction with hydroxyl radicals; the half-life for the reaction has been estimated at around 130 hours. TBBPA is also susceptible to direct photodegradation using UV-radiation (e.g. 254 nm and >290 nm wavelengths) but the significance of the process in the environment is unclear. TBBPA is not expected to undergo significant hydrolysis in the environment (ECB, 2008b).

TBBPA has been shown to undergo biodegradation in both aerobic and anaerobic test systems (ECB, 2008b). Although TBBPA is not readily biodegradable in standard test systems, primary degradation of TBBPA has been found to occur in sediment and soil systems under aerobic conditions. Around 36-55% degradation of TBBPA was shown to occur over 56 days in a sediment system at 25°C; between 18 and 64% degradation occurred in soils over 64 days at 21.5°C. Mineralisation in soil has also been shown to occur, with around 18-22% mineralisation occurring over six months (mineralisation half-life >>6 months). There is some evidence that TBBPA can undergo O-methylation by certain bacterial strains. However, only trace amounts of the dimethyl ether or diethyl ether derivatives were found to be formed in aerobic degradation studies using soil systems. The other primary degradation products formed as a result of aerobic biodegradation of TBBPA are unclear.

Primary degradation of TBBPA has also been demonstrated under anaerobic conditions (ECB, 2008b). Around 10 to 56% degradation was seen over 64 days at 24°C in anaerobic soil systems, with the degradation rate being higher in a sandy loam and silty loam (approximate half-life of 60 to 70 days) than in clay soil (10% degradation in 64 days). The primary degradation half-life for TBBPA in an uncontaminated freshwater anaerobic sediment/water system was determined to be around 24-28 days at 20°C (the half-life in the sediment phase alone was around 28-42 days) and TBBPA was found to be degraded more rapidly in a contaminated sediment system with a high salt content (85% degradation in ten days at 30°C). The half-life of TBBPA in anaerobic marine sediments was determined to be around 25-30 days at 30°C. In sewage sludge the primary degradation half-life of TBBPA was determined to be 19 days at 35°C. The main primary degradation product formed under anaerobic conditions is bisphenol-A.

Overall it is concluded that it is possible that TBBPA may be degraded to bisphenol-A in anaerobic freshwater and marine sediments. Another possible metabolite/degradation product of TBBPA is tetrabromobisphenol-A-bis(methyl ether), which is potentially more bioaccumulative than TBBPA itself, although this is considered to be a minor degradation product based on the currently available data (ECB, 2008b and EC, 2008).

TBBPA has a high log Kow (log Kow 5.9) and a low vapour pressure and so in the environment it preferentially distributes to environmental compartments other than the atmosphere (ECB, 2008b). As tetrabromobisphenol-A is a weak acid that may be dissociated at environmentally relevant pHs, the adsorptive behaviour of TBBPA is expected to vary with pH of the soil or sediment system. An analysis of the available soil and sediment adsorption data was carried out in ECB (2008b); this suggested that the Koc value for TBBPA was around 49,700 l/kg but higher values up to around 2,000,000 l/kg have also been measured. The analysis also indicated that a substantial amount of the adsorption could be governed by factors other than the organic carbon content (i.e. adsorption to mineral fractions could be important). Level III fugacity modelling (ECB, 2008b) predicted that when TBBPA is released to air it will distribute mainly to the soil compartment, while when released to soil it will remain in the soil with only a small fraction distributing to water and sediment. When released to water, it will distribute to sediment, with a small but significant fraction also predicted to be present in the water phase. The potential for long-range transport of TBBPA was predicted to be comparatively low.

The bioconcentration of TBBPA in fish has been investigated in a number of studies using either parent compound analysis or radiolabelled TBBPA. The results from studies using parent compound analysis are reasonably consistent, giving BCF values in the range ~170-485 l/kg. The studies

using radiolabelling generally result in higher BCF values in the range ~1,234-1,300 l/kg. The higher values obtained reflect the fact that TBBPA is extensively metabolised in fish and so, based on radiolabel analysis, the BCF includes the contribution from these metabolites (ECB, 2008b). Similarly the bioconcentration factors for TBBPA determined in invertebrates are around 148-160 l/kg based on parent compound analysis and 780-870 based on radiolabel measurements (ECB, 2008b). Excretion of TBBPA from aquatic organisms is rapid, with a half-life generally of the order of <1 day in fish to 3-5 days in marine oysters.

The available avian and mammalian data show that, although the substance is absorbed through the gut, it has a low potential for bioaccumulation on repeated exposure because it is rapidly excreted via faeces (ECB, 2008b).

In comparison to TBBPA, the environmental fate of derivatives of TBBPA has been much less studied. ECB (2008b) considered that some of the simple ether derivatives of TBBPA, for example the bis(allyl ether) TBBPA-BAE, the bis(2-hydroxyethyl ether) (TBBPA-BHEE) and the bis(2,3-dibromopropyl ether) (TBBPA-BDBPE) derivatives appear, at least theoretically, to have some potential to form TBBPA in the environment through a (bio)degradation process but the significance of this is unknown. The persistence of TBBPA-BDBPE in a sediment mesocosm has recently been investigated by De Jourdan *et al.* (2013). This study found that the median dissipation time for TBBPA-BDBPE was around 32 days in the particulate phase and 102 days in the sediment phase. TBBPA was detectable in some of the samples as a degradation product.

Environment Canada/Health Canada (2012) considered the environmental fate of two derivatives of TBBPA, the bis(allyl ether) derivative (TBBPA-BAE) and the bis(2-hydroxyethyl ether) derivative (TBBPA-BHEE), and concluded that the biodegradation half-lives of these two derivatives were likely to be 182 days or more in soil and water and 365 days or more in sediment based on modelled data. The atmospheric half-lives for reaction with hydroxyl radicals were estimated to be 0.159 and 0.418 days respectively (Environment Canada/Health Canada (2012)). Environment Canada/Health Canada (2012) considered that, based on modelled data, the environmental distribution of these derivatives would be similar to that of TBBPA itself. Environment Canada/Health Canada (2012) further considered the bioaccumulation potential of TBBPA-BAE and TBBPA-BHEE to be low based on the available experimental data (the BCF for TBBPA-BHEE in fish was determined to be 10 to 53 l/kg) and modelled data.

Bergman *et al.* (2012a) gives estimated log Kow values and Koc values for several derivatives of TBBPA. These are summarised in Table 35. The derivatives all have relatively high log Kow and Koc values, indicating that they will partition preferentially onto sediment and soil in the environment.

TABLE 35
SUMMARY OF LOG KOW AND KOC VALUES FOR DERIVATIVES OF TBBPA (FROM BERGMAN *ET AL.*, 2012A)

Abbreviation	TBBPA derivative	Log Kow	Koc (l/kg)
TBBPA-BME	bis(methyl ether) derivative	10.35	1×10 ⁷
TBBPA-BOAc	bis(acetate) derivative	9.45	3.28×10 ⁶
TBBPA-BHEE	bis(2-hydroxyethyl ether) derivative	8.51	1.01×10 ⁶
TBBPA-BAE	bis(allyl ether) derivative	11.42	1×10 ⁷
TBBPA-BA	bis(acrylate) derivative	9.37	2.99×10 ⁶
TBBPA-BGE	bis(glycidyl ether) derivative	8.87	1.60×10 ⁶
TBBPA-BP	bis(propanoate) derivative	10.47	1×10 ⁷
TBBPA-BHEEBA	bis(2-hydroxyethyl ether) bisacrylate derivative	10.76	1×10 ⁷
TBBPA-BDBPE	bis(2,3-dibromopropyl ether) derivative	12.99	1×10 ⁷

5.2.4 DBDPE and EBTEBPI

DBDPE

The environmental fate and behaviour of DBDPE has been reviewed in detail in Environment Agency (2007). This review considered hydrolysis to be an insignificant removal process for DBDPE in the aquatic environment and concluded that DBDPE is unlikely to be rapidly degraded by reaction with OH radicals if released to the atmosphere. DBDPE is not readily biodegradable in standard test systems; predictions carried out by Environment Agency (2007) suggest that DBDPE is unlikely to biodegrade rapidly in the aquatic environment under aerobic conditions. Environment Agency (2007) considered that there was a potential for DBDPE to undergo reductive debromination by analogy with decaBDE and Wang *et al.* (2012) have shown that DBDPE may have potential to undergo photolytic debromination reactions; however, the environmental significance of such reactions is currently unknown.

Based on the high log Kow (7-10 or more), DBDPE is expected to adsorb strongly to organic matter in sewage sludge, soils and sediments. Environment Agency (2007) estimated the Koc value to be of the order of 1×10⁶ l/kg for DBDPE. The relatively low vapour pressure and high adsorption to particulate matter suggest that volatilisation to the atmosphere from aquatic and terrestrial compartments is unlikely to be a significant distribution process for DBDPE. DBDPE present in the atmosphere would be expected to be associated with atmospheric particulates and removed by processes such as wet or dry deposition, but long-range atmospheric transport on such particulates is also a possibility (Environment Agency, 2007).

The available information on the bioaccumulation potential of DBDPE is limited and, in some cases, of uncertain reliability (Environment Agency, 2007). A bioconcentration study with fish appears to show a low level of accumulation (a limit value for the BCF is <25 l/kg). However, there are uncertainties over the actual dissolved concentration to which the fish were exposed and, assuming the actual exposure concentration was close to the solubility limit of DBDPE, the actual BCF could be higher at around 1,600 l/kg. Data from a field study found DBDPE to be present in some fish species sampled, but Environment Agency (2007) considered that it was not possible to estimate a reliable biomagnification factor or trophic magnification factor owing to the low concentrations and detection frequency involved, as well as uncertainties about the state of the system over the study period. Overall, Environment Agency (2007) concluded that there was currently insufficient reliable

data with which to quantify the bioaccumulation potential of DBDPE in both aquatic and terrestrial organisms.

EBTEBPI

In contrast to DBDPE, few experimental data appear to be available on the environmental fate of EBTEBPI. The substance was considered in a recent review by the European Food Safety Authority (EFSA, 2012a) and the log K_{ow} and K_{oc} were reported to be 6.63 and 96,500 l/kg respectively, which indicates that the substance will adsorb strongly to sediment and soil. The BCF in fish was reported to be low (<33 l/kg) but the EFSA (2012a) report considered the potential for accumulation in mammals to be high based on modelling. The overall environmental persistence (P_{ov}) was estimated to be >500 days, again based on modelling.

EBTEBPI has previously been evaluated in the EU by the TC NES sub-group on identification of PBT and vPvB substances consisting of Member State representatives and European Chemical Bureau staff (TC NES, 2008). According to the evaluation, EBTEBPI was not considered a PBT substance. EBTEBPI meets the P/vP (persistent/very persistent) criteria based on screening data, but the substance does not meet the B (bioaccumulative) criterion based on indicators of limited bioaccumulation potential. It also does not meet the T (toxic) criterion in mammals (TC NES, 2008).

5.2.5 Other BFRs

As mentioned above, there are numerous other BFRs currently on the market, or becoming available. Only limited information is generally available for many of these BFRs. A recent review by the European Food Safety Authority (EFSA, 2012a) considered the environmental fate of these substances, and a summary of their findings is given in Table 36. The EFSA review of brominated phenols and their derivatives does not include a summary on environmental persistence and bioaccumulation potency but data for four substances which are either registered under REACH or reported in surveys of BFRs in the environment are included in the table below: DBP, TBP and TBP-AE and PBP.

The EFSA (2012a) review considered the overall environmental persistence (P_{ov}) based on modelled data and the potential for bioaccumulation (considering modelled and experimental data where possible). In Table 36 these data have been supplemented with information on the environmental effects based on the classification supplied in the ECHA C&L database. For comparison purposes, the available information on the BFRs reviewed in the previous sections is also summarised.

Many, but not all, of the BFRs have log K_{ow} values of 5-6 or higher and so are potentially bioaccumulative, although it is possible that bioavailability of some of the very large molecules (those with molecular weights above 700 g/mole) may be low, leading to a bioaccumulation potential that is lower than expected based on log K_{ow} alone. EFSA (2012a) concludes that based on the limited experimental data on environmental behaviour, BTBPE and HBB were identified as compounds that could raise a concern for bioaccumulation.

The formation of environmentally problematic degradation products has not been reviewed in detail as part of this survey, as it will differ from substance to substance and an assessment has been beyond the limit of the study. Gouteux *et al.* (2007) have demonstrated that TBBPA carbonate oligomer, bromostyrene oligomers and pentabromobenzyl acrylate oligomer (with a molecular weight ranging between 3,500 and 80,000 Da) by thermal stress release substances which were identified as substituted alkyl benzenes or phenols with two to six bromine atoms. The results of an evaluation of the environmental persistence and potential to bioaccumulate of these substances indicated that the majority of these compounds were expected to bioaccumulate in the food chain (Log K_{ow} > 5 and/or BCF > 5,000) and to persist in the environment. The results indicate that further evaluation of degradation products of other BFRs is necessary for a full assessment of the potential environmental impacts of the flame retardants.

TABLE 36
SUMMARY OF ENVIRONMENTAL FATE AND EFFECTS OF OTHER BFRS AS COMPARED TO THE MAIN BFRS

Substance		CAS No	MW *2	Log Kow*2	Env. persistence	Bioaccumulation potency *2		Env. toxicity *3
Abbreviation *1	Name				*2	Environment	Mammals	
TBBPA	Tetrabromobisphenol A	79-94-7	543	5.9 (see Section 5.1.4)	Mineralisation half-life in soil > 6 months. Primary degradation occurs under aerobic and anaerobic conditions (see Section 5.1.4)	BCF ≤1,300 l/kg		Aquatic Acute 1 Aquatic Chronic 1 (harmonised class.)
PBDEs	Polybrominated diphenyl ethers	1163-19-5 (DecaBDE) 32536-52-0 (OctaBDE) 32534-81-9 (PentaBDE)	959 (decaBDE) 801 (octaBDE) 565 (PentaBDE)	>>6 (DecaBDE and OctaBDE) 6.57 (PentaBDE) (see Section 5.1.2)	Degradation half-life >1 year. Debromination of decaBDE to form more toxic and accumulative lower brominated congeners can occur (see Section 5.1.2)	Increases with decreasing bromine content. BCF around 66,700 l/kg for tetraBDE, 17,700 l/kg for pentaBDE, 5,600 l/kg for hexaBDE but low for decaBDE (see Section 5.1.2)		Aquatic Chronic 4 (DecaBDE; some self classifications) Not classified (OctaBDE; harmonised class.) Aquatic Acute 1 Aquatic Chronic 1 (PentaBDE; harmonised class.)
HBCDD	Hexabromocyclododecane	25637-99-4 3194-55-6		5.62 (see Section 5.1.3)	Degradation half-life 119 days or more in soil and ~200 days in sediment (see Section 5.1.3)	BCF 18,100 l/kg (see Section 5.1.2)		Not classified (harmonised class.) Aquatic Acute 1 Aquatic Chronic 1 (some self classifications)
4'-PeBPO-BDE208	Pentabromophenoxy-nonabromodiphenyl ether	58965-66-5	1367	12.67 16.894	Pov>500 days May be susceptible to photolytic debromination	No data BCF = 34	No data	Not classified (data lacking)

Substance		CAS No	MW *2	Log Kow*2	Env. persistence	Bioaccumulation potency *2		Env. toxicity *3
Abbreviation *1	Name				*2	Environment	Mammals	
BDBP-TAZTO	1,3-Bis(2,3-dibromopropyl)-5-(2-propen-1-yl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	75795-16-3	569	3.55	No data	No data	No data	No data
BEH-TEBP	Bis(2-ethylhexyl) tetrabromophthalate	26040-51-7	706	9.34	No data Median dissipation time in sediment >200 days ⁵	Low (MW ≈ 700 Da)	No data	Not classified (data lacking)
BTBPE	1,2-Bis(2,4,6-tribromophenoxy) ethane	37853-59-1	688	8.31	Pov>500 days Median dissipation time in sediment ~187 days ⁵	Log BAF 3.3-6.1 ⁵	High	Not classified (no details)
DBDPE	Decabromodiphenyl ethane	84852-53-9	971	11.1	Pov>500 days (see also Section 5.1.5)	Low (MW > 700 Da)	Unclear	Aquatic Chronic 4
DBE-DBCH	4-(1,2-Dibromoethyl)-1,2-dibromo cyclohexane	3322-93-8	428	4.82	No data	No data	High	Not classified (data lacking)
DBHCTD	5,6-Dibromo-1,10,11,12,13,13-hexachloro-11-tricyclo[8.2.1.0 _{2,9}] tridecene	51936-55-1	541	7.62	Pov>500 days	No data	High	No data
DBNPG	Dibromoneopentylglycol	3296-90-0	262	0.41	No data	No data	No data	Aquatic Chronic 4
DBP	2,4-Dibromophenol *	615-58-7	252	3.47	No data	Predicted BCF: 24	No data	Not classified (data lacking)
DBP-TAZTO	1-(2,3-dibromopropyl)-3,5-diallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	57829-89-7	409	2.66	No data	No data	No data	No data
DBS	Dibromostyrene	31780-26-4	262	No data	No data	No data	High	Not classified (no details)
EBTEBPI	Ethylenebis (tetrabromophthalimide)	32588-76-4	951	6.63	Pov>500 days	No data	High	Not classified (data lacking)

Substance		CAS No	MW *2	Log Kow*2	Env. persistence	Bioaccumulation potency *2		Env. toxicity *3
Abbreviation *1	Name				*2	Environment	Mammals	
EH-TBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate	183658-27-7	550	7.73	No data	No data	High	No data
HBB	Hexabromobenzene	87-82-1	551	6.11	Pov>500 days	Log BAF 3.3-5.5 ⁵	High	Not classified (data lacking/inconclusive)
HBCYD	Hexabromocyclodecane	25495-98-1	614	No data	Pov>500 days	No data	High	No data
HCTBPH	1,2,3,4,7,7-Hexachloro-5-(2,3,4,5-tetrabromophenyl)-bicyclo[2.2.1]hept-2-ene	34571-16-9	693	10.24	Pov>500 days	No data	High	No data
HEEHP-TEBP	2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	20566-35-2	628	1.04	No data	No data	No data	Aquatic Chronic 3
OBTMPI	Octabromotrimethylphenyl indane	1084889-51-9 1025956-65-3 893843-07-7 155613-93-7	868	15.11	Pov>500 days	No data	No data	No data
PBB-Acr	Pentabromobenzyl acrylate	59447-55-1	557	5.60	Pov>500 days	No data	High	Aquatic Chronic 4
PBEB	Pentabromoethylbenzene	85-22-3	501	6.76	Pov>500 days	Log BAF 2.7-4.1 ⁵	High	Not classified (data lacking)
PBP	Pentabromophenol *	608-71-9	489	5.22	No data	Predicted BCF: 3,100	No data	No data
PBT	Pentabromotoluene	87-83-2	487	6.25	Pov>500 days	BCF = 270 Log BAF 2.0-4.8 ⁵	High	Aquatic Acute 1 Aquatic Chronic 1
TBCO	1,2,5,6-Tetrabromocyclooctane	3194-57-8	428	5.28	No data	No data	High	No data
TBNPA	Tribromoneopentyl alcohol	1522-92-5	325	2.06	No data	No data	No data	Not classified (data lacking/inconclusive)
TBP	2,4,6-tribromophenol *	118-79-6	331	4.40	No data	BCF: 120	No data	Aquatic Acute 1
TBP-AE	2-(allyloxy)-1,3,5-tribromobenzene *	3278-89-5	371	5.04	No data	No data	No data	No data

Substance		CAS No	MW *2	Log Kow*2	Env. persistence	Bioaccumulation potency *2		Env. toxicity *3
Abbreviation *1	Name				*2	Environment	Mammals	
TBX	2,3,5,6-Tetrabromo-p-xylene	23488-38-2	422	6.20	Pov>500 days	No data	High	Not classified (data lacking)
TDBPP	Tris(2,3-dibromopropyl) phosphate	126-72-7	698	3.71	No data	No data	No data	Aquatic Acute 1 Aquatic Chronic 1
TDBP-TAZTO	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-trione	52434-90-9	729	4.45	No data	No data	No data	Aquatic Chronic 4
TTBNPP	Tris(tribromoneopentyl) phosphate	19186-97-1	1018	7.55	Pov>500 days	No data	No data	No data
TTBP-TAZ	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine	25713-60-4	1067	12.97	Pov>500 days	No data	No data	No data

Sources:

*1 Bergman *et al.*, 2012a.

*2 EFSA, 2012a, unless otherwise indicated ("No data" is indicated in the EFSA assessment). For substances marked with a * by substance name, data are from EFSA, 2012b (for these "no data" indicates that no data are provided in the EFSA review).

*3 C&L database. Substances indicated with "harmonised class" have a harmonised classification in accordance with the CLP Regulation. No data indicates that there is no entry for the substance within the database. Where the substance is not classified for environmental effects the reason for the "not classified" is given in brackets where available.

*4 Letcher and Chen (2013).

*5 De Jourdan *et al.* (2013).

*6 Wu *et al.* (2011).

5.3 Environmental exposure

5.3.1 Sources of release

Releases in Denmark

No detailed assessment of releases of BFRs in Denmark is available.

The 1999 substance flow analysis for BFRs estimated a total emission of BFRs to air of 0.2-1.6 t/y to air (nearly 100% from product service life), 0.005-0.07 t/y to water (effluent from sewage treatment plants) and 0.03-0.3 t/y to soil (application of sewage sludge) on the basis of limited data. The study did not provide a split between the different BFRs, but stated that the majority would be additive flame retardants.

The most recent monitoring data concerning municipal sewage treatment plants from the NOVANA programme are shown in the table below. Both the average and the median for the measured PBDEs are below the detection level of 0.01 µg/l. Monitoring data for other BFRs have not been available, but some data from regional programmes are described in section 4.1.

TABLE 37
MOST RECENT MONITORING DATA FOR BROMINATED FLAME RETARDANTS IN OUTLETS FROM POINT SOURCES FROM THE NATIONAL MONITORING AND ASSESSMENT PROGRAMME

Substance	Point source	Number of samples *1	Average µg/l	Median µg/l	Year	Source
BDE-47 BDE-99 BDE-209	WWTP outlet	30-40	<0,01	<0,01	2011	Naturstyrelsen 2012
BDE-47 BDE-99 BDE-100 BDE-153 BDE-154 BDE-183	WWTP outlet	37 (0)	<0,01	<0,01	2007-09	Naturstyrelsen 2010
BDE-209	WWTP outlet	37 (0)	<0,03	<0,03	2007-09	Naturstyrelsen 2010

*1 Number of positive samples in brackets

*2 From bar chart in Table 9.13 in reference, Y axis is logarithmic.

<d.l. : Below detection level. n.i.: not indicated

The Danish national surveillance programme for the aquatic environment (formerly NOVA 2003, now NOVANA) includes monitoring of trace elements and organic xenobiotics in discharges from sewage treatment plants and other point sources since 1998. With the objective of enabling the use of the resulting information in the planning of future surveillance programmes and for assessment of the total amount of substances discharged from Danish sewage treatment plants, the point source data on hazardous substances for the period 1998-2009 were analysed (Kjølholt *et al.*, 2011). The maximum reported concentration for each congener in inlets was in the range of 0.01 (e.g. BDE-100) to 0.4 µg/l (BDE-209) and in the outlets between 0.01 (e.g. BDE-100) to 0.5 µg/l (BDE-209). For none of the nine monitored PBDEs could a national means for inlet and outlet be established because all measurements were below the detection limit. Consequently, the total releases from sewage treatment plants could not be estimated.

Releases at EU level – EU Risk Assessments

Worst case release estimates have been developed as part of the EU Risk Assessments for the PBDEs, HBCDD and TBBPA (ECB, 2002, 2008a, 2008b). The releases from production processes may today be significantly lower, as described below, whereas releases from other sources may still be of the same magnitude for the three substances still used in significant amounts: decaBDE, TBBPA and HBCDD.

DecaBDE – The total releases of decaBDE in the continental scenario were estimated at approximately 0.01-0.1 t/y to air, 0.1 t/y to waste water, 9.4 t/y to surface water, 28 t/y to industrial/urban soil and 6,700 t/y to landfill/incineration (as updated in ECB, 2004). The major sources of release to air were rubber and polymer processing and textile disposal. The major source to waste water was textile formulation and backcoating, while textile "disposal particulate loss" (uncontrolled losses of textiles) was the major source of decaBDE in direct releases to surface water and industrial/urban soil.

HBCDD – The total release of HBCDD is estimated at 0.06 t/y to air, 2.9 t/y to waste water and 0.9 t/y to surface water (ECB, 2008a) in the continental scenario. The emissions to air were mainly from formulation and industrial uses of the flame retarded plastics, whereas emissions from service life accounted for less than 10%. The releases to waste water and direct release to surface water occurred mainly from industrial backcoating of textiles (>90%).

TBBPA - The total releases of TBBPA in the continental scenario were 0.2 t/y to air, 1.1 t/y to waste water, 0.3 t/y to surface water and 0.05 t/y to industrial urban soil (ECB, 2007). The major sources of releases to air, waste water and surface water were compounding of ABS and manufacture of epoxy and polycarbonate resin. Volatilisation during service life of articles from additive flame retardants use was approximately 15% of the total emissions to the air whereas other losses from the service-life of articles were considered negligible.

DBDPE – According to the Environmental Risk Evaluation from Environment Agency (2007), no specific information is available about either direct releases of DBDPE from industrial applications or indirect releases from treated articles in service and at disposal. The risk evaluation was therefore based on generic industry information and a number of assumptions. Overall, environmental releases were expected to be highest from textile backcoating applications because these are wet processes. Diffuse emissions from treated articles over their lifetime will undoubtedly occur, and are difficult to quantify, but the releases are estimated to be relatively small compared to the predicted local releases from industrial sites (Environment Agency, 2007). The estimated release figures were not included in the public version of the Risk Evaluation.

Other BFRs - Data on total releases of other BFRs at the EU level have not been identified.

Releases from production processes – EU level

The EU Risk Assessment for the BFRs identified the need for reducing the releases of the substances from production processes. A Voluntary Emissions Control Action Programme (VECAP) was developed and first implemented in 2004 by three major producers of flame retardants in partnership with downstream user industries. The VECAP programme addresses decaBDE, TBBPA and HBCDD and prepares annual reports on used volumes and emissions from manufacturers and industrial downstream users in Europe. The reported volumes sold are shown in Chapter 3 while emissions for the period 2007 to 2012 are shown in Table 38 (VECAP, 2011). In 2010, a total of 16,000- 22,000 tonnes of the three BFRs were sold for downstream uses in Europe.

VECAP does not physically measure emissions from chemical production processes, but rather calculates or estimates potential emissions associated with user and producer processes and practice, based on practical experience and studies.

In 2011 total emission factors for all processes were (in gram per tonne sold to downstream users) (VECAP, 2012):

- DecaBDE: 31 g/t to land, 18 g/t to water and 11 g/t to air.
- HBCDD: 1 g/t to land, 2 g/t to water and 36 g/t to air.
- TBBPA: 0 g/t to land, 0.2 g/t to water and 1 g/t to air.

TABLE 38
TOTAL EMISSIONS BY MEMBERS OF THE VECAP PROGRAMME (VECAP, 2012)

Substance	Total potential emission from manufacturers and downstream users in Europe, t/y *1					Coverage 2011 *2
	2007	2008	2009	2010	2011	
DecaBDE	<4	<1.5	<1.5	<0.5	<0.3	84%
HBCDD	<2.5	<0.5	<0.65	<0.5	<0.25	98%
TBBPA	<1	<0.15	<0.5	<0.005	< 0.003	95%

*1 The emissions in a specific year are referred to in the report as the survey results of the subsequent year. In this table, the emission data from the 2011 survey are referred to as 2010 emission.

* Indicates the percentage of the total volumes sold by EFRA member companies covered by the survey.

Releases in the Baltic Sea Region

Based on a substance flow analysis approach, sources of releases of PBDEs (all PBDEs taken together) and HBCDD in the Baltic Region have been estimated as part of the regional project "Control of hazardous substances in the Baltic Sea region", COHIBA (COHIBA, 2012). The substance flow diagrams for the PBDEs and HBCDD prepared as part of the COHIBA project are shown in Annex 4.

PBDEs - The emissions of PBDEs to environmental compartments within the Baltic Sea region as estimated in the COHIBA project tend to originate mainly from the application of contaminated sewage sludge, followed by emissions during the service life of flame retardant products in the form of release via the indoor environment. The emissions to the indoor environment (300-900 kg/year) are estimated to be of a similar order of magnitude as the total emissions to the outdoor environment. The amount reaching the environmental compartments from the indoor environment is estimated to be lower (3-60 kg). According to COHIBA (2012), this is possibly an effect of dust removal indoors, but could also be due to incomplete figures from some of the countries. A recent Swedish study (referred to in COHIBA, 2012) indicated that indoor air may contribute as much as 86% of the total releases to outdoor air. The modelling study part of the COHIBA project indicates low potential for transport of PBDEs from inland soil to the Baltic, but it is possible that certain extreme conditions (e.g. flooding, erosion etc.) not considered in the model scenarios, could lead to such release (COHIBA, 2012).

The estimated emissions to air in the Baltic Region (4-100 kg) are about a factor of 10-20 lower than the estimated atmospheric deposition in the area (approximately 100-700 kg/year for BDEs-47, -99, -100, -209), indicating that long-range transport followed by deposition is likely to be important for these substances (COHIBA, 2012). The difference could also indicate that the emissions from the indoor to the outdoor environment are underestimated in the study (comment by the authors of this report).

HBCDD - The major sources of HBCDD to environmental compartments in the Baltic region are construction and demolition of buildings and manufacturing of flame retardant products (COHIBA, 2012). Manufacture of HBCDD does not occur within the Baltic Sea Region. The estimated emis-

sions from the demolition of buildings may be part of a future scenario, as many buildings with HBCDD-containing insulation material are not yet being demolished. Moreover, HBCDD is emitted during its service life, albeit in smaller quantities. It was estimated that part of the service life emissions would end up in wastewater; in the WWTP the majority of the HBCDD is removed from the water phase by partitioning to sludge. To the extent this sludge is used on agricultural soils, the substance would enter the environment by this route.

5.3.2 Monitoring data

The Danish NOVANA assessment programme

The national environmental monitoring and assessment programme, NOVANA, includes measurements of three PBDE congeners in point sources and of total PBDE in two marine species (Table 39). The data are not reported annually, but rather approximately every third year. Other BFRs are not regularly monitored.

Some measurements of HBCDs and other BFRs have been included in regional surveys in the Nordic or Baltic environments and are mentioned in this context below.

TABLE 39
BROMINATED FLAME RETARDANTS INCLUDED IN THE NATIONAL MONITORING AND ASSESSMENT PROGRAMME FOR THE AQUATIC AND TERRESTRIAL ENVIRONMENT, NOVANA 2011-2015 (NOVANA, 2011)

Substance	Point sources	Marine Environment	Ground water
BDE-47	x *1		
BDE-99	x *1		
BDE-209	x *1		
PBDE		x (flounder, eelpout)	

*1 Only in a small, simple WWTP.

An initial screening in 2000 of the PBDEs at ten sediment stations and fifteen mussel stations showed that the highest contamination was found in sediments (21.5 ng/g dry weight) and mussels (0.811 ng/g wet weight) close to populated areas (Christensen and Platz, 2001). Notably, the concentration of decaBDE (BDE209) in sediments in most stations was significantly higher than the concentration of tetra- to hexaBDEs (Figure 1).

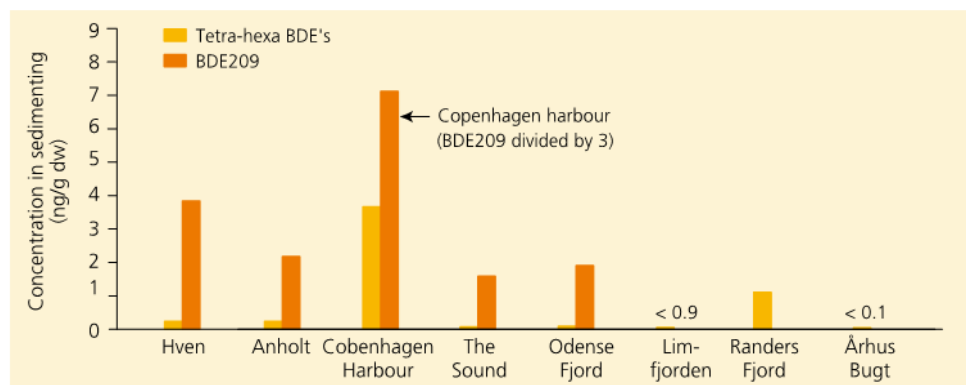


FIGURE 1
CONCENTRATIONS OF PBDE IN MARINE SEDIMENTS IN DENMARK. BDE 209 IS decaBDE. (CHRISTENSEN & PLATZ, 2001 AS CITED BY DAHLLÖF AND ANDERSEN, 2009)

In blue mussels, the sum of the 4 lower brominated congeners (BDE47, BDE99, BDE100, and BDE153) was in the range of 0.08-0.81 µg/kg wet weight. Generally, freshwater sediments contained higher levels of PBDEs compared to marine sediments, except for the high levels found in Copenhagen harbour. Ranking of the concentration of PBDEs in sediment from Denmark gave the following order: BDE-209 >> BDE-99 > BDE-47 > BDE-100 > BDE-153 (Christensen and Platz, 2001).

The results from the NOVANA monitoring in 2009 revealed that of 10 monitored PBDEs, only 3 were demonstrated in more than one sample of blue mussels: BDE-47 in 8 of 34 samples, BDE-99 (pentaBDE congener) in 22, and BDE-154 in 24. The highest concentrations were for BDE-47 (0.95 µg/kg wet weight) and BDE-99 (1.25 µg/kg wet weight). Sediment samples were not reported.

According to the most recent assessment of the PBDEs in *Vandmiljø og Natur 2008 [Aquatic environments and Nature 2008]*, no environmental criteria for PBDEs have yet been established within the context of OSPAR (Nordemann Jensen *et al.*, 2010). Only one of the substances, BDE-47, is subject to a quality criteria within the Norwegian classification system, and the Danish results are assessed on the basis of this system. In around 4% of the samples of mussels examined, the content of BDE-47 was at a level corresponding to the classification of "moderately polluted". BDE-47 and BDE-99 were observed in around half of all sediment samples in 2008; however, in all samples the concentrations were low. (Nordemann Jensen *et al.*, 2010)

In a survey of 25 Danish lakes in 2008, BDE-47 (tetraBDE), BDE-99 (pentaBDE), and BDE-100 (pentaBDE) could be detected in the sediment of only one of the lakes, at levels of 0.6-1.9 µg/kg. BDE 153, BDE 154 and BDE 209 could not be detected in any of the lakes (Bjerring *et al.*, 2010).

HELCOM assessments of BFRs in the Baltic Sea

Two assessments of PBDEs and HBCDD in the Baltic Sea have been published by HELCOM in the assessment reports: "Hazardous substances of specific concern to the Baltic Sea" (HELCOM, 2009) and "Hazardous substances in the Baltic Sea" (HELCOM, 2010).

PBBDEs - According to HELCOM (2010), PBDEs mainly spread to the Baltic Sea environment by diffuse distribution via the atmosphere and rivers. The environmental distribution differs between the lower-brominated BDEs and the higher-brominated BDEs. Higher-brominated BDEs have low water solubility and are mainly distributed in the sediments. They are not easily transported from the sediment and suspended particulate material to marine organisms. Deca-BDE is therefore found only in low concentrations in fish, in contrast to the lower-brominated BDEs, which are commonly found in marine organisms.

The concentrations of BDE-47 (pentaBDE congener) in herring and perch muscle and in blue mussel varied throughout the Baltic Sea. In the southern regions outside the coast of Poland, levels were more than threefold higher than the threshold level of 0.005 mg/kg lw⁷. In the other parts of the region, the level was below 0.005 mg/kg lw or slightly above. Several time series of BDE-47 concentrations in herring muscle tissue from the Bothnian Sea, the Baltic Proper and the Kattegat showed significant decreasing trends, with half-lives in the herring populations of about 6–8 years.

In marine top predators, PBDE concentrations indicate a cause for concern according to HELCOM. For example, white-tailed sea eagles in the Baltic Sea (Nordlöf *et al.* 2007 as cited by HELCOM, 2010) have BDE concentrations (sum of four BDEs with four to six bromines) up to four times higher than the reported effect levels in exposed American kestrels, which were causing adverse effects (Ferne *et al.* 2005a, 2005b, 2009 as cited by HELCOM, 2010).

DecaBDE has generally not been analysed in fish from the Baltic Sea or has been found in low concentrations. However, Burreau *et al.* (2004 as cited by HELCOM, 2010) reported relatively high levels (median 48 µg/kg lw) in roach from the Archipelago Sea (Åland). DecaBDE was also found in perch (1.3 µg/kg lw) and pike (1.7 µg kg⁻¹ lw) from the same area.

According to HELCOM (2009), in general the results show that BDE-47 is the dominant congener in biota of the Baltic Sea. Ranking the BDE congeners according to the concentration in biota of the Baltic Sea yields the following order: BDE-47 > BDE-99 & BDE-100 > BDE-209. The levels in biota are, in general, low and always lower than the PNEC⁸ level. The high BDE-209 levels found in roach muscle are alarming; according to HELCOM (2009), more information on the BDE-209 levels in biota of the Baltic Sea is needed.

Relatively few studies have reported PBDEs in marine sediment from the HELCOM region. HELCOM (2009) refers to the Danish study mentioned above (Christensen and Platz, 2001), where decaBDE was reported to be the dominant BDE congener compared to lower-brominated congeners. The highest levels of pentaBDE were found in the Limfjord, Denmark. The Swedish sediment monitoring programme, covering 16 stations in the coastal and offshore areas of the Baltic Sea, showed that concentrations of BDE-47, BDE-99 and BDE-100 were clearly the highest in the Kattegat with concentrations at 0.44, 0.62 and 0.08 µg/kg d.w., respectively, at station Fladen (SGU 2003 as cited by HELCOM, 2010).

Ranking the BDE congeners according to concentration in the Baltic Sea sediments yields the following order: BDE-209 >> BDE-99 > BDE-47. In general, the levels in the sediment are low and do not exceed the PNEC level (HELCOM, 2009).

HBCDD - HBCDD mainly spreads to the environment by diffuse distribution via the atmosphere and rivers (HELCOM, 2010). HBCDD concentrations in herring muscle were found to exceed the threshold value at all monitoring stations near the Swedish coast from the Bothnian Bay to the Kattegat. Time series of HBCDD from monitoring sites along the Swedish coasts showed no significant trends in herring muscle tissue, whereas a clear increasing trend of about 3% per year ($p < 0.001$) was detected in eggs from common guillemot (*Uria aalge*) collected from Stora Karlsö in the Western Gotland Basin (HELCOM, 2010). An increasing trend in the HBCDD content of marine animals has been reported from many areas of the world (Bergman *et al.*, 2012b)

According to HELCOM 2009, Swedish results show that HBCDD levels in Baltic Sea fish are generally low and always lower than the estimated PNEC level of 1.53 mg/kg w.w. in prey tissue. Also, the

⁷ Threshold levels are threshold values that are either commonly agreed quality criteria or proposed levels below which toxic effects are not found in the environment (HELCOM, 2010) They are not equal to PNEC values.

⁸ PNEC: predicted no effect concentration

levels in the sediments of the Swedish coastal area are low compared to the estimated PNEC level of 0.170 mg/kg d.w..

Other BFRs - The HELCOM assessments do not include monitoring data for other BFRs.

Screening of BFRs in the Nordic Environment

A joint Nordic screening of environmental contaminants financed by the Nordic Council of Ministers has investigated the presence of a range of "new"⁹ brominated flame retardants and other related compounds in various parts of the Nordic environment (Schlabach *et al.*, 2011). Sixteen different brominated substances were included in this screening, and 16 PBDE congeners were also analysed as reference compounds, to provide for a more relevant discussion of the results.

The overall results of the screening showed that the "new" brominated flame retardants were regularly found in all the sample matrices indicating a widespread distribution in the Nordic environment. However, there were geographic differences and differences in occurrence among substances and groups of substances.

Some flame retardants (FRs) were frequently found in air. Phenolic BFRs occurred in air both from urban and background sites. DBP and TBP were most frequently found; the levels varied from <0.8 to 21 pg/m³ and <0.3 to 27 pg/m³, respectively. PBP was only found in urban air, in one sample from Oslo (1.5 pg/m³). The concentrations of the BFR ethers and esters varied for different substances and sites. EHTeBB and BTBPE were the substances most frequently detected while DPTE was measured in the highest concentration (3.2 pg/m³). TBA was determined in four of the air samples with the highest concentration at 13 pg/m³. The presence of BFRs in background air indicates that long-range transport in the atmosphere of these substances may take place. The air concentrations were generally higher in urban areas compared to background areas and increased concentrations of some BFRs were measured in indoor air.

Concentration ranges for the most frequently detected BFRs in biota, sediment and sludge are shown in Table 40. The phenolic BFRs, DBP and TBP, may originate from the industrial use of the substances, but they are also naturally formed in the marine environment (Schlabach *et al.*, 2011).

Some of the "new" BFRs were like the reference substances (PBDEs) widespread in fish, mussels and guillemot eggs in the Nordic region and several of the BFRs was present in all biota samples. The highest concentrations were found in fish liver samples collected in affected areas. The detection frequency of BFRs in sediments was high. Most of the sediment samples were, however, collected in urban areas where emissions from municipal sewage treatment plants and other diffuse sources may affect the concentrations. Increased concentrations of BFRs were also found in sediment taken in harbours and marinas. The BFRs were present in sludge from sewage treatment plants, storm water sludge and sludge from landfills. The frequent occurrence in the different sludge samples indicates a widespread use of these substances in the Nordic countries.

The concentrations of the "new" BFRs are, with a few exceptions, of the same order of magnitude or lower compared to the sum of BDE congeners BDE-28, -47, -99, -100, -153 and -154 (congeners of commercial PBDE included as priority substances under the Water Framework Directive). A comparison of the sediment concentrations as measured in the survey with the pentaBDE quality standard for marine sediment (QS sediment, 310 µg/kg d.w.) showed that the measured concentrations were below the QS, with the exception of the concentration of sum DBE-DBCH (350 ng/g d.w.) in one sample. According to the authors, data on ecotoxicological effects of the "new" BFRs are scarce. In a Norwegian screening study (Møskeland, 2010 as cited by Schlabach *et al.*, 2011), the predicted no-effect concentration (PNEC) were thus assigned to these substances by read-across from the BDEs and for TBBPA which have PNEC values derived in EU Risk Assessments and by the Swedish Chemicals Agency.

⁹ "New" indicates that the substances are new in a monitoring context – some of the substances have been marketed for decades.

The concentrations measured in biota were converted to concentrations in water using the formulae given in the EU Technical Guidance Document (see Schlabach *et al.* (2011) for details). The phenolic substances were predicted by this approach to have the highest water concentrations (TBP, max 0.13 µg/l; DBP max 0.059 µg/l), which were above the pentaBDE quality standard for marine water (0.053 µg/l). According to the authors, the initial risk assessment based on “read-across” from pentaBDE indicates that concentrations of the more water soluble substances may in some cases be at levels that can cause negative effects on the pelagic community. For the sediment compartment, the limit value was only exceeded in one sample. However, it was not possible to assess the ecotoxicological risk satisfactorily. Substance specific PNEC values need to be developed.

More specifically for substances in focus in this survey, the study found:

DBDPE - Sediment was analysed from 11 isolated Swedish lakes along a transect running from central Stockholm through the Stockholm archipelago to the Baltic Sea. DBDPE was present in all samples. In lake sediment, the levels ranged from 0.23 to 11 ng/g d.w. and were similar to the levels of decaBDE (0.48-11 ng/g d.w.). Since the lakes have no known point sources of BFRs, their presence in the sediments provides evidence for long-range atmospheric transport and deposition. In the marine sediment, the DBDPE and decaBDE levels decreased by a factor of 20-50 over 40 km from the inner harbour to the outer archipelago. In the outer archipelago, the DBDPE and decaBDE levels were similar to the levels in nearby isolated lakes. The results indicate that contamination of the Swedish environment with DBDPE has already approached that of decaBDE, and that this contamination is primarily occurring via the atmosphere.

EBTEBPI was not included in the study.

Screening of phenolic substances in the Nordic environments

In a screening study of phenolic substances in the Nordic environments, TBBPA was found in sewage sludge samples at concentrations of <5-1,138 µg/kg d.w., but not in any of the other investigated matrices: Fish liver, mussels, marine mammals, sediment, landfill effluents, waste water influent and effluents, and different types of surface water. The concentration of methylated TBBPA was below the detection level in all matrices (Hansen and Lassen, 2008).

OSPAR assessment of BFRs in the North Sea

The OSPAR background document on certain BFRs (OSPAR, 2009) provides information on monitoring data for PBDEs, PBBs and HBCDD from the OSPAR Parties. The report does not include time trends of concentrations of the BFRs in the North Sea biota or sediments. According to the OSPAR Quality Status Report for BFRs (OSPAR, 2010), data from the period 2000 – 2005 show widespread contamination of the marine environment with PBDEs and HBCDD in all components of marine ecosystems. Regular monitoring of these substances in the marine environment, which commenced at an OSPAR scale in 2008, needs to be continued to evaluate whether any of the actions that have been taken thus far are effective in terms of reducing this burden on the marine environment. Monitoring data on an OSPAR scale have not yet been reported in published documents.

TABLE 40
CONCENTRATION RANGES FOR THE SUBSTANCES MOST FREQUENTLY DETECTED IN BIOTA,
SEDIMENT AND SLUDGE (SCHLABACH *ET AL.*, 2011)

Substance *5	Biota (µg/kg fw) *1	Sediment (µg/kg d.w.) *2	Sludge (µg/kg d.w.) *3
Phenolic BFRs			
DBP	<0.02–6.4	<0.03–2.9	<0.04–40
TBP	<0.03–86	<0.03–7.8	<0.01–100
BFR esters & ethers			
BTBPE	<0.0052–0.2	<0.0081–1.7	<0.075–3.9
TBA	0.013–14	0.0009–0.66	0.00034–2
BEH-TEBP	<0.026–0.46	<0.013–3.3	<0.13–42
EH-TBB	<0.006–0.18	<0.0082–0.21	<0.25–2.6
Other BFRs			
HBB	0.0058–0.072	<0.022–0.19	<0.14–0.72
PBT	0.0015–0.021	<0.011–2.7	<0.027–5.2
PBEB	<0.00034–0.0044	<0.0098–0.046	<0.00095–0.13
DBDPE	<0.082–0.12	<0.00001–2.4	<2.5–160
DBE-DBCH	0.0032–1.6	0.010–350	0.018–9.0
Reference compounds			
pentaBDE *4	0.062–36	0.096–13	0.18–76

The values are min-max; “<” indicates concentration under the limit of quantification (LOQ), and the lowest LOQ is listed here. For individual compounds in groups, concentrations below the LOQ have been set to 0.5×LOQ.

*1 Matrices: egg, fish muscle, fish liver and mussel.

*2 Marine, brackish and freshwater sediments.

*3 Landfill/waste deposit, STP sludge and stormwater sludge.

*4 Sum of congeners -28, -47, -99, -100, -153 and -154 present in commercial pentaBDE.

*5 Abbreviations are here changed to be in accordance with abbreviations used in this report.

BFRs in the Arctic

BFRs in the Arctic are monitored within the framework of the Arctic Monitoring and Assessment Programme (AMAP). The results of the monitoring of BFRs and other organic pollutants in the Arctic have been reviewed in 2010 as part of the AMAP POPs Assessment, published as a series of scientific papers (Letcher *et al.*, 2010; Muir and de Wit, 2010; Hung *et al.*, 2010; De Wit *et al.*, 2010). The following is, to a large extent, extracted from these papers.

According to the review "Brominated flame retardants in the Arctic environment – trends and new candidates", PBDEs containing two to 10 bromines are ubiquitous in the Arctic, in both abiotic and biotic samples (de Wit *et al.*, 2010). Hexabromocyclododecane (HBCDD) is also ubiquitous in the Arctic, with the γ -HBCDD isomer predominating in air, the α -HBCDD isomer predominating in biota and similar concentrations of α -, β and γ -HBCDD found in marine sediments. Other brominated flame retardants (BFRs) found in some Arctic samples are PBBs, TBBPA, BTBPE, HBB, PBEB, PBT and DBE-DBCH.

Temporal trends of tetra- to heptaBDEs and HBCDD show increasing concentrations or a tendency to levelling off depending on the matrix (air, sediment, biota) and location, but no uniform picture for the Arctic emerges (De Wit *et al.*, 2010). BDE-209 concentrations are increasing in air. PBDEs and HBCDD spatial trends in seabirds and marine mammals are similar to those seen previously for polychlorinated biphenyls (PCBs), with the highest concentrations found in organisms from East Greenland and Svalbard. These trends indicate western Europe and eastern North America as important source regions of these compounds via long range atmospheric transport and ocean currents. Latitudinal trends showed lower concentrations and fluxes of PBDEs at higher latitudes. The tetraBDE, hexaBDE and α -HBCDD biomagnify in the Arctic food webs. Results for BDE-209 are more conflicting, showing either only low or no biomagnification potential. PBDE and HBCDD concentrations are lower in terrestrial organisms and higher in marine top predators, such as some killer whale populations in Alaska and glaucous gulls from the Barents Sea area. Higher concentrations are seen near populated areas, indicating local sources. Findings of BTBPE, HBB, PBEB, PBT and DBE-DBCH in seabirds and/or marine mammals indicate that these compounds reach the Arctic, most likely by long range atmospheric transport, and accumulate in higher trophic level organisms; it is concluded that their increasing use as PBDE replacements will lead to increasing concentrations

DecaBDE have been demonstrated to be the dominant PBDE in air samples from one Arctic station (Alert on Ellesmere Island) but was reported to be non-detectable in another (Zeppelin in Svalbard), probably due to the sampling technique and detection limit (Muir and de Wit, 2010). The presence of BDEs, including BDE-209, in the Arctic terrestrial environment and food chains involving herbivores (plant eaters) is a new observation. The detection of BDE-209 and other BDEs in moose and grouse in northern Norway provides evidence for entry of these BFRs into the terrestrial food web. However, the BDE concentrations were low (sub- $\mu\text{g}/\text{kg}$ lipid weight) (Muir and de Wit, 2010).

Long-term temporal trend studies of tetra- to hexaBDE congeners in biota in the Arctic are ongoing, using archived and present day samples. Most studies are now showing a levelling off or decline of BDE-47, while BDE-99 and BDE-209 concentrations appear to be increasing in air. Strong seasonal trends in air concentrations of all the PBDEs, however, make interpretation of air trends challenging (Muir and de Wit, 2010).

For HBCDD, different isomers dominate in different media. The γ -HBCDD isomer predominates in air at Svalbard, and the α -HBCDD isomer in biota, while similar concentrations of α -, β and γ -HBCDD were found in marine sediments (Muir and de Wit, 2010). Eight time-trend studies on biota have included HBCDD, but most of them could not identify any clear trends as the HBCDD concentration was highly variable. Increases were found in northern fulmar eggs (Canada) and ringed seal from several sites in Canada, while decreases were reported for ivory gull eggs (Canada) and beluga (Canada). (Muir and de Wit, 2010)

The first reports of BFRs that are used as substitutes for phased-out substances have emerged during the period 2005–2008 (Muir and de Wit, 2010). These include BTBPE, DBE-DBCH, HBBz, PBEB, and PBT in seabirds and/or marine mammals. This indicates that these compounds reach the Arctic, most probably by long-range atmospheric transport and bioaccumulate in higher trophic level organisms. Furthermore, TBBPA is present at low levels in several Arctic animals and plants, but more data are needed to assess its potential to undergo long-range transport (Muir and de Wit, 2010).

Flame retardants were analysed in adipose tissue from 11 circumpolar *Ursus maritimus* (polar bear) subpopulations in 2005–2008 spanning Alaska east to Svalbard. Although 37 PBDEs, total-(α)-hexabromocyclododecane (HBCDD), 2 PBBs, PBT, PBEB, HBB, BTBPE and DBDPE were screened, only 4 PBDEs, total- α -HBCDD and BB-153 were consistently found. Total- α -HBCDD

levels (<0.3-41.1 µg/kg lw) were lower than ΣPBDE levels in all subpopulations except in Svalbard, consistent with greater European HBCDD use versus North American pentaBDE product use. Comparing earlier polar bear studies, ΣPBDE and total-α-HBCDD levels consistently declined. (McKinney *et al.*, 2011)

Concentrations of HBCDD were recently determined in a combination of archived and fresh blubber samples of juvenile ringed seals from East Greenland collected between 1986 and 2008 (Vorkamp *et al.*, 2011). α-HBCDD was the only diastereoisomer consistently above levels of quantification and showed a significant log-linear (exponential) increase from 2.0 to 8.7 ng/g lipid weight (median concentrations) with an annual rate of +6.1%.

In a recent Norwegian study, seven animal species from Svalbard were screened for the presence of 12 "new" BFRs (Sagerup *et al.*, 2010). Detection of these BFRs in Arctic biota implies long-range transport, because local sources are not present. EH-TBB was detected in all the seven species and BEH-TEBP was found in five of the seven species. Due to a lack of data points above detection limits no statistical analysis could be performed. The lipid normalized concentrations of TBB indicated that this compound may biomagnify in the marine food chain. BEH-TEBP did not show the same ability. According to the authors, the results from the study indicate that two of the 12 analysed BFRs undergo long-range transport to the Arctic (EH-TBB and BEH-TEBP) and that one compound (TBB) may undergo biomagnification in the Arctic marine food chain. Three other BFRs, BTBPE, DBDPE and TBP were found at very low levels (mean 0.05-0.7 ng/g wet weight) and should be included in future analyses of BFRs in Arctic biota. The authors recommended that TBB and BEH-TEBP are monitored in Arctic species, or in similar species at lower latitudes to clarify their distribution and bio-accumulation capacity.

Brominated flame retardants were determined in adipose tissues from 294 polar bears (*Ursus maritimus*) sampled in East Greenland in 23 of the 28 years between 1983 and 2010 (Dietz *et al.* 2012). Significant linear increases were found for ΣPBDE, BDE-100, BDE-153, and HBCDD. Average increases of 5.0% per year (range: 2.9-7.6%/year) were found for the subadult polar bears. BDE-47 and BDE-99 concentrations did not show a significant linear trend over time, but rather a significant non-linear trend peaking between 2000 and 2004. The average ΣPBDE concentrations increased 2.3 fold from 25.0ng/g lw (95% C.I.: 15.3-34.7ng/g lw) in 1983-1986 to 58.5ng/g lw (95% C.I.: 43.6-73.4ng/g lw) in 2006-2010. Similar but fewer statistically significant trends were found for adult females and adult males, likely due to smaller sample size and years. According to Dietz *et al.* (2012), these increasing concentrations of organobromine contaminants contribute to a complex organohalogen mixture, already causing health effects to the East Greenland polar bears.

Several potential PBDE alternatives were assessed in Greenland sharks caught in waters around Iceland between 2001 and 2003. Non-PBDE flame retardants detected were PBEB, BTBPE and TBX. The concentrations were lower than levels of BDE-47 but similar to other PBDE congeners previously reported in Greenland shark. (Strid *et al.*, 2013)

The Danish Centre for Environment and Energy, Aarhus University, has recently prepared a review of the occurrence of brominated flame retardants (among other new pollutants) in the Arctic which are not covered by the current monitoring activities in Greenland and assessed their relevance for further studies in Greenland, for example under the AMAP Core Programme (Vorkamp and Rigét, 2013). The summary of BFRs identified is shown in the following table. Based on the initial assessments, a final list of 11 compounds which could accumulate in Greenlandic animals, and would be particularly relevant for further studies in Greenland, was proposed. This list includes five BFRs: DPTE, BEH-TEBP, EH-TBB, BTBPE, and DBDPE.

TABLE 41
BFRS SHOWN IN ARCTIC ANIMALS (TRANSLATED FROM VORKAMP AND RIGÉT, 2013)

Substance *1	Demonstrated	Not demonstrated	Comment	References *2
BATE *3	Hooded seals and harp seals from the Barents Sea and the Greenland Sea.	Black guillemot eggs from the Faroe Islands, fish from the Faroe Islands and Iceland.	Possibly degradation product of DPTE; can cross the blood-brain barrier.	Von der Recke & Vetter (2007); Schlabach <i>et al.</i> (2011)
BEH-TEBP	Black guillemot eggs from the Faroe Islands; fish, birds, bird eggs, seals from Svalbard.	Fish from the Faroe Islands and Iceland, Arctic fox and polar bear from Svalbard	Replacement product for pentaBDE; also used as plasticizer.	Sagerup <i>et al.</i> (2010); Schlabach <i>et al.</i> (2011)
BTBPE	Fulmar eggs from the Faroe Islands; beluga and ringed seals from Canada; Glaucous gull from Bjørnøya; black guillemot eggs from the Faroe Islands, fish from the Faroe Islands and Iceland; guillemot eggs from Svalbard.	Ringed seals from East Greenland, pilot whales from Faroe Islands, minke whales from Norway, fish, birds, Arctic fox, polar bears from Svalbard	Replacement product for octaBDE. Possibly decomposes into 2,4,6 tribromophenol.	Karlsson <i>et al.</i> (2006); CECPB (2008); de Wit <i>et al.</i> (2010); Verreault <i>et al.</i> (2007); Sagerup <i>et al.</i> (2010); Schlabach <i>et al.</i> (2011); Dam <i>et al.</i> (2011)
DBDPE	Guillemot eggs from Svalbard; black guillemot eggs from the Faroe Islands.	Ringed seals from Canada; fish from the Faroe Islands; birds, fish or mammal from Svalbard, seals or whales from the NE Atlantic.	Replacement product for for decaBDE	Sagerup <i>et al.</i> (2010); de Wit <i>et al.</i> (2010); Schlabach <i>et al.</i> (2011); Dam <i>et al.</i> (2011)
DBE-DBCH	Beluga, Canada; black guillemot eggs from the Faroe Islands, fish from the Faroe Islands and Iceland.	-	Only beta- DBE-DBCH shown in beluga.	Tomy <i>et al.</i> (2008); Schlabach <i>et al.</i> (2011)
DBP	Fish from the Faroe Islands and Iceland.	Birds' eggs from the Faroe Islands.	Can also be formed naturally.	Schlabach <i>et al.</i> (2011)
DPTE	Hooded seal and harp seal from the Barents Sea and Greenland Sea; higher concentrations than PBDE.	Black guillemot eggs from the Faroe Islands, fish from the Faroe Islands and Iceland. Biota samples (fish, birds, eggs of birds, mammals) from Svalbard.	-	Von der Recke & Vetter (2007); Schlabach <i>et al.</i> (2011); Sagerup <i>et al.</i> (2010)
EH-TBB	Black guillemot eggs from the Faroe Islands, fish (but not all) from the Faroe Islands and Iceland, all biota samples (fish, birds, bird eggs, mammals) from Svalbard.	-	Replacement product for pentaBDE.	Sagerup <i>et al.</i> (2010); Schlabach <i>et al.</i> (2011)

Substance *1	Demonstrated	Not demonstrated	Comment	References *2
HBB	Glaucous eggs from Arctic Norway, pilot whale and minke whale in the NE Atlantic, of Greenland polar bears; black guillemot eggs from the Faroe Islands, fish from the Faroe Islands and Iceland.	Birds, bird's eggs, fish or mammals from Svalbard.	-	Verreault <i>et al.</i> (2007); Letcher (2007); Sagerup <i>et al.</i> (2010); Dam <i>et al.</i> (2011); Schlabach <i>et al.</i> (2011)
PBB	Arctic birds and mammals including Greenland and the Faroe Islands. Seals, minke whales and polar bears from Greenland and pilot whale and fulmar from the Faroe Islands.	Polar bear samples from 1967	Substance group, with BB-153 as the most bio-accumulative single substance. Stockholm Convention Annex A (Elimination)	Derocher <i>et al.</i> (2003); Vorkamp <i>et al.</i> (2004a); de Wit <i>et al.</i> (2010); Dam <i>et al.</i> (2011)
PBEB	Black guillemot eggs from the Faroe Islands (low); glaucous gulls from Bjørnøya (Norway).	Birds, bird's eggs, fish or mammals from Svalbard.	-	Verreault <i>et al.</i> (2007); Sagerup <i>et al.</i> (2010); Schlabach <i>et al.</i> (2011)
PBT	Glaucous eggs from Arctic Norway, with high detections frequency; black guillemot eggs from the Faroe Islands, fish from the Faroe Islands and Island.	Birds, bird's eggs, fish or mammals from Svalbard; <DL in marine mammals from NE Atlantic.	Possibly degradation product from DBDPE.	Verreault <i>et al.</i> (2007); Sagerup <i>et al.</i> (2010); Dam <i>et al.</i> (2011); Schlabach <i>et al.</i> (2011)
TBBPA	Shown in Norwegian cod, eggs of Norwegian peregrine falcon and golden eagle	Peregrine eggs from Greenland; fish and seabirds from Svalbard, Greenland minke whales and polar bears, in pilot whales from the Faroe Islands ; Faroese black guillemot eggs, fish from the Faroe Islands and Iceland.	Degradation product dimethyl-TBBPA shown in peregrine eggs from Greenland.	Fjeld <i>et al.</i> (2004); Herzke <i>et al.</i> (2005); Vorkamp <i>et al.</i> (2005); Frederiksen <i>et al.</i> (2007); Evenset <i>et al.</i> (2009); Schlabach <i>et al.</i> (2011)
TBP	Fish from the Faroe Islands; birds and seals from Svalbard.	Birds' eggs and mammals from Svalbard.	Reactive flame retardant, but also many other applications. Can also be formed naturally. Degradation product of PBDEs, byproduct in BTBPE.	Sagerup <i>et al.</i> (2010); Schlabach <i>et al.</i> (2011); Covaci <i>et al.</i> (2011)
TBP-AE	Hooded seals and harp seals from the Barents Sea and the Greenland Sea.	Black guillemot eggs from the Faroe Islands, fish from the Faroe Islands and Iceland.	Possibly degradation product of DPTE.	Von der Recke & Vetter (2007); Schlabach <i>et al.</i> (2011)

*1 Abbreviations changed in order to be in consistent with abbreviations used in this survey.

*2 See Vorkamp and Rigét (2013) for full reference.

*3 2-Bromallyl 2,4,6 tribromophenyl ether. Possibly degradation product of DPTE.

Summary of findings from the Nordic and Arctic environment

A recent Norwegian report on Nordic screening data relevant for PBT evaluation summarises data from the Nordic countries and Norwegian part of the Arctic for TBP, TBBPA, TBPA, BEH-TEBP, and DBDPE. Between 160 and 370 results for each of these substances are summarized, including air, sediment, biota, and sewage samples.

TBPA was not found in any of the studies. The levels found in the different environmental matrices of the four other BFRs are shown in for Figure 3. As mentioned above, besides emissions from industrial processes, TBP is also formed by natural processes in the environment.

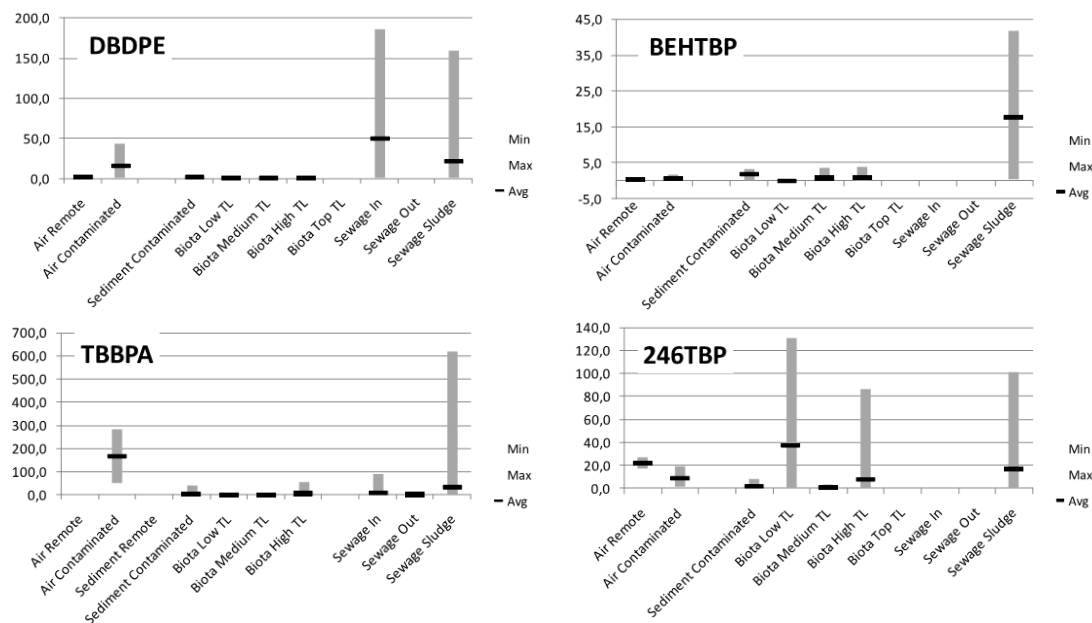


FIGURE 3 RANGE AND AVERAGE OF THE INDIVIDUAL CONCENTRATIONS FOR DBDPE FOR DIFFERENT ENVIRONMENTALLY RELEVANT MATRICES IN THE NORDIC AND ARCTIC ENVIRONMENT. CONCENTRATION GIVEN IN ng/m³ FOR AIR; ng/g d.w. FOR SEDIMENT AND SLUDGE; ng/g W.W. FOR BIOTA AND ng/L FOR SEWAGE WATER. NOTE DIFFERENT Y-AXES SCALES. BEHTBP = BEH-TEBP; 246TBP = TBP. (SCHLABACH, 2012)

5.4 Environmental impact

It is beyond the scope of this survey to provide an environmental impact assessment. The following shortly summarises the findings of existing Risk Assessments or preliminary assessments prepared on the basis of monitoring data e.g. in the context of HELCOM or AMAP.

PBDEs - The four PBDEs covered by the Stockholm Convention (main constituents of c-pentaBDE and c-octaBDE) are demonstrated to have the potential for possessing risks to the environment: they are persistent, bioaccumulative and have the potential for long-range transport. The EU Risk Assessment for pentaBDE concludes that there is a risk of secondary poisoning in the environment at both local and regional level (ECB, 2001). High levels of pentaBDE have been both predicted and measured in fish and earthworms which may lead to secondary poisoning a higher level in the food chain. The EU Risk Assessment for octaBDE likewise concludes that there is a need for reducing the risk of secondary poisoning via the earthwork route (ECB, 2003).

The EU Risk assessment update for decaBDE concluded that there is a need for further information and/or testing regarding the PBT assessment. Furthermore, it concluded that there was no need for further information and/or testing or for risk reduction measures beyond those which are being applied at present (ECB, 2004). The latter conclusion applied to the assessment of surface water and sediment (freshwater and marine), sewage treatment plants, the terrestrial compartment, the

air compartment and secondary poisoning for all life cycle stages using the PEC/PNEC assessment approach. The Annex XV report for decaBDE (UK, 2012) suggests that decaBDE meets the PBT and vP/vB criteria, but the Annex XV report does not include an environmental impact assessment.

An environmental risk evaluation report from Environment Agency (2009) concludes that whilst a risk arising from direct toxicity of decaBDE has not been identified, and it does not itself meet the Annex XIII criteria of the REACH Regulation, there continue to be concerns related to its presence in food chains (including top predators) and degradation pathways. The latest evidence suggests that detection of hazardous degradation products (e.g. hexaBDE congeners which themselves have highly persistent and bioaccumulative properties in sediment, sewage sludge and biota may be linked to emissions of decaBDE, although it is still difficult to estimate the rates and amounts of formation (Environment Agency, 2009).

According to a proposal for nomination of decaBDE for uptake under the Stockholm Convention, decaBDE can be considered to meet the screening criteria for persistence, bioaccumulation, long-range transport and adverse effects under the Stockholm Convention (Norway, 2013). Adding to this concern is the potential debromination to other POPs and the possibility of combined effects. According to the nomination report, several assessments have concluded that there is a high probability that decaBDE is transformed in the environment and in biota to form substances or act as precursors to lower brominated PBDEs. The nomination report further states that reported *in vitro* data suggest the possibility that the different PBDEs could act in concert to induce additive or synergistic effects.

According to HELCOM, in marine top predators, PBDE concentrations indicate a cause for concern. For example, white-tailed sea eagles in the Baltic Sea (Nordlöf *et al.* 2007 as cited by HELCOM 2010) have BDE concentrations (sum of four BDEs with four to six bromines) up to four times higher than the reported effect levels in exposed American kestrels, which were causing adverse effects (Fernie *et al.* 2005a, 2005b, 2009 as cited by HELCOM, 2010).

A new report "State of the Science of endocrine disrupting chemicals from UNEP and WHO (Bergman *et al.*, 2012b) mentions that evidence of relationships between exposure to chemicals and thyroid hormone disruption in wildlife species has increased in the last decade, especially in relation to exposure to the flame retardant PBDEs and PCBs, but other chemicals are inadequately studied.

HBCDD - The EU Risk Assessment for HBCDD concluded that there is a need for limiting the risks. The conclusion applies to sites involved in EPS and XPS formulation, formulation of polymer dispersions for textiles, industrial use of XPS and sites involved in textile backcoating (ECB, 2008a).

The POPs Review Committee under the Stockholm Convention concluded that HBCDD is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects (POPRC, 2011).

According to HELCOM, HBCDD concentrations in herring muscle were found to exceed the threshold value at all monitoring stations near the Swedish coast from the Bothnian Bay to the Kattegat. In contrast, HBCDD did not exceed the threshold level in the muscle of flounder and perch in the coastal waters of Lithuania, in the Gulf of Riga, in the Gulf of Finland or in Szczecin Lagoon (Lilja *et al.* 2009 as cited by HELCOM, 2010).

The "State of the Science of endocrine disrupting chemicals from UNEP and WHO (Bergman *et al.*, 2012b) mention that in harbour porpoises, once the effect of age and nutritional condition were taken into account, the data so far suggest that higher POP concentrations (PCB, HBCDD and DDE) tended to be associated with lower numbers of corpora scars, possibly indicating that high contaminant levels were inhibiting ovulation. The review notes that the lower contaminant loads found in

breeding females could simply be reflective of the maternal transfer to the offspring, rather than any true causative association with the reproductive status of these females.

TBBPA - The EU Risk Assessment for TBBPA concluded that there was a need for limiting the risks for surface water and sediment; this conclusion applied to compounding sites where TBBPA was used as an additive flame retardant in ABS (ECB, 2007). For the terrestrial compartment, this conclusion applied to the use of TBBPA as an additive flame retardant in ABS from compounding and conversion sites. The conclusion for conversion sites was dependent on whether or not sewage sludge from the site is applied to agricultural land (no risk is identified where sewage sludge is not applied to land). For ABS compounding sites, a risk was identified regardless of the assumptions made over the spreading of sewage sludge. For the risks to sewage treatment processes, the atmosphere and from secondary poisoning, for all sources of TBBPA it was concluded that there were no need for risk reduction measures beyond those which were being applied already.

No assessments from international organisations of a possible environmental impact of TBBPA have been identified.

DBDPE - The environmental risk assessment for DBDPE by Environment Agency (England and Wales) concludes that overall, the risks arising from direct toxic effects of DBDPE are low, especially in a UK context (Environment Agency, 2007). According to the risk assessment there are, however, concerns over bioaccumulation potential and the potential products of degradation processes that require further investigation. First, further studies on uptake and accumulation in wildlife are needed (preceded by a more reliable Kow value, if possible). Second, the identity, properties and the rate of formation of DBDPE principal metabolites and degradation products should be established, and their environmental impact assessed.

Other BFR

The results from the screening of "new" BFRs in the Nordic environment showed that the measured levels of the BFRs in sediments were below the established quality standard (QS for) pentaBDE, with the exception of the concentration of sum DBE-DBCH in one sample. The initial risk assessment based on "read-across" from pentaBDE cannot exclude negative effects on the pelagic community (organisms living in the water phase). However, it was not possible to assess the ecotoxicological risk satisfactorily.

Impact of BFRs in the Arctic

An exposure and effects assessment of persistent organohalogen contaminants (OHC, among which are PBDEs and other BFRs) in Arctic wildlife and fish, prepared as part of the AMAP POPs Assessment, concludes that there remains minimal evidence that organohalogen contaminants are having widespread effects on the health of Arctic organisms, with the possible exception of East Greenland and Svalbard polar bears and Svalbard glaucous gulls (Letcher *et al.*, 2010). According to the authors, however, the true effects of POPs in Arctic wildlife have to be put into the context of other environmental, ecological and physiological stressors (both anthropogenic and natural) that render an overall complex picture.

For polar bears from the East Greenland and Svalbard regions there are substantial reports on organic hazardous compounds (OHC) concentration associations with changes in various biomarker responses (e.g. endocrine and immune-related), although these do not directly establish cause-effect relationships. The effects are not specifically attributed to the BFRs. A number of glaucous gull field studies carried out on Bjørnøya (Bear Island, Svalbard) during the incubation period have reported significant relationships between circulating levels of endogenous hormones and blood (or plasma) concentrations of major OHC classes, including organochlorine substances, BFRs and OH-containing analogues. Overall, these studies strongly suggest that the high exposure to OHCs may

contribute to disrupting endocrine functions and homeostasis in nesting glaucous gulls from Bjørnøya (Letcher *et al.*, 2010).

5-5 Summary and conclusions

Environmental fate and effects

There is a wide range of BFRs currently on the market and it is difficult to generalise the environmental fate and effects of BFRs as a whole, particularly as there is only limited information about many of the BFRs.

Many, but not all, of the BFRs have log K_{ow} values of 5-6 or higher and so are potentially bioaccumulative, although there is some evidence that bioaccumulation potential for some substances with high log K_{ow} values (e.g. decaBDE and DBDPE) is low, possibly as a result of reduced bioavailability of large molecules. A high level of accumulation has been demonstrated for pentaBDE and HBCDD in particular.

BFRs as a group are generally relatively persistent, although data are not available for all BFRs. Although persistent, it is also necessary to consider possible breakdown products on a case-by-case basis. For example, there is evidence that decaBDE can undergo debromination reactions in the environment to form products that are more toxic and accumulative than decaBDE, and TBBPA can undergo debromination under anaerobic conditions to form bisphenol-A.

As a group, BFRs tend to have limited solubility in water and so, in many cases, little or no toxicity has been seen in acute ecotoxicity tests at concentrations up to the water solubility. However, in longer-term tests, pentaBDE, TBBPA and HBCDD have demonstrated toxicity with some aquatic organisms with no-effect concentrations (NOECs) below 10 µg/l for pentaBDE and HBCDD and around 13 µg/l for TBBPA.

In terms of PBT properties, hexaBB, four PBDEs and HBCDD are listed as POPs in Annex A of the Stockholm Convention. In addition, decaBDE have been identified as substances of very high concern (SVHC) under REACH and recently proposed for Annex A of the Stockholm Convention. DecaBDE was identified as a SVHC on the basis that it can undergo debromination in the environment to form substances with PBT or vPvB properties, and is currently included on the Candidate List.

Other BFRs, for example TBBPA and DBDPE, do not meet the REACH PBT criteria based on the currently available data; however, there are currently insufficient reliable data for DBDPE. Few data are currently available for a large number of other BFRs; the PBT status of these substances is currently unknown.

Environmental releases and exposure

The EU Risk Assessment for the BFRs identified production processes as the major sources of releases of decaBDE, HBCDD and TBBPA and called for a reduction of the releases of the substances from production processes. A Voluntary Emissions Control Action Programme (VECAP) was developed and first implemented in 2004 by three major producers of flame retardants in partnership with downstream user industries. During the period 2007-2011, the total releases from production and industrial downstream uses from the companies included in the programme decreased by a factor of 10 (representing in 2011 84 % of decaBDE, 98% of HBCDD by volume and 95% of TBBPA of the supply from the manufacturers).

The Danish environmental monitoring programme, NOVANA, includes regular monitoring of the PBDEs only. A screening survey of 16 BFRs in the Nordic environment indicated that the concentrations of the "new" BFRs, with a few exceptions, are of the same order of magnitude or lower compared to the sum of BDE congeners included as priority substances under the Water Framework

Directive. Available data indicate that DBDPE levels in the environment in the Nordic countries have approached the levels of decaBDE, and that this contamination primarily occurs via the atmosphere.

Whilst the levels of lower brominated PBDEs in the Arctic have been decreasing, many studies have demonstrated the presence of "new" BFRs in the air and biota in the Arctic, indicating the potential for long-range transport of these flame retardants. Based on a review of the available data on BFRs in Arctic biota and abiotic media, combined with information on the substances' potential for bioaccumulation, the Danish Centre for Environment and Climate include five "new" brominated flame retardants in a list of candidates for inclusion in the Arctic monitoring programme: DPTE, BEH-TEBP, TBB, BTBPE, and DBDPE.

Environmental impact

The potential for environmental impact of the lower brominated PBDEs and HBCDD and the background for the listing of the substances' inclusions under the Stockholm Convention is well established. The potential environmental impact of decaBDE is, as has been mentioned, mainly linked to the potential debromination to other lower brominated PBDEs; the different PBDEs may act in concert to induce additive or synergistic effects. However, it is still difficult to estimate to what extent debromination of decaBDE contributes to the actual environmental levels of the lower brominated PBDEs or contributes to additive or synergistic effects. Environmental impact of TBBPA has mainly been associated with compounding sites where TBBPA was used as an additive flame retardant. DBDPE have properties of concern, but an environmental risk assessment concludes that more information is needed. The results from a screening of "new" BFRs in the Nordic environment showed that the measured levels of the BFRs in sediments, with the exception of the concentration of sum DBE-DBCH in one sample, was below the established quality standard (QS for) pentaBDE. The initial risk assessment based on "read-across" from pentaBDE cannot exclude negative effects on the pelagic community of some of the more water soluble compounds. However, it was not possible to assess the ecotoxicological risk satisfactorily.

Data gaps

Monitoring data and data on environmental fate and effects of "new" BFRs are scarce and constrain a comprehensive ecotoxicological risk assessment.

6. Human health effects and exposure

6.1 Human health hazard

In this chapter the human health aspects of selected brominated flame retardants will be reviewed. The main focus will be on the substances most used at present. These are tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCDD) and decabromodiphenyl ether (decaBDE); however, the polybromodiphenyl ethers (PBDEs) in the banned commercial mixtures of pentabromodiphenyl ether (pentaBDE) and octabromodiphenyl ether (octaBDE) and their ingredients are also covered because of

- their continued presence in humans,
- the many available studies, and
- the potential formation by a degradation of decaBDE.

6.1.1 Classification

According to Annex VI of the CLP Regulation (EC) No 1272/2008, only three chemicals have a harmonized classification:

- OctaBDE is classified as toxic for reproduction in Category 1B,
- PentaBDE is classified for acute and chronic toxicity in the aquatic environment in Category 1, for specific target organ toxicity – repeated exposure in Category 2, and with adverse effects on or via lactation (Lact.),
- TBBPA is classified as hazardous to the aquatic environment, acute Category 1 and chronic Category 1.

In December 2010, the ECHA Committee for Risk Assessment adopted a classification proposal for HBCDD submitted by Sweden in 2008, suggesting that HBCDD is toxic for reproduction in Category 2 (Repr.2) and with adverse effects on or via lactation (Lact.) with the hazard statements: “suspected of damaging fertility and the unborn child” (H361) and “may cause harm to breast-fed children” (H362).

6.1.2 PBDEs (with focus on decaBDE)

Toxicokinetics and metabolism

Toxicokinetics in adult animals have indicated that absorption, distribution, metabolism and excretion of PBDEs are congener-, species- and gender-dependent.

The absorption of the lower PBDEs after oral administration to animals is rather complete and mostly >70%. DecaBDE (BDE-209) has, however, a much lower absorption. BDE-209 is a large, bulky molecule, with a molecular weight of 959, and because of its size it cannot easily be absorbed through the intestinal tract. In rats, some older studies found an oral absorption for BDE-209 of 6-9% and a body half-life of <24 hours (ECB, 2002). The oral bioavailability in rats of decaBDE (BDE-209), defined as the fraction of administered parent compound reaching systemic circulation, was determined to be 26 %, with the maximum plasma concentration of 264 pmol/mL occurring 6 hours after dosing. Data indicates that BDE-209 can be absorbed into the human body and is dis-

tributed to the blood and the adipose tissue. Quantitative oral absorption data in humans were not located (EFSA, 2011b).

There are no data on inhalation or dermal absorption of BDE-209, but these are assumed to be low with a maximum of 1% (ECB, 2002).

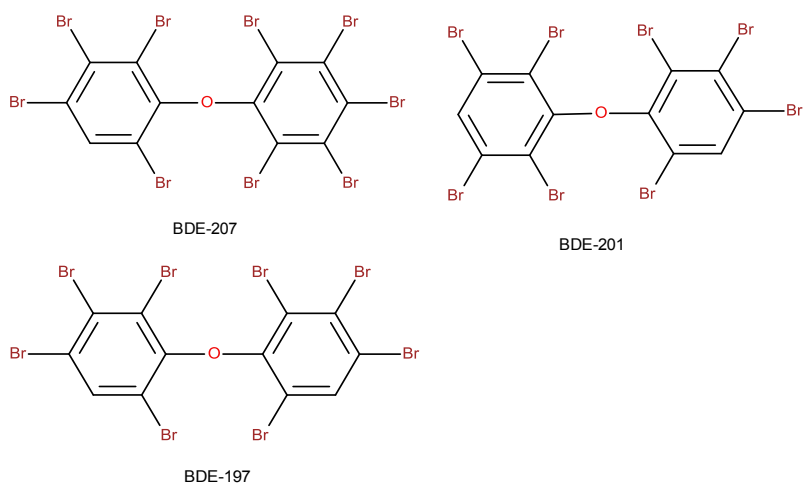
The lower brominated congeners are also metabolized to mono- and di-hydroxylated metabolites, which may have toxicological relevance, and appear to bioaccumulate in serum. In contrast, decaBDE may be metabolized to lower brominated congeners, which then may be hydroxylated. Male mice have a higher rate of urinary excretion compared to female mice or rats. Young animals have a reduced ability to excrete PBDEs, which contributes to a higher body burden (Costa *et al.*, 2008). The lower PBDEs have a preference for the lipid-rich tissues such as adipose tissue and breast milk. Substantial differences were observed between BDE-209 and other PBDE congeners. A few days after oral administration of BDE-209 to male rats, the highest concentrations on a fresh weight basis were in adrenals, kidneys, heart, and liver. Based on lipid weight, blood plasma and liver had the highest concentrations, and adipose tissue had the lowest concentrations. Oral exposure of BDE-209 to pregnant rats showed that 0.5% of the dose was found in foetuses, demonstrating that BDE-209 residues are able to cross the placental barrier in rats. In all tissue extracts, most of the radioactivity was associated with unchanged BDE-209 (EFSA 2011b).

BDE-209 is also able to penetrate the blood-brain barrier to some extent in neonatal mice (ECB, 2002).

BDE-209 has been determined in blood serum from 19 workers dismantling electronic products alongside other PBDEs, therefore, absorption occurred. The median concentration was 5.0 pmol or 4.8 ng BDE-209/g fat (ECB, 2002).

BDE-209 is also able to cross the placental barrier in humans. It is detected in cord blood in France (Antignac *et al.*, 2009), and it is found to account for approximately 50 % of the total PBDE congeners present in 50 human placental samples collected in Denmark (Frederiksen *et al.*, 2009).

In an organism, PBDEs are more or less transformed into various hydroxylated metabolites (OH-PBDEs) depending on chemical structure and bromine substitution. Because of the fully brominated benzene rings in BDE-209, hydroxylation requires previous reductive debromination steps. Debromination of BDE-209 was confirmed where nona- and octaBDEs and hydroxylated octaBDE were identified as metabolites in tissues and excreta from pregnant rats exposed orally to deca-BDE (Riu *et al.*, 2008). Some of the debromination products are BDE-197, BDE-201 and BDE-207.



All investigated PBDEs were mainly excreted via faeces, whereas urine represents a minor route of elimination (0.01%). In rodents using different routes of administration, BDE-209 is eliminated faster than some lower brominated diphenyl ethers such as BDE-47 (EFSA, 2011b).

The transfer rate of BDE-209 to milk was estimated to be in the 0.16-0.24 % range in lactating cows exposed to a naturally contaminated diet (Kierkegaard *et al.*, 2007).

The whole body half-life of BDE-209 in rats was 8.6 days, which is shorter than for the lower PBDEs (EFSA, 2011b). Available data suggests the human PBDEs' half-life tends to increase by the bromination of the PBDE congener. The calculated apparent half-life for BDE-209 was 15 days and much smaller than the half-lives of 18-39 days and 37-91 days, respectively, for three nonaBDEs and four octaBDE congeners (Thuresson *et al.*, 2006b).

Acute toxicity

All PBDEs have low acute toxicity, with oral LD50s of >5 g/kg.

For example, decaBDE exhibits low acute oral toxicity in rats, because all rats survived single doses of up to 2,000 mg/kg b. w. of a decaBDE mixture with no signs of toxicity during the 14 day observation period (ECB, 2002).

Acute inhalation studies indicated no effects in rats upon 1–2 h exposure to commercial BDE-209 products at concentrations of 48 mg/l or 200 mg/l, and no toxicity was also observed in rabbits upon dermal exposure of BDE-209 (unknown purity) at doses up to 8000 mg/kg (reported in Hardy *et al.*, 2009).

Irritation and sensitization

Studies with commercial undissolved solid decaBDE and rabbits showed no skin irritation but the method was questionable. However, mild eye irritation was observed in rabbits after application of solid commercial decaBDE (ECB, 2002). Neither of the PBDEs has demonstrated any skin sensitization potential (ECB, 2002).

In 50 human subjects, repeated application of a suspension of 5% DBDPO in petrolatum 3 times a week for 3 weeks and challenged two weeks subsequent to the last induction application did not result in skin sensitization. Skin irritation was observed in 9 out of the 50 persons (as cited by ECB, 2002).

Sub-chronic and chronic toxicity

Upon chronic exposure to PBDEs, target organs are the liver, the kidney and the thyroid gland. PBDEs have been reported to decrease levels of total and free T₄ in adult animals and in adolescent animals. Different PBDEs appear to have similar toxicological profiles, with decaBDE being less potent than other lower brominated congeners. For example, in sub-chronic toxicity studies in rats, no-observed-effect-levels are usually in the g/kg/day range for decaBDE, but less than 10 mg/kg/day for pentaBDE (Costa *et al.*, 2008).

A short-term acute toxicity study conducted by the National Toxicology Program (NTP) found no effects in rats or mice fed BDE-209 (99% pure) up to 100,000 ppm (approximately equivalent to 10,000 mg/kg/day in rats, and 20,000 mg/kg/day in mice in the diet for two weeks (NTP, 1986). In a 28-day oral rat toxicity study with decaBDE, the most sensitive effects in the liver were induction of CYP1A and CYP2B (BMD10s 0.5-0.7 mg/kg b. w. per day for a 10 % increase), and decaBDE also caused an increase of T₃ at a BMDL10 value of 33 mg/kg b. w. (van der Ven *et al.*, 2008). In an older 30 days study with an impure technical product, the NOAEL was assumed to be 100 ppm (8 mg/kg/day), with a LOAEL of 1,000 ppm (ECB, 2002).

The available data on the effects of PBDEs provide convincing evidence that they have the potential to disrupt endocrine systems at multiple target sites. While the thyroid hormone system appears to be the main target, experiencing the most significant effects of these compounds, recent studies demonstrated *in vivo* effects on both the estrogen- and androgen-mediated processes as well (EFSA, 2011b).

Effect on reproduction and offspring

Reproductive toxic effects of PBDEs have been reported. Thyroid hormones are known to play an important role in brain development and hypothyroidism has been associated with a large number of neuroanatomical and behavioural effects. In that respect it is relevant that PBDEs have been reported to decrease levels of total and free T4 following developmental exposure. PBDEs can be phototoxic, but usually at maternally toxic doses, and there is no evidence of teratogenicity (Costa *et al.*, 2008).

Many of the older studies of decaBDE have been carried out using commercial products of low purity. Based on data from these limited studies, it was assumed that the maternal NOAEL is 1,000 mg/kg/day and the foetal LOAEL is 10 mg/kg/day (ECB, 2002).

In an unpublished study it was shown that animal exposures to decaBDE during gestation and/or postnatally had no reproductive or developmental toxicity at doses up to 500 mg/kg b. w. per day, which was considered a NOAEL value (EFSA, 2011b).

In rodents, decaBDE exposure can also result in decreased immune function during pregnancy and lactation (Liu *et al.*, 2012).

The available data indicate the nervous system as one of the main systems vulnerable to PBDE-induced toxicity. The main concern relates to the substances' potential developmental neurotoxicity. BDE-209 induced changes in spontaneous behaviour and habituation after oral administration of 6.7 mg/kg b. w. in rats and 20.1 mg/kg b. w. in mice on PND3 (Viberg *et al.*, 2007).

The BDE-209 has demonstrated toxic effects during development of central nervous system in neonatal rats, especially in large doses; dams exposed to BDE-209 for more than 14 weeks (0.3 g/kg bw/day) showed decrease in body and spleen weight. Maternal BDE-209 exposure during pregnancy decreases the ability to learn and memory function in mice (Zhang *et al.*, 2010).

DecaBDE probably exerts its developmental neurotoxicity via the accumulation of debrominated metabolites in the brain (Costa and Giordano, 2011).

Mutagenicity/Genotoxicity

PBDEs do not appear to be genotoxic. Some older, limited, and unpublished mutagenicity tests carried out on five strains of *Salmonella typhimurium* with a technical product of decaBDE and commercial decaBDE in a concentration of up to 5 mg/plate, set up with and without metabolic activation, were negative (ECB, 2002). Similarly, studies in eukaryotic cells utilizing yeast (*Saccharomyces cerevisiae*) and the TK locus of the mouse lymphoma cell line L5178Y with and without metabolic activation were negative. Commercial decaBDE did not induce unscheduled DNA synthesis, chromosomal aberrations or sister chromatid exchanges in Chinese hamster ovary cells with or without metabolic activation (EFSA, 2011b).

Carcinogenicity

PBDEs are generally not carcinogenic. Specifically, decaBDE has been evaluated by IARC as Group 3 - not classifiable as to its carcinogenicity to humans (IARC, 1990).

Whilst the pure congener BDE-209 has not been tested for carcinogenicity, decaBDE (97% purity) has been studied in rats and in mice, with some evidence for an increase in liver adenoma in male rats exposed to dietary levels of 25 g decaBDE/ kg feed, and liver adenoma and carcinoma were similarly produced in male mice (IPCS, 1995).

In male mice exposed to 25,000 and 50,000 ppm deca-BDE for 103 weeks, thyroid gland follicular cell adenomas or carcinomas were observed at marginally increased incidence (control, 0/50; low dose, 4/50; high dose, 3/50; historical incidence in male, $1.7 \pm 2\%$). The significance of this lesion in males was supported by an increased incidence of follicular cell hyperplasia in males (control, 2/50; low dose, 10/50; high dose, 19/50). It should, however, be noted that only one carcinoma was observed in one male at the lowest dose and (ECB, 2002). A LOAEL for carcinogenicity of 1,120 mg/kg bw/day was assigned based on the increased incidence of liver neoplastic nodules from the lowest tested dose (1,120 mg/kg bw/day) (ECB, 2002).

BDE-209 caused hepatic hypertrophy and induction of CYP enzymes typical of activation of CAR/PXR receptor(s). Other compounds that act in this way are tumour promoters in rodent liver. Tumours occur only after prolonged, high dose exposure, and precursor effects are reversible. There is evidence that CAR/PXR activation in humans does not support a number of the key events necessary for tumor promotion, such as hepatic hyperplasia. It is therefore concluded that BDE-209 does not present a carcinogenic risk to humans (EFSA, 2011b).

Mechanisms and interactions

In neuronal cells, PBDE neurotoxicity was prevented by antioxidants (119), suggesting that PBDEs may induce oxidative stress (Reistad *et al.*, 2006).

PBDEs do not appear to activate the Ah receptor-AhR nuclear translocator protein-XRE complex, although they can bind to the Ah receptor. Various PBDEs have been reported to induce mixed-type monooxygenase *in vivo* (Costa *et al.*, 2008).

The mechanism of BDE-209-induced toxicity may be induction of lipid peroxidation, suppression of thyroid hormone receptor-mediated gene transcription, and inhibition of differentiation of rat neural stem cells into neurons and neurite outgrowth (EFSA, 2011b).

6.1.3 HBCDD

Toxicokinetics and metabolism

In rodents orally administered HBCDD in the feed, the substance was easily absorbed with an extent of 50-100% from the gastro-intestinal tract and rapidly distributed in different tissues. The body distribution in mice of α -HBCDD, observed one day after dosing, were in the following order: liver > muscle > adipose tissue > blood > brain > kidney, whereas adipose tissue had the highest levels after four days (Sweden, 2008; EFSA, 2011a).

The absorption of HBCDD through intact skin was low (0.01%) in an *in vitro* study with human skin preparations but 1.35% did accumulate in the outer skin (Roper *et al.*, 2007). A value of 4 % was assumed to be applicable for uptake of powder by the dermal route by the EU Annex XV document.

There is no information about uptake after inhalation, but it was considered by the EU Annex XV document to be 100% or equal to the oral absorption.

Debromination and hydroxylation seem to be the major metabolic pathways for HBCDDs. There are some differences in metabolism observed between the γ - and α -stereoisomers. γ -HBCDD was more rapidly metabolized and changed to α - and β -isomers. Mainly α -HBCDD was found to accumulate in adipose tissue (EFSA, 2011a).

Furthermore, elimination of α -HBCDD and γ -HBCDD was primarily in faeces and to a lesser extent in urine, and mono- and dihydroxylated pentabromocyclododecane metabolites were found in faecal extracts (Szabo *et al.*, 2011a). There are differences in tissue distribution of HBCDD isomers between adult and developing mice, the latter retaining more HBCDD (Szabo *et al.*, 2011b).

Elimination of HBCDD and its metabolites in rats occurs mainly via faeces with a minor part excreted in urine. Elimination from body fat appears to be markedly slower than from other tissues, with an elimination half-life of the three stereoisomers possibly being in the order of weeks to months.

Based on HBCDD concentrations in adipose tissue, the elimination half-lives of HBCDD stereoisomers have been calculated to vary from 2-6 days for γ -HBCDD and to 17 days for α -HBCDD in female mice. The average half-life of total HBCDD in humans has been estimated to be 64 days (range 23-219 days) on the basis of extrapolation from animal studies and human adipose fat levels (EFSA, 2011a).

Acute toxicity

Acute toxicity from exposure to technical HBCDD is low, and an LD₅₀ value has not been determined. The oral lethal dose is more than 20 g/kg b. w. in rats and more than 40 g/kg b. w. in mice (ECB, 2008). Regarding acute toxicity by inhalation and skin contact, the minimum lethal doses were considered greater than 200 mg/l and greater than 20 g/kg, respectively, by the EU Annex XV document.

Irritation and sensitization

HBCDD was mildly irritating to the eye but not irritating to the skin, according to the EU Annex XV document. This document also concludes that there was no concern for skin sensitization caused by the HBCDD available on the EU market. No information was available on respiratory sensitization.

Sub-chronic and chronic toxicity

In animal experiments HBCDD mainly targets the liver, the thyroid, and the pituitary gland. In the liver it induces hepatic microsomal enzymes (CYP2B and CYP3A) affecting key metabolic pathways, such as the metabolism of lipids and sex hormones. Females were most sensitive. In rats, the most consistent effect found after repeated doses was a dose-dependent increase in liver weight with a no-observable-adverse-effect-level (NOAEL = BMD-L₂₀) of 22.9 mg/kg per day estimated for this effect in female rats exposed to HBCDD for 28 days (van der Ven 2006). Pituitary and thyroid weight also increased significantly, accompanied by thyroid follicular cell hypertrophy. This effect on the pituitary gland induced the synthesis of thyroid-stimulating hormone (TSH). The NOAEL for this effect was 2 mg HBCDD/kg b. w. per day. HBCDD also had an effect on bone mineral density in this study.

There were no available repeated dose toxicity studies by inhalation or dermal application.

Effect on reproduction and offspring

Exposure to HBCDD can have wide-ranging and potentially severe effects, particularly to the neuroendocrine system and to offspring during the early phases of neurodevelopment. Several studies on HBCDD's reproductive effects indicate this (EFSA, 2011a).

In a two-generation study by Ema *et al.* (2008), the main effects seen were a dose-dependent decrease (8-14%) in fertility index in both generations. Thyroid effects were observed both in dams and in offspring, with a NOAEL of 10 mg/kg b. w. per day. In addition, in the F2 generation at the highest dose level, increased pup mortality during lactation was observed.

Another study indicated that neonatal HBCDD exposure may cause statistically significant changes in spontaneous behaviour and learning and may also induce memory defects (Eriksson *et al.*, 2006). An indicative lowest-observable-adverse-effect-level (LOAEL) of 0.9 mg/kg b. w. per day was also deduced from this study.

A one-generation reproduction feeding study found that HBCDD induces disturbances in hearing function and changes in dopamine-dependent behaviour. The immune system was also affected, showing a statistically significant dose-response for decreased lymphocyte fraction and a decreased whole white blood cell count in the blood and increased blood cell count in the bone marrow. The most sensitive effect in this study on reproductive organs was decrease in weight of the testes with a benchmark dose limit (BMDL₅) of 11.5 mg/kg b. w. per day (van der Ven *et al.*, 2009).

Mutagenicity/Genotoxicity

HBCDD was not mutagenic in the Ames test with *Salmonella typhimurium* bacteria and caused no chromosomal aberrations in an *in vitro* mammalian cytogenetic test using human peripheral blood lymphocytes and an *in vivo* micronucleus test. Based on the available studies, it was concluded that HBCDD was not genotoxic (EFSA, 2011a).

Carcinogenicity

In an older 1984 long-term toxicity/carcinogenicity study B6C3F1 mice were exposed in 18 months to up to 10,000 mg HBCDD/kg of the feed or equivalent to an intake of 1300 mg/kg b. w. per day. The results indicated that the incidence of altered foci in the liver of males was increased, as was the incidence of liver carcinoma in females, but without a dose-relationship and within the range of background levels for this strain of mice. EFSA concluded that this study and the lack of genotoxicity showed that carcinogenicity was not a critical effect in the risk assessment of HBCDD (EFSA, 2011a). There is no human data or data from animal bioassays using exposure routes other than oral.

Further, ECHA concluded in 2009 that the data available on carcinogenicity did not suggest a classification of HBCDD according to EU criteria. However, the lack of acceptable cancer bioassays in both mice and rats makes these conclusions premature and gives no incentive to undertake such studies. Modern research also shows that lack of direct dose-effect relationships and lack of genotoxicity may not be decisive as regards hormone-related carcinogens having a U-shaped dose-response curve.

Mechanisms and interactions

Experimental studies *in vivo* indicate that reproductive and neurodevelopmental toxicity, disturbance of thyroid homeostasis, hepatic hypertrophy and immunotoxicity are the major effects of HBCDDs. α -HBCDD has been reported to suppress AhR-mediated gene expression, with IC₅₀ = 7.4 μ M (EFSA, 2011a).

Neurodevelopmental effects might be associated with modulation of thyroid hormone homeostasis and the involved processes include direct interaction of HBCDDs with thyroid hormone receptors, induction of CAR/PXR-dependent hormone-metabolizing enzymes, and/or perturbation of thyroid hormone transport (EFSA, 2011a). HBCDD has also been shown in *in vitro* tests to interact with calcium levels and neurotransmitter release in cells (Dingermans *et al.*, 2009).

6.1.4 TBBPA and derivatives

Toxicokinetics and metabolism

The limited toxicokinetics data suggest that oral bioavailability of ¹⁴C-labelled TBBPA in rats is above 70 % (EFSA, 2011c). In a new study (Knudsen *et al.*, 2013) following oral administration of [¹⁴C]-TBBPA, the primary route of elimination of radioactivity was in faeces with dose recoveries in 72 hours between 94 and 98%, depending on dose size.

After oral exposure to TBBPA dissolved in corn oil, the highest tissue concentrations (radioactivity = TBBPA + metabolites) were found in the liver, adipose tissue and in the gonads. The half-life of TBBPA in the blood in rats was 13-20 hours, and it was 71 hours in adipose tissue. Most of the radioactivity (>90%) was excreted via the bile in faeces. Glucuronide or sulfate conjugates of TBBPA were identified in the bile. Tribromobisphenol A has been identified in faeces, suggesting that debromination of TBBPA can occur in mammals (EFSA, 2011c).

In one human study, only TBBPA glucuronide was detected in the blood and with a half-life appearing to be between 48 and 72 hours (Schauer *et al.*, 2006). In another older study with occupationally exposed individuals (Hagmar *et al.*, 2000) the half-life was about 2 days. In that study the serum concentrations were between <2 and 7.4 pmol/g lipid weight.

Rat experiments with oral administration of TBBPA indicate that the trans-placental transfer is less than 0.01% (EFSA, 2011c). However, this study only had a general oral absorption of 0.5%, which is in contrast to other studies reporting >70% absorption. The detection of TBBPA in cord serum collected from French women volunteers during caesarean deliveries (Cariou *et al.*, 2008) confirms that trans-placental transfer of TBBPA occurs in humans.

The studies demonstrate the presence of TBBPA in breast milk and suggest that milk represents a substantial route of excretion for TBBPA in humans (EFSA, 2011c).

Acute toxicity

The acute toxicity of TBBPA was reported as low in rodents with an oral LD₅₀ >50 g/kg b. w. in rats and >10 g/kg b. w. in mice (ECB 2006). However, in single administration studies, TBBPA has an established LD₅₀ of greater than 5 g/kg bw when administered by gavage to rats, and LD₅₀ in mice was about 4.5 g/kg b. w. (IPCS 1995). The dermal LD₅₀ in rabbits and guinea pigs were respectively >2 g/kg b. w. and >1 g/kg b. w. (IPCS, 1995).

Irritation and sensitization

TBBPA was not irritating to skin when 500 mg was applied to intact and shaved rabbit skin for 24 hours, and it was neither a sensitizer in guinea-pigs nor humans (IPCS 1995). Installation of TBBPA powder in rabbit eyes caused a slight redness but the chemical was not considered irritating to the eyes (IPCS, 1995).

Sub-chronic and chronic toxicity

Animal studies with TBBPA have been carried out using different experimental designs with single or repeated administration during gestation, postnatally or in adulthood. The general toxicity is low, and ECB (2006) considered 1000 mg/kg b. w. per day as a NOAEL in rats exposed for 90 days. For mice, the NOAEL for weight and blood changes in a similar study was 700 mg/kg b. w. per day (IPCS, 1995).

TBBPA exhibits some signs of hepatotoxicity in rats and mice, particularly in juvenile mice, in the gram per kg b. w. dose range (EFSA, 2011c).

Available studies indicate that TBBPA can affect the host immunity in mice after administration of 1,700 mg/kg b. w. per day for 28 days (EFSA, 2011c).

Effect on reproduction and offspring

The available studies did not indicate any reproductive or teratogenic effects of TBBPA. A few studies have provided contradictory results especially with regard to the developmental neurotoxic potential of TBBPA (EFSA, 2011c).

In a one-generational reproductive study in rats, TBBPA exposures resulted in decreased circulating thyroxin levels, while other endocrine effects increased weight of testis and male pituitary gland. The hypothyroxinemia correlated to a cluster of developmental parameters including delayed sexual development in females, decreased pup mortality, and effects on brainstem auditory evoked potentials (Van der Ven *et al.*, 2008). A previous study by the same group has indicated that TBBPA exposure, especially in females, affects thyroid-dependent neurobehavioral functions in offspring, such as auditory responses examined with brainstem auditory evoked potentials (BAEPs) (Lilienthal *et al.*, 2008). The BMDL values for elevation of hearing thresholds in females were in the range of 1-40mg/kg body weight, depending on frequency.

Mutagenicity/Genotoxicity

The available *in vitro* data such as Ames test with bacteria, chromosomal aberrations in human peripheral lymphocytes, sister chromatid exchanges in Chinese hamster ovary (CHO) cells etc. indicated that TBBPA was not genotoxic *in vitro*; *in vivo* data were lacking (EFSA, 2011c).

Carcinogenicity

There are no long-term toxicity/carcinogenicity studies for TBBPA. However, based on the weight of evidence (absence of genotoxicity *in vitro*, no indications for proliferative changes or cytotoxicity in studies with up to 90 days repeated administration, no immunosuppression, except possibly at high doses), the EFSA CONTAM Panel concluded that there were no indications that TBBPA might be carcinogenic (EFSA, 2011c).

Mechanisms and interactions

The main target for TBBPA toxicity is thyroid hormone homeostasis, and most of the studies indicated a decrease in serum T₄; in addition, weak estrogenic potency has been found, but TBBPA did not induce CYP1, CYP2B1 or CYP3A mRNA, protein and respective monooxygenase activities. The BMDL₁₀ of 16 mg/kg b. w. for changes in circulating thyroid hormone levels could, in principle, be used as the basis to derive a human health based guidance value (EFSA, 2011c).

TBBPA also induces oxidative stress in cerebellar granule cells *in vitro* (Reistad *et al.*, 2007)

6.1.5 DBDPE and EBTEBPI

Toxicokinetics and metabolism

A single administration of 1 000 mg DBDPE /kg b. w. was poorly absorbed in rats by the oral route (EFSA, 2012a).

Only trace amounts of radiolabel were found in examined tissues of rat (liver, kidney, brain, skeletal muscle and body fat) 2 days after dosing of ¹⁴C-Labelled EBTEBPI. Tissue levels declined by an order of magnitude over the subsequent 28 days (no data provided on levels in fat) (EFSA, 2012a).

Acute toxicity

The acute toxicity of BTBPE is very low with an oral LD₅₀ of >10 g/kg b. w. for both rats and dogs (EFSA, 2012a).

The acute toxicity of EBTEBPI is very low with an oral LD₅₀ of >7.5 g/kg b. w. for both rats and dogs (EFSA, 2012a).

Irritation and sensitization

No information.

Sub-chronic and chronic toxicity

Statistically significant differences in absolute and relative liver weights were found between control and female rats dosed 1 000 mg DBDPE /kg b. w. per day for 90 consecutive days, but no clinical signs, changes in clinical chemistry or hematology were observed (Hardy *et al.*, 2002).

This study was insufficient for the EFSA CONTAM Panel to identify a no-observed adverse effect level (NOAEL) (EFSA, 2012a).

On the other hand, in another study where male rats were orally exposed to 100 mg/kg b. w. per day of DBDPE for 90 days, no significant changes in body, liver and kidney weight were observed. However, DBDPE induced changes in various clinical parameters and a significant increase in the triiodothyronine (T₃) level, suggesting that DBDPE did alter thyroid hormone homeostasis. DBDPE also induced CYP3A biotransformation enzymes and constitutive androgen receptor (CAR)-dependent gene expression and, consequently, may cause possible adverse effects (Wang *et al.*, 2010).

Groups of 15 male and 15 female Sprague Dawley rats were administered EBTEBPI in their diet at concentrations of up to 1 % (10 000 mg/kg feed) for 90 days. The NOAEL was the highest dose tested: 1 % of the diet, which is equivalent to about 1 000 mg/kg bw per day. (as cited by EFSA, 2012a)

Effect on reproduction and offspring

No evidence of maternal toxicity, developmental toxicity or teratogenicity was reported in rats and rabbits treated with DBDPE at dose levels up to 1 250 mg/kg b. w. per day from gestation day (GD) - 6 to GD15 for rats and GD6 to GD18 for rabbits (Hardy *et al.*, 2010).

In a study of New Zealand White rabbits administered EBTEBPI orally, the NOAEL for maternal and developmental toxicity was 1 000 mg/kg bw per day, the only dose tested (as cited by EFSA, 2012a).

Mutagenicity/Genotoxicity

DBDPE was not genotoxic in bacterial assays such as the Ames-test with *Salmonella typhimurium* and in *Escherichia coli* WP2 reverse mutation assays, and no chromosomal aberrations were reported in Chinese hamster lung cells (Hardy *et al.*, 2010).

The mutagenicity of EBTEBPI has been investigated in a number of *in vitro* systems. EPTEBPI was not mutagenic in *Salmonella typhimurium* strains TA1535, TA1537, TA1538, TA98 and TA100, and in *Saccharomyces cerevisiae* (D4), with and without metabolic activation. (as cited by EFSA, 2012a).

Carcinogenicity

No information.

Mechanisms and interactions

No information.

Human health impacts

No information.

6.1.6 Other brominated flame retardants

EFSA (2012a) evaluated a number of emerging and novel BFRs. Some available toxicological properties are shown in Table 42 which also indicates the self-classification from the C&L database.

Due to the limited available information on occurrence, exposure and toxicological hazards, the CONTAM Panel concluded that it was not possible to perform a risk characterization for any of the emerging or novel BFRs considered (EFSA, 2012a).

However, from the available toxicological information it is evident that tris(2,3-dibromopropyl) phosphate (TDBPP; “Tris”) is genotoxic and carcinogenic, and therefore is a health concern (Blum and Ames, 1977). This flame retardant has been a priority chemical for a long period of time and was banned in textiles in the 1980s.

EFSA (2012a) concludes that dibromoneopentyl glycol (DBNPG) is genotoxic in the Ames test with TA100 strain and metabolic activation, carcinogenic in mice, and demonstrative of reproductive toxicity, and therefore could be of potential health concern.

The toxicity of the highly persistent hexabromobenzene (HBB) was not especially noted by EFSA (2012a); however, this chemical is closely related to hexachlorobenzene (HCB), a highly toxic and banned POP chemical once used as fungicide on seed grains, which gave rise to serious mass poisoning, e.g. in Turkey in the 1950s. About 500 people were fatally poisoned and more than 4,000 people fell ill by eating bread made with HCB-treated seed that was intended for agriculture use. Most of the sick were affected with a liver condition called *porphyria cutanea tarda*, which disturbs the metabolism of hemoglobin and results in skin lesions. HBB has a long residence time in rats with a half-life of 48 days. Exposed rats have increased excretion of porphyrins in the urine, analogous to exposure to HCB. Therefore, this chemical should not be used as flame retardant.

TBECH diastereomers activate the human androgen receptor (AR) in *in vitro* assays, indicating potential endocrine disruption (Khalaf *et al.*, 2009).

TABLE 42
SUMMARY OF AVAILABLE DATA ON HUMAN HEALTH EFFECTS

Abbreviation *1	Name	CAS No	Occurrence Food *2	Human sam- ples *2	Reproductive and developmental toxicity *2	Genotoxicity /carcinogenicity *2	Self classification *3
4'-PeBPO- BDE208	Pentabromophenoxy- nonabromodiphenyl ether	58965-66-5	No data	No data	No data	No data	No classification indicated
BDBP- TAZTO	1,3-Bis(2,3- dibromopropyl)-5-(2- propen-1-yl)-1,3,5-triazine- 2,4,6(1H,3H,5H)-trione	75795-16-3	No data	No data	No data	No data	Not in C&L
BEH-TEBP	Bis(2-ethylhexyl) tetra- bromophthalate	26040-51-7	No data	No data	No data	DNA strand breaks (Firemaster)	Eye Irrit. 2
BTBPE	1,2-Bis(2,4,6- tribromophenoxy) ethane	37853-59-1	<4 ng/g fat	Plasma (SE) <1.3 ng/g fat	No hatching effects (chicken)	Not mutagenic in Ames test and <i>S. cerevisiae</i>	No hazard class
DBDPE	Decabromodiphenyl ethane	84852-53-9	Up to 7 ng/g fat	Plasma (SE) <1 ng/g fat	No developmental or teratogenic effects (rats), depressed hatching (fish)	Not mutagenic in Ames test, CHL cells	No hazard class
DBE-DBCH	4-(1,2-Dibromoethyl)-1,2- dibromo cyclohexane	3322-93-8	No data	No data	No data	Mutagenic in mouse lymphoma cells	Eye Irrit. 2
DBHCTD	5,6-Dibromo- 1,10,11,12,13,13- hexachloro-11- tricyclo[8.2.1.0 _{2,9}] tride- cene	51936-55-1	No data	No data	No hatching effects (chicken)	No data	Not in C&L
DBNPG	Dibromoneopentylglycol	3296-90-0	No data	No data	Impaired reproduction (mice)	Mutagenic in Ames test and in CHO cells, and <i>in vivo</i> . Increased tumor incidence in male and female rats and mice	Acute Tox. 4 Eye Irrit. 2 Muta. 1B Carc. 1B STOT RE 2

Abbreviation *1	Name	CAS No	Occurrence Food *2	Human samples *2	Reproductive and developmental toxicity *2	Genotoxicity /carcinogenicity *2	Self classification *3
DBP	2,4-Dibromophenol *4	615-58-7	Up to 6 ng/g fat *4	Plasma (Canada) 148 (< 50-4 100) ng/l	No data	No data	Acute Tox. 2 Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 STOT SE 3
DBP-TAZTO	1-(2,3-Dibromopropyl)-3,5-diallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	57829-89-7	No data	No data	No data	No data	Not in C&L
DBS	Dibromostyrene	31780-26-4	No data	No data	No data	No data	No hazard class
EBTEBPI	Ethylenebis (tetrabromophthalimide)	32588-76-4	No data	No data	No effects in rats (highest dose)	Not mutagenic in Ames test.	No hazard class
EH-TBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate	183658-27-7	No data	No data	No data	DNA strand breaks (Firemaster)	Not in C&L
HBB	Hexabromobenzene	87-82-1	Up to 5 ng/g fat	Serum (CHINA) 0.05 ng/g fat Milk (JP) 0.27-0.46 ng/g fat	Not teratogenic (rats)	Not mutagenic in Ames test	Acute Tox. 4 Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 STOT SE 3
HBCYD	Hexabromocyclodecane	25495-98-1	No data	No data	No data	No data	Not in C&L
HCTBPH	1,2,3,4,7,7-Hexachloro-5-(2,3,4,5-tetrabromophenyl)-bicyclo[2.2.1]hept-2-ene	34571-16-9	No data	No data	No data	No data	Not in C&L
HEEHP-TEBP	2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	20566-35-2	No data	No data	No data	Not mutagenic in Ames test and <i>S. Cerevisiae</i> .	No hazard class
OBTMPI	Octabromotrimethylphenyl indane	1084889-51-9 1025956-65-3 893843-07-7 155613-93-7	No data	No data	No data	No data	Not in C&L
PBB-Acr	Pentabromobenzyl acrylate	59447-55-1	No data	No data	No data	No data	Not in C&L

Abbreviation *1	Name	CAS No	Occurrence Food *2	Human samples *2	Reproductive and developmental toxicity *2	Genotoxicity /carcinogenicity *2	Self classification *3
PBEB	Pentabromoethylbenzene	85-22-3	<10 ng/g fat	Serum (CHINA) <LOD 0.01 ng/g fat	No data	Not mutagenic in Ames test	Skin Irrit. 2 Eye Irrit. 2 STOT SE 3
PBP	P entabromophenol *4	608-71-9	<0.04 ng/g fat *4	No data	No data	PBP was not mutagenic in <i>Salmonella typhimurium</i> No data on carcinogenicity	Acute Tox. 3 Skin Irrit. 2 Eye Irrit. 2 STOT SE 3
PBT	Pentabromotoluene	87-83-2	No data	No data	No foetotoxicity (rats)	Not mutagenic in Ames test	Skin Irrit. 2 Eye Irrit. 2 STOT SE 3
TBCO	1,2,5,6-Tetrabromocyclooctane	3194-57-8	No data	No data	No data	No data	Not in C&L
TBNPA	Tribromoneopentyl alcohol	1522-92-5	No data	No data	No data	Mutagenic in Ames test (with metabolic act.)	Eye Irrit. 2
TBP	2,4,6-Tribromophenol *4	118-79-6	Up to 13 ng/g fat *4	Plasma (Canada) 58 (< 5-280) ng/l Umbilical cord (Japan) 33 pg/g wet weight (±8.2)	NOAELs for maternal and developmental toxicity 1 000 and 300 mg/kg bw per day, respectively	Not mutagenic in Ames test No data on carcinogenicity	Skin Sens. 1 Eye Irrit. 2
TBP-AE	2-(Allyloxy)-1,3,5-tribromobenzene *4	3278-89-5	<0.04 ng/g fat *4	No data	No data	No data	Not classified (no information provided)
TBX	2,3,5,6-Tetrabromo-p-xylene	23488-38-2	No data	<1 ng/g fat	No data	No data	Skin Irrit. 2 Eye Irrit. 2 STOT SE 3
TDBPP	Tris(2,3-dibromopropyl) phosphate	126-72-7	No data	No data	No data	Mutagenic in bacterial and mammalian cells, chromosomal aberrations <i>in vitro</i> and <i>in vivo</i> . Kidney tumours in male rats and mice	Eye Irrit. 2
TDBP-TAZTO	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-trione	52434-90-9	No data	No data	Depressed hatching (fish)	No data	Skin Irrit. 2 Eye Irrit. 2 STOT SE 3

Abbreviation *1	Name	CAS No	Occurrence Food *2	Human sam- ples *2	Reproductive and developmental toxicity *2	Genotoxicity /carcinogenicity *2	Self classification *3
TTBNPP	Tris(tribromoneopentyl) phosphate	19186-97-1	No data	No data	No data	No data	Not in C&L
TTBP-TAZ	2,4,6-Tris(2,4,6- tribromophenoxy)-1,3,5- triazine	25713-60-4	No data	No data	No data	No data	Not in C&L

*1 Abbreviations changed to be in consistence with Bergman *et al.*, 2012a.

*2 Source: EFSA, 2012a

*3 C&L database. Self-classification regarding human health – indicated by more than 25% of notifiers. Data from Appendix 6. "No hazard class" indicates the the substance in the C&L database is registered as "no t classified".

*4 Data extracted from EFSA, 2012b. Data on occurrence in food include data from Europe only.

6.1.7 Combination effects

Simultaneous occurrence of more brominated flame retardants with similar toxicological mechanism will result in additive effects at a minimum. There may also be a possibility for synergistic effects. Thyroid hormones are critically involved in brain development and PBDE (+ metabolites) induced developmental neurotoxicity may be caused by disruption of thyroid hormone homeostasis (Dingermans *et al.*, 2011). Since most of the BDEs, other brominated flame retardants and other environmental pollutants can affect thyroid homeostasis, combinational effects are likely to occur.

Neurotoxicological effects have been seen in mice several months after administration of a single dose of specific PBDE congeners and TBBPA on day 10 after birth (results from Eriksson *et al.*, 1998).

6.2 Human exposure

Human exposure to BFRs has recently been reviewed by the EFSA Panel on Contaminants in the Food Chain (CONTAM) and reported in five assessments on PBDE (EFSA, 2011b), PBB (EFSA, 2010a), HBCDD (EFSA, 2011a), TBBPA and its derivatives (EFSA, 2011c), emerging and novel BFRs (EFSA, 2011a) and brominated phenols and their derivatives (EFSA, 2012b). The following section is largely based on these assessments and many paragraphs are direct citations of the assessments with a focus in the substances still in use in the EU.

To the extent Danish data have been identified, they are included in the following; i.e. if nothing is mentioned, no Danish data have been identified.

The brominated flame retardants are solids with a low vapour pressure (volatility), thus air exposures will mainly be to particle-bound substances. The water solubility is also low but these chemicals are persistent and lipophilic and can be accumulated and magnified through the aquatic food chains.

Humans may be directly exposed to brominated flame retardants in occupational settings that involve handling these chemicals, or materials containing these chemicals. Consumers may be directly exposed to these chemicals through exposure to consumer products. Releases from such products may also cause elevated levels in indoor air and dusts. The general population may further be potentially exposed to BFRs in polluted ambient air, in polluted soil (children mainly) and in polluted drinking water.

6.2.1 Direct exposure

The direct exposures are exposures from the direct handling of the BFRs and mixtures and articles containing the BFRs in occupational settings and by consumers.

Consumer exposure

PBDEs – Non-dietary human exposure to PBDEs and other BFRs can occur via inhalation of gas-phase PBDEs and PBDEs on particles, as well as oral intake of house dust. Such exposure can occur in homes as well as in the workplace. No reports could be identified which indicate that dermal exposure should be of any importance for the total human exposure (EFSA, 2011b). The main non-dietary human exposure routes are described in section 6.2.2 addressing indirect exposure.

HBCDD – According to EFSA (2011a), no reports could be identified which indicate that dermal exposure should be of any importance for the total human exposure (EFSA, 2011a). The main non-dietary human exposure route is described in section 6.2.2 addressing indirect exposure.

TBBPA - According to the EU Risk Assessment, consumer exposure to TBBPA is likely to be insignificant (ECB, 2006).

Other BFRs – No data on direct exposure of consumers to other BFRs have been identified.

Occupational exposure

Occupational exposure to the main BFRs is described in the EU Risk Assessments and summarised from these, although the occupational exposure has likely decreased as a consequence of the activities under VECAP, although the emission reduction programme does not specifically target occupational exposure.

PBDEs – According to the EU Risk Assessment, the main occupational exposures to decaBDE are by handling of the substance such as filling or emptying bags, adding the substance by formulation processes (e.g. hotmelt adhesives) or sewing decaBDE treated textiles (ECB, 2002). The occupational exposure from the end-use of flame retardant products is considered negligible (ECB, 2002).

A number of studies from the last ten years demonstrate that workers in EEE recycling facilities may be exposed to the BFRs over and above the level of the general population. Elevated exposure to PBDE of workers in EEE recycling facilities has been demonstrated in China, Sweden, Norway and the USA (as reviewed by Schechter *et al.* (2009)). A Swedish study showed the median total PBDE blood level in EEE recycling facility workers was seven times higher than the reference group, which consisted of hospital workers and computer clerks (Sjodin *et al.*, 1999 cited by Schechter *et al.*, 2009). A later study showed that dust-reducing industrial hygiene improvements clearly reduced the occupational exposure to higher brominated diphenyl ethers. In 2000, the BDE-209 concentrations did not differ from levels observed in a reference population whereas the levels of hexa- to nonaBDEs still were elevated (Thuresson *et al.*, 2006a).

Schechter *et al.* (2009) showed an approximate 6-fold to 33-fold increase in electronic recycling facility workers' PBDE exposure as compared with the US general population.

Rosenberg *et al.* (2011) measured PBDEs, TBBPA, DBDPE, HBCDD and BTBPE and a chlorinated FR at four EEE recycling facilities in Finland. The three most abundant FRs in personal air samples were PBDEs (comprised mostly of deca-BDE, TBBPA, and DBDPE), with mean concentrations ranging from 21 to 2,320 ng/m³, from 8.7 to 430 ng/m³, and from 3.5 to 360 ng/m³, respectively. The authors conclude that the concentrations reported may pose a health hazard to the workers, although evaluation of the association between BFR exposure and adverse health effects is hampered by lack of occupational exposure limits.

HBCDD – The main occupational exposures to HBCDD is from handling of the substance such as filling or emptying bags, adding the substance by formation processes or sewing HBCDD treated textiles (ECB, 2008a). Other occupational exposure scenarios may be at building sites handling insulation boards or other materials containing HBCDD. These scenarios probably result in much lower exposure levels than the scenarios arising during direct handling of the pure substance (ECB, 2008a).

TBBPA –The EU RISK assessment for TBBPA did not review occupational exposure to TBBPA, but makes reference to a study of Thomsen *et al.* (2001, as cited by ECB, 2008) determined the concentration of TBBPA in blood plasma from humans in three occupational groups in Norway: electronic equipment dismantlers, circuit board producers and laboratory personnel. The levels found in the various populations were from 0.64 to 1.8 µg/kg lipid (mean 1.3 µg/kg lipid) in the electronic equipment dismantlers, from not detected to 0.80 µg/kg lipid (mean 0.54 µg/kg lipid) in the circuit board producers and from not detected to 0.52 µg/kg lipid (mean 0.34 µg/kg lipid) in the laboratory personnel.

TBBPA - Elevated indoor air concentrations, up to several orders of magnitude above those found in outdoor air, have been reported for specific occupational environments, such as electronics dismantling plants (EFSA, 2011c).

Other BFRs – No data have been identified on occupational exposure to other BFRs apart from the data from recycling facilities mentioned above. The main occupational exposures to other BFRs is likely from handling of the substance such as filling or emptying bags or adding the substance through formulation processes, and for handling some of the substances from EEE recycling.

6.2.2 Indirect exposure

The indirect exposure routes include exposures to hazardous substances via the environment (in ambient air, food, drinking water, etc.), the indoor climate (indoor air and dust) or other indirect exposures (e.g. from packaging or drinking water installation).

Ambient air

In general, exposure via ambient air does not appear to be a significant source of BFRs; measurements in air are used rather to indicate the potential of long-range transport of the substances.

PBDEs - There are several factors indicating long-range transboundary transport of PBDEs in the environment: they have a high persistency in air and monitoring has detected a widespread occurrence in the European atmosphere (EFSA, 2011b). Recorded levels of tri- to hexaBDEs in the UK, Canada and Kuwait ranged from 0.49 to 32 pg/m³, whereas BDE-209 (decaBDE) was recorded from the limit of detection up to 105 pg/m³ in Ontario, Canada (Harrad *et al.*, 2010, as cited by EFSA, 2011b).

A study of trends of PBDEs in European background air sampled at eleven sites (southern England to northern Norway) during 2000 to 2008 showed a general decline in PBDE levels over time. A consistent decline was only observed at four sites and declines could only be calculated for BDE-47, -49, -99, -100, -153 and -154, for which half-lives ranged from 1.4 to 4.0 years. The absolute decline of the sum of PBDE levels between 2000-2002 and 2006-2008 ranged from 35 to 57 % and the concentration in air declined by 50 % every 2.2 ± 0.4 years. (Schuster *et al.*, 2010, as cited by EFSA, 2011b)

HBCDD - HBCDDs have been found in Arctic air (Svalbard) at mean concentrations of 7.1 pg/m³ (2006) and 6.5 pg/m³ (2007). γ -HBCDD was the predominant stereoisomer followed by α -HBCDD and a low contribution of β -HBCDD. Earlier results from remote stations in Sweden and Finland ranged from 2 to 280 pg/m³. (EFSA, 2011a)

TBBPA - Comparable concentrations of TBBPA were found at a rural site in northern Germany (ranging from <0.04 to 0.85 pg/m³) and over the Wadden Sea (ranging from 0.31 to 0.69 pg/m³), whereas the concentrations over the Northeast Atlantic Ocean ranged from <0.04 to 0.17 pg/m³, with the highest concentration present in a sample collected at the West Norwegian coast, indicating an input source from land to ocean (Xie *et al.*, 2007 as cited by EFSA, 2011c). The levels of TBBPA in ambient air are considerably lower than the levels of HBCDD mentioned above.

Other BFRs – Other BFRs in air in the Nordic countries have been analysed by Schlabach *et al.* (2011) and are further described in section 5.3.2.

Soil

The dominating source of BFRs in arable soil is via application of sludge from sewage treatment plants (EFSA, 2011b). The releases to soil by application of sludge are discussed in section 4.1. The EFSA reviews provide limited data on BFRs in soil and no estimates of the possible exposure to

BFRs from intake of soil. For infants and toddlers the intake by from house and car dust, mentioned later, seems to be a more significant exposure source.

Drinking water

The EFSA reviews generally do not provide any data on the BFRs in drinking water and the possible exposure to BFRs via drinking water.

Food

According to the EFSA reviews, for the general population food is the major source of exposure to BFRs.

PBDEs - Analyses of PBDE in food in Denmark have been undertaken by the Danish Veterinary and Food Administration in 2009 and 2010. In 2010, samples of beef (54 samples), pork (46 samples), milk (10 samples), egg (7 samples) and lamb (4 samples) were examined for contents of PBDE (DVFA, 2010). All samples had contents just below the tolerable level of 100 ng/g fat determined by the Danish Veterinary and Food Administration. The same was the case for all samples analysed in 2009.

A European level monitoring program has been carried out since 2006. The results obtained from the analyses of 19 PBDE congeners on 3,971 food samples were provided to EFSA by 11 European countries, covering the period from 2001 to 2009 (EFSA,2011b). The following focuses on the data for decaBDE (BDE-209).

The levels of BDE-209 were the highest in almost all of the food categories except for “Fish and other seafood (including amphibians, reptiles, snails and insects)” and “Food for infants and small children”, where BDE-47 was the congener with the highest levels. The food categories that contribute most to the exposure to BDE-209 are animal and vegetable fats and oils, and milk and dairy products, with relative contributions of 43.5 % and 41.7 % respectively (maximum upper bound (UB)¹⁰ across European countries and surveys).

The highest dietary exposure is due to BDE-47 and BDE-209. The estimated mean chronic dietary exposure for average consumers across the dietary surveys in European countries ranges from 0.35 (minimum lower bound (LB)) to 2.82 (maximum UB) ng/kg bw per day for BDE-209. For high consumers, the minimum LB and maximum UB dietary exposure estimates of BDE-47 are for BDE-209 - 0.7 and 4.58 ng/kg bw per day, respectively.

For children from 1 to 3 years old, the dietary intake of BDE-47, -99, -153 and -209, for average and high consumers, is about 3-6 times higher than for adults. The CONTAM Panel noted that exposure to BDE-99 for this age group could be overestimated due to one high sample in the category “Food for infants and small children”. (EFSA,2011b)

EFSA (2011b) concludes that the available data indicate a potential health concern for dietary exposure for young children (1-3 years) to BDE-99. For other congeners, the estimated dietary intake for the different population groups indicates that current dietary exposure is unlikely to raise a health concern (EFSA, 2011b).

HBCDD

Denmark - The Danish National Food Institute has evaluated the content of chemical contaminants in food in the period 2004-2011 at the request of the Danish Veterinary and Food Administration (DTU Food, 2013). The study presents data on the occurrence of Σ HBCDD and TBBPA in fish

¹⁰ EFSA use an approach for data reported to be below the limit of detection (LOD) or limit of quantification (LOQ) where results below the LOD or LOQ are either represented by a value equal to the LOD/LOQ (upper bound, UB) or zero (lower bound, LB) (EFSA, 2010b)

from Danish waters and the exposure of Danish adults and children to Σ HBCDD are estimated. The results show that α -HBCDD was present in the highest amounts, followed by γ -HBCDD and β HBCDD. The highest levels of the sum of the HBCDD isomers (Σ HBCDD) were found in cod liver that is used e.g. for the production of vitamin supplies (Vitamin D). The cod liver contained 37-66% lipid and 11 ng/g w.w. Σ HBCDD. Salmon, being a fatty fish with lipid levels from 10-23%, contained the second largest contaminant levels, 2.45 ng/g w.w.. The mackerel taken from the North Sea contained 23-29% lipid and an average Σ HBCDD level of 0.93 ng/g w.w. In conclusion, the results of 63 fish samples for food consumption showed Σ HBCDD levels from <0.01-16.7 ng/g w.w. or <0.1-110 ng/g lipid.

The distribution of Σ HBCDD exposure from fish for the adult population in Denmark showed that a large proportion of the population has a low exposure to HBCDD from fish. The curve decreases slowly, as some individuals have a relatively high HBCDD exposure from fish. The mean exposure for adults is 0.19 ng/kg body weight per day, and the 95th percentile is 0.75 ng/kg bw/day. The Σ HBCDD exposure for children aged 4-14 is 0.23 ng/kg bw/day and the exposure for high consumers, estimated as the 95th percentile, is 1.28 ng/kg bw/day. The Σ HBCDD exposure is mainly derived from eating salmon and herring. The Margin of Exposure (MOE) was calculated relative to the effect of the most sensitive end-point, and based on the mean and the 95th percentiles (representing high consumption). The calculated intake and the MOEs are shown in Table 43. The authors concluded that the MOEs are of no food safety concern.

TABLE 43
CALCULATION OF MOE OF Σ HBCDD FOR DANISH ADULTS (AGED 15-75) AND CHILDREN (AGED 4-14) (DTU FOOD, 2013)

	Effect level (μ g/kg bw/day)	Exposure group	Danish adults (ng/kg bw/day)	MOE	Danish children (ng/kg bw/day)	MOE
BMDL10 neurodevelopmental effects on behaviour	790	Mean	0.19	4.1×10^6	0.23	3.4×10^6
		95th percentile	0.75	1×10^6	1.28	617,000

EU - The mean dietary exposure to HBCDDs across dietary surveys in European countries was estimated by EFSA (2011a) for children from three to ten years old ("Other children"), ranging from 0.15 - 1.85 ng/kg body weight (bw) per day for the minimum lower bound (LB) and maximum upper bound (UB), respectively. Total dietary exposure for adults is about half the exposure for "Other children", with minimum LB and maximum UB, respectively, of 0.09 and 0.99 ng/kg bw per day. Dietary exposure to HBCDDs is decreasing with increasing age down to 0.06 - 0.54 ng/kg bw per day for the minimum LB and maximum UB, respectively, for 'Very elderly' (from 75 years of age and older). Similar exposure patterns across age classes are found for the dietary intake of high consumers (95th percentile). For a specific population group consisting of high consumers of fish, the total mean dietary UB intake of HBCDD (maximum UB across European surveys) is 2.76 ng/kg bw per day. The total dietary UB intake of consumers of fish liver (once a week) is estimated to be 1.94 ng/kg bw (EFSA, 2011a).

Considering the LB estimates, the contribution of 'Fish meat and products' to the median intake of HBCDDs across European dietary surveys vary from 83 to 88.2 % for the different age classes. The second highest dietary source of dietary exposure to HBCDDs is the food group 'Meat and meat products', with median LB contribution across European dietary surveys, ranging from 6.1 to 8.9 %, and median UB from 9.8 to 15.3 %, for different age classes (EFSA, 2011a).

EFSA (2011a) concluded that the estimated dietary intake for the different population groups indicate that current dietary exposure to HBCDDs in the European Union does not raise a health concern.

TBBPA – The Danish study of content of chemical contaminants in food in the period 2004-2011 included analyses of TBBPA in samples of fish (DTU Food, 2013). TBBPA was almost undetectable in the samples, typically at a level of less than 1% of the level of Σ HBCDD. The highest value was 0.02 ng/g w.w. from 20 samples of herring. No assessment of the intake of TBBPA was included in the study.

EFSA's CONTAM Panel concluded that the submitted occurrence data were not suitable to carry out a reliable dietary exposure assessment for the general population or specific population groups such as infants, children or vegetarians (EFSA, 2011c). A hypothetical worst case dietary exposure estimate for TBBPA was considered for the specific group of adult high fish consumers by 1) substituting the concentration levels of TBBPA in fish, all reported as not quantified, by the LOQ of 1 ng/g wet weight and 2) assuming a daily high fish consumption of 2.6 g/kg body weight (bw) The resulting "upper bound" exposure estimate was 2.6 ng/kg bw per day. According to EFSA (2011c), the available data indicates that current dietary exposure to TBBPA in the EU does not raise a health concern.

DBDPE – A total of 100 composite samples of various food commodities were prepared after collection of individual sub-samples at the production or processing stage in the UK. No sample contained DBDPE levels above the limit of detection (range as reported by the authors) of 0.9-3 (milk), 1.2- 2.7 (carcass fat), 1.42-7.97 (liver) and ND-6.01 (eggs) ng/g fat (Tlustos *et al.*, 2010 as cited by EFSA, 2011). The CONTAM Panel noted, however, that observations in wildlife, particularly in fish, indicate that DBDPE might also be present in food.

Other BFRs - According to EFSA (2011b), limited information could be identified on other BFRs in food, although the observations in wildlife, particularly in fish, indicate that many of the BFRs might also be present in food.

Indoor climate

The indoor climate may be a significant source of exposure to some of the BFRs, especially for children.

PBDEs - A Danish exposure study from 2009 of pregnant women and their unborn children demonstrated positive correlations for BDE-28, -47, -100, -209 and Σ PBDE in maternal plasma and house dust, as well as for Σ PBDE in umbilical cord plasma and house dust. (Frederiksen *et al.*, 2010) The positive correlations between the levels of PBDEs in house dust and the various biological matrices indicated that house dust was a significant source of PBDE exposure in Denmark.

EFSA (2012b) reviews a number of studies on PBDEs in dust and the relation between exposures and the levels in humans. EFSA's CONTAM panel summarises that the available exposure estimates indicate that house and car dust can be important routes of exposure especially for children to BDE-209. Concentrations in dust appear to influence blood/human milk/placenta concentrations significantly. However, the CONTAM panel also noted that exposure from dust is of no health concern (EFSA, 2011b).

The highest concentrations of BDE-209 in dust worldwide were detected in the UK, which is the only EU country with specific requirements for flame retardancy in domestic upholstery (Vorkamp, 2012)

HBCDD - Dust in homes, classrooms and cars can be a source of exposure to HBCDDs for children.

Based on the level of total HBCDD in dust, Abdallah *et al.* (2008b, as cited by EFSA, 2011) identified dust ingestion as an important pathway of exposure to HBCDD for the UK population. Average dust ingestion was estimated to constitute 23.9 % of total exposure to HBCDDs for adults and 62.6 % for toddlers. High dust intake scenarios (95th percentile) resulted in values of 57.9 % and 91.5 %, respectively. Inhalation was found to be a minor exposure pathway to HBCDDs contributing 1.2 % or less in all scenarios.

Assuming a body weight of 20 kg the exposure through dust in homes, classrooms and cars was estimated to be 0.55, 5.9 and 330 ng/kg bw for three scenarios, respectively (EFSA, 2011a). The three scenarios were a 'low-end' scenario where the child ingests 50 mg dust per day contaminated at the 5th percentile concentration, one 'typical' scenario where 50 mg dust per day contaminated at the median concentration is ingested, and one 'high-end' scenario where the child ingests 200 mg dust per day contaminated at the 95th percentile concentration. The CONTAM Panel concluded that the 'typical' exposure scenario provided the most realistic estimate of exposure to HBCDDs from dust.

The available studies indicate according to EFSA (2011a) that the daily non-dietary exposure, mainly through dust in homes, offices, schools, cars and the public environment can substantially contribute, and in some cases even dominate the total human exposure to HBCDDs, especially for toddlers and children. Taking into account the uncertainties in the dust exposure estimates and considering the use of UB dietary intake estimates, the CONTAM Panel, however, concluded that the available information indicates that it is unlikely that additional exposure to HBCDDs from dust raises a health concern.

TBBPA - Dust in homes, classrooms and cars can be an additional source of exposure to TBBPA, particularly for children. Mean concentrations of TBBPA in indoor dust from homes, offices, cars and public microenvironments were reported to be in the range of 6-220 ng/g dust (EFSA, 2011c). Considering the 95th percentile TBBPA concentration in dust of 460 ng/g, the exposure based on a typical or high end exposure scenario would be 1.2 or 4.6 ng/kg bw per day, respectively (EFSA, 2011c). The CONTAM Panel concluded that the available data indicate that exposure of children to TBBPA from dust does not raise a health concern (EFSA, 2011c).

DBDPE – A number of studies of DBDPE in indoor air and dust have been performed. Karlsson *et al.* (2007) studied DBDPE in house dust sampled in five homes from three Swedish cities and found DBDPE in all but one sample in concentrations ranging from 20.8 to 121 ng/g dust. The authors also analysed the vapour phase and found DBDPE in only one sample, 0.0229 ng/m³. Harrad *et al.* (2008) reported the levels of DBDPE in dust samples from UK homes, offices and cars. Average (and maximum) concentrations were found to be 270 (3,400), 170 (860) and 900 (2,900) ng/g dust, respectively. Similar levels were found by Ali *et al.* (2011) in dust samples collected in Belgian homes and offices, and in UK child-care centre and primary school classrooms (n = 36) in 2007 and 2008. The median (min-max) concentrations were 153 (55-2,126) ng/g dust, 721 (170 – 1 846) ng/g dust and 98 (< 20 - 2 467) ng/g dust, respectively. The typical (median) exposure via high dust ingestion was calculated to be 1.89 and 0.18 ng/kg bw per day for toddlers and adults, respectively. These concentrations were high compared to the concentrations found for other BFRs as discussed below.

Other BFRs – In a study from the Nordic Countries the levels of brominated ethers and esters were higher in the indoor air samples compared to outdoor air (Schlabach *et al.*, 2011). In indoor air, BTBPE was found in the highest concentrations, ranging from 9-19 pg/m³ while BEHTBH was found in concentrations around 7 pg/m³, and DPTE in concentrations around 1 pg/m³. ATE, BATE and EHTeBB could not be detected.

Ali *et al.* (2011) studied brominated flame retardants in dust sampled in schools and offices in Belgium and the UK. The following BFRs were quantified: DBDPE (<20–2470 ng/g), BTBPE (<0.5–1,740 ng/g), TBBPA-DBPE (<20–9,960 ng/g), TBB (<2–436 ng/g) and TBPH (range <2–6,175 ng/g). DBHCTD was below the detection limit in all samples. Typical exposure with high dust ingestion estimates for adults and toddlers were estimates at: BTBPE (0.01 / 0.05), DBDPE (0.2 / 1.9), TBB (0.01 / 0.08), TBPH (0.02 / 0.4) and TBBPA-DBPE (0.08 / 1.12) ng/kg bw/d. Compared to the other analysed BFRs, the exposure to DBDPE in the dusts was significantly higher.

Stapleton *et al.* (2008 as cited by EFSA 2012a) found BEH-TEBP and EH-TBB in dust samples, collected in homes in Boston in concentrations of 3.5–10,630 ng/g dust (mean 142 ng/g dust) for BEH-TEBP and 6.6–15,030 ng/g dust (mean 133 ng/g dust) for EH-TBB. Stapleton *et al.* (2009) studied 50 further dust samples, and found BEH-TEBP in 30 of these samples in concentrations ranging from < 300 to 47,110 ng/g dust (mean = 650 ng/g dust) and EH-TBB in concentrations <450–75,000 ng/g (mean = 840 ng/g dust).

Karlsson *et al.* (2007 as cited by EFSA, 2012a) studied BTBPE in house dust sampled in five homes from three Swedish cities and found BTBPE in all samples in concentrations ranging from 2.52 to 8.15 ng/g dust, with a mean of 4.8 ng/g dust. The authors also analysed the vapour phase but they did not detect BTBPE above LOD (0.0118 ng/m³).

Harrad *et al.* (2008 as cited by EFSA, 2012a) reported the levels of BTBPE in dust samples from UK homes, offices and cars. Average (and maximum) concentrations were found to be 120 (1,900), 7.2 (40) and 7.7 (29) ng/g dust, respectively.

Zhu *et al.* (2008 cited by EFSA, 2012a) identified DBHCTD in residential indoor dust in Ottawa, Canada at a mean concentration of 1,600 ng/g dust and a maximum concentration of 93,000 ng/g dust. In residential indoor air the mean concentration was 240 pg/m³ and the maximum concentration 3,000 pg/m³.

Shoeb *et al.* (2012 as cited by EFSA, 2012a) analysed OBTMPI in dust in vacuum cleaner bags collected in Vancouver during 2007–2008. OBTMPI was detected in 8 % of the samples with a mean concentration of 13 ng/g (in detectable samples only) and a maximum concentration of 46 ng/g.

Perinatal exposure (placental transfer and breast milk)

With regard to the toxicity endpoints, exposure to BFR is particularly critical during the human brain growth spurt, covering the third trimester of pregnancy and extending to the first 2 years of the child's life. (Vorkamp, 2012). In utero exposure to BFRs can take place if the compounds cross the placental barrier. Neonatal exposure occurs primarily through breast milk, while direct ingestion of and contact with BFRs becomes increasingly important with increasing mobility. Little is known about transfer mechanisms *in utero*. Several studies have shown the presence of BFRs in umbilical cord blood; these have documented that placental transfer does take place and that the foetus is exposed to BFRs (Vorkamp, 2012).

DecaBDE – The PBDE concentrations in umbilical cord blood reflect that pentaBDE was used more extensively in the US. The US studies have reported median levels of 20–40 ng/g lw, whereas European levels are one order of magnitude below these concentrations, as shown in studies from many European countries (Vorkamp, 2012). Maternal and umbilical cord levels of PBDEs are generally highly correlated. Several studies have found decreased placental transfer with increasing degree of bromination; however, independence of the level of bromination has also been postulated. Findings for BDE-209 are inconsistent and difficult to interpret, partly because no clear trends have been established for adult blood either, and partly because of analytical challenges (Vorkamp, 2012). Higher brominated BDEs (octa- to decaBDEs) were found to account for approximately 90% of the total PBDE burden in umbilical cord blood in some studies. Other studies, however, found

BDE-209 at concentrations close to or below detection limits (as reviewed by Vorkamp, 2012). In a Danish study the Σ PBDE concentration in the umbilical cord samples varied between 213 and 54,346 pg/g lw, with a median of 958 pg/g lw (Frederiksen *et al.*, 2009). In the maternal samples where the BDE-209 analysis was successful, the concentrations of BDE-209 contributed on average 50% to the total PBDE burden (range: 19–86%). In the umbilical cord plasma samples, BDE-209 was detected in all samples, but the concentrations were below or close to those found in the blanks. According to the authors, other studies have detected BDE-209 in cord blood with LOQs similar to those of this study, indicating that, to some extent, transport of BDE-209 does take place (Frederiksen *et al.*, 2009).

The average concentrations of the predominant PBDE congeners in human milk show a comparable mean contamination across various European countries (EFSA, 2011b). BDE-47 was generally the predominant congener with mean concentrations across countries of 0.14–3.0 ng/g fat. The average concentrations across European countries for BDE-99 and BDE-153 were found to be <0.03–1.1 ng/g fat and 0.10–2.4 ng/g fat, respectively. However, the individual contamination may differ considerably as indicated by the wide concentration ranges for several PBDEs from various countries. For BDE-209, mean concentrations between 0.21 and 2.9 ng/g fat were reported for seven European countries.

For breast-fed infants with average human milk consumption, the mean daily exposure of BDE-47, -99 and -153 across countries ranges from 0.64–13.8, <0.14–5.05 and 0.46–11.0 ng/kg bw. For BDE-209, the exposure scenario based on average human milk consumption results in a range of 0.96–13.3 ng/kg bw per day. For infants with a high human milk consumption the respective mean daily exposure across European countries for BDE-47, -99 and -153 ranges from 0.96–20.6, <0.14–7.57 and 0.69–16.5 ng/kg bw. For BDE-209 the exposure scenario based on high human milk consumption amounts to 1.44–20.0 ng/kg bw per day.

Evidence exists regarding elimination of BDE-209 in human milk as shown by Antignac *et al.* (2008) who found that this compound was one of the major PBDE congeners found in human milk collected between the 3rd and 6th day after delivery in 93 volunteer women.

HBCDD - For breast-fed infants with average human milk consumption (800 mL per day) the reported range for total HBCDD in human milk (0.13–31 ng/g fat) results in daily exposures of 0.60–142 ng/kg bw. For infants with high human milk consumption (1,200 mL per day) this is 0.90–213 ng/kg bw (EFSA, 2011a). The concentration of HBCDD in human milk in Sweden increased during the period 1980–2010 as shown in section 6.4.2. EFSA (2011a) concludes that it is unlikely that exposure of breast-fed infants via human milk raises a health concern.

TBBPA – The detection of TBBPA in cord serum collected from French women during caesarean deliveries (Cariou *et al.*, 2008 as cited by EFSA, 2012c) confirms that trans-placental transfer of TBBPA occurs in humans.

Data on levels of TBBPA in human milk are scarce (EFSA, 2011c). For 3 month old breast-fed infants in France with average human milk consumption (800 mL per day), concentrations of TBBPA in human milk (ranging from 0.06 to 37.3 ng/g fat) result in daily exposures of 0.28 to 171 ng/kg b.w (Cariou *et al.*, 2008 as cited by EFSA, 2011c). For infants with high human milk consumption (1,200 mL/day) the respective daily exposures range from 0.41 to 257 ng/kg bw (EFSA, 2011c). The data from the French study showed the widest range and the highest median and average concentrations. The CONTAM Panel noted that, in contrast to the other studies, the analytical method applied in the French investigation included a hydrolysis step in the sample preparation in order to cleave potential glucuronide or sulphate conjugates. This may explain the higher values reported.

EFSA (2011c) concludes that exposure of breast-fed infants to TBBPA via human milk does not raise a health concern.

Other BFRs - For all other BFRs there is a lack of basic information on their occurrence in human samples, including human milk. Fujii *et al.* (2012 as cited by EFSA, 2012a) analysed HBB in human milk samples (n = 40) from mothers living in Japan. HBB was detected in all samples but one, with a median and mean concentration of 0.32 and 0.53 ng/g fat, respectively (middle bound approach, LOQ 0.05 ng/g fat).

6.3 Bio-monitoring data

Biomonitoring data for BFRs have recently been reviewed by EFSA's CONTAM panel and Vorkamp (2012) and the following is, to a large extent, extracted from these reviews.

Since BFRs are persistent organic pollutants and lipophilic, they are associated with fat, and the highest levels are measured in the lipid-rich tissues. In monitoring exercises all results are therefore calculated on a fat basis in order to get more relevant comparisons and trends.

Most human bio-monitoring investigations of BFRs have studied human milk samples, many have studied human blood serum/plasma and only a few have studied adipose tissue or hair samples.

6.3.1 Blood serum and adipose tissue

PBDE - In human adipose tissue and liver samples reported in the literature from different European countries, BDE-153 was the most predominant congener (1.0-2.5 ng/g fat) followed by BDE-47. In placental tissue, serum or blood BDE-47 was the predominant congener (0.16-7.0 ng/g fat) followed by BDE-153 and BDE-99. (EFSA, 2011b).

When analysed, BDE-209 was reported to be the most predominant congener in serum or blood samples (0.77-37 ng/g fat) (EFSA, 2011b).

HBCDD - According to EFSA (2011a), the median concentration of total HBCDD in serum and adipose tissue samples was in general not higher than 3 ng/g fat, except when considering occupational exposure where the levels were reported to be up to 101 ng/g fat. α -HBCDD was found to be the dominating isomer in serum and adipose tissue samples, while β - and γ -HBCDD were not detected or contributed only 1-3 % to the total. In contrast, in serum samples from workers exposed to HBCDDs, the contribution of γ -HBCDD was reported to be much higher (39 %) pointing to direct exposure to the technical HBCDD where γ -HBCDD is predominant (about 78 %). Therefore, higher levels of γ -HBCDD than α -HBCDD might indicate recent exposure to technical HBCDD.

Lignell *et al.* (2011) studied the temporal trends of HBCDD in blood serum from mothers pregnant for the first time from Uppsala (Sweden) between 1996 and 2010. The concentrations of HBCDD were below the LOQ in more than 70 % of the samples. The mean concentration in the period 1996-2010 was 0.28 ng/g fat. After linear regression analysis, the authors reported that the HBCDD level in serum decreased significantly during the study period. This decrease reported by the authors is in contrast to a steady increase observed in pooled human milk samples from Stockholm.

TBBPA – EFSA (2011c) concludes that the studies in the literature reporting levels of TBBPA in human samples other than human milk are limited and no studies have been found reporting levels of TBBPA derivatives. The levels found varies among the studies which may be attributed to different analytical methods. In Norway, Thomsen *et al.* (2007 as cited by EFSA, 2011c) analysed TBBPA in archived pooled serum samples from Norway sampled from different county hospitals yearly since 1975. TBBPA was found in all serum pools from 1982 to 2003, as well as methylated TBBPA. The concentration for the sum of both TBBPA and methylated TBBPA ranged from <LOQ (0.1 ng/g fat) to 2.0 ng/g fat. In France, Cariou *et al.* (2008 as cited by EFSA, 2011c) analysed the concentra-

tion of TBBPA in maternal and cord serum, and adipose tissue sampled from volunteers during caesarean deliveries, and human milk. TBBPA was not detected in any of the adipose tissue samples analysed (n=44). In maternal serum, TBBPA was quantified in 29 out of the 91 samples analysed with a median (min-max) concentration of 16.14 (0.23-93.22) ng/g fat, while in cord serum it was quantified in 27 out of the 90 samples analysed with a median concentration of 54.76 (2.09-649.45) ng/g fat. No significant correlation could be established by the authors between the concentrations of TBBPA in maternal and cord serum. No relation was found between the age of the volunteer women and the concentration in maternal serum.

DBDPE – DBDPE could not be identified above the LOD (1.03 ng/g fat) in 5 human plasma samples from Sweden (Karlsson *et al.*, 2007 as cited by EFSA, 2012a).

Other BFRs - BTBPE was analysed in human plasma samples (n = 5) from Sweden, but was not identified in any of these samples above the LOD of 1.31 ng/g fat (Karlsson *et al.*, 2007 as cited by EFSA, 2012a).

6.3.2 Human milk

PBDEs – The average concentrations of the predominant PBDE congeners in human milk are rather comparable across various European countries (EFSA, 2011b). BDE-47 was the most predominant congener with mean concentrations across countries of 0.14-3.0 ng/g fat. The mean concentration of BDE-99 across European countries was <0.03-1.1 ng/g fat, and of BDE-153 it was 0.10-2.4 ng/g fat. However, the individual contamination may differ considerably as indicated by the wide concentration ranges for several PBDEs from various countries. BDE-209 was analysed in seven studies with mean concentrations between 0.21 and 2.8 ng/g fat (EFSA, 2011b). In a Danish-Finnish study on breast milk, the sum of PBDEs in breast milk did not differ between Denmark and Finland (median, 3.52 vs. 3.44 ng/g fat), but significant differences in some individual congeners were found (Main. *et al.*, 2007).

The PBDE level in Swedish human milk almost doubled every four years for the period 1972 to 1997 and peaked around at the end of 1990s. This trend makes it clear that the peak of contamination occurred at the end of the 1990s (EFSA, 2011b). According to data from the Swedish monitoring program, the sum of the eight PBDE congeners showed mean levels of 2.7, 2.0 and 2.5 ng/g fat from the years 2003, 2004 and 2007, respectively. A comparable trend was found by Fångström *et al.* (2008 as cited by EFSA, 2011b) who analysed pooled human milk samples from Sweden between 1980 and 2004. The levels for BDE-47 as the predominant congener continuously increased from 0.14 to 2.24 ng/g fat between 1980 and 1995 and then decreased to 0.92 ng/g fat in 2004. For BDE-153 the concentrations increased between 1980 and 2001 from 0.05 ng/g fat to 1.35 ng/g fat and then decreased to 0.90 ng/g fat in 2004 (Fångström *et al.*, 2008). While the median concentration of BDE-209 was found to be 1.1 ng/g fat in 2007, this congener was only detected in 6 out of the 29 individual human milk samples collected in 2008-2009/10 and then in the range of 0.12-6.48 ng/g fat (Bergman *et al.*, 2010 as cited by EFSA, 2011b).

HBCDD - More and more studies of HBCDD in human milk are published. Most of the data is not stereospecific but reports only total HBCDD. EFSA (2011a) reports that for the total HBCDD concentration the concentration in Europe ranged from 0.13 to 13 ng/g fat. Where reported, the mean and median levels were below 2 ng/g fat. Extremely high levels (mean: 47 ng/g fat) were measured in Spain. The data from Spain were not included in EFSA's assessment as the data indicated a specific contamination source.

The best trend study is from Sweden, addressing pooled samples from Stockholm showing annual fluctuations but with a clear upward trend for the period 1980-2010 as shown in the figure below. A similar increasing trend of HBCDD in human milk has been demonstrated in Japan (as discussed in Vorkamp *et al.*, 2012).

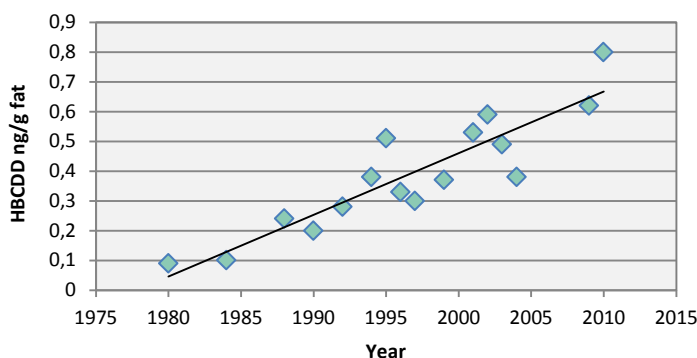


FIGURE 4
TIME TREND OF HBCDD IN HUMAN MILK FROM STOCKHOLM, SWEDEN, 1980-2010 (EFSA, 2011A BASED ON DATA FROM FÄNGSTRÖM ET AL., 2008 AND BERGMAN ET AL., 2010)

The levels of HBCDD in human milk from Sweden are rather low compared with average levels more ten times higher in single samples analysed, for instance, in Canada, Australia and China.

In samples from 12 provinces of China in 2007, the average concentration of HBCDD (mainly α -HBCDD) was about 1 ng/g fat with a maximum of 2.7 ng/g fat (Shi *et al.*, 2009).

TBBPA - Data on TBBPA in human milk are scarce and limited to three studies from Europe and one study from China (EFSA, 2011c). The TBBPA concentrations range from <0.04 to 37.34 ng/g fat with average levels between 0.06 and 4.11 ng/g fat (EFSA, 2011c). In a Norwegian study, TBBPA was detected for the first time in samples from 1986 and increased slightly up to 0.65 ng/g lw in 1999 (Thomsen *et al.*, 2002 as cited by Vorkamp, 2012).

Other BFRs - For all other BFRs there is a lack of basic information on their occurrence in human samples, including human milk. Fuji *et al.* (2012, as cited by EFSA, 2012a) analysed HBB in human milk samples (n = 40) from mothers living in Japan. HBB was detected in all samples but one, with a median and mean concentration of 0.32 and 0.53 ng/g fat, respectively (middle bound approach, LOQ 0.05 ng/g fat).

6.3.3 Hair

The identified reviews do not summarise studies in BFRs in hair and no European studies of BFRs in hair has been identified.

Several studies of BFRs in hair have been undertaken in China and other Asian countries.

Zheng *et al.* (2011) analysed BFR levels and sources of brominated flame retardants in human hair from urban, e-waste, and rural areas in South China. BFR concentrations in hair from occupational e-waste recycling workers were higher than those from non-occupationally exposed residents in other sampling areas. PBDEs and DBDPE were the two major BFRs in hair samples. The PBDE congener profiles in hair from the e-waste area were different from those from urban and rural areas, with relatively higher contributions of lower brominated congeners. DBDPE, instead of BDE-209, was the major BFR in non-e-waste recycling areas. Significant correlations were found between hair level and dust level for DBDPE and BTBPE but not for PBDEs. The different PBDE congener profiles between dust and hair may suggest that exogenous exposure to the PBDE adsorbed on dust is not a major source of hair PBDEs.

Detection of polybrominated biphenyl ethers (PBDEs) in newborn and children's hair have been evaluated as a tool for determining *in utero* exposure. PBDEs were detected in all of the newborn and child hair in a study from Canada (Alaksa *et al.*, 2011). The Σ PBDE ranged from 0.038 to 1.01 pg/mg in newborn hair and from 0.208 to 2.695 ng/mg in child hair. The most abundant PBDE in newborn hair was BDE-153, while in child hair the variable PBDEs were BDE-47 and BDE-99. The highest molecular weight congener BDE-209 was detected in 10/24 paediatric hair samples.

6.4 Human health impact

PBDEs – Main *et al.* (2007) reported significantly higher levels of PBDEs (measured as a sum of BDE-47, -153, -99, -100, -28, -66, and -154) in breast milk of mothers to newborn boys with cryptorchidism (undescended testicles) than in breast milk of the mothers of boys without cryptorchidism (Main *et al.*, 2007), in a prospective Danish-Finnish study.

A large number of epidemiological studies on the effects of PBDEs on thyroid and endocrine disruption, cancer, diabetes and metabolic syndrome, effects on fertility and offspring and neurodevelopment effects have been reviewed by EFSA (2011b). The data were summarized as follows by the CONTAM panel (EFSA, 2011b): Most epidemiological studies suggested an association between PBDEs and (sub)clinical hyperthyroidism (overactive thyroid), and with neuropsychological functioning (motor, cognitive and behavioural performance, and mental and physical development in children). The CONTAM Panel noted, however, that the observed effects on thyroid hormone levels were not always consistent, and that exposure to other halogenated contaminants could have confounded the outcome of these studies.

In three human studies, effects on neuropsychological functioning were associated with exposure to PBDEs, but these results were heterogeneous. Although one study controlled for PCBs, DDT, DDE and HCB, in general, exposure to other halogenated contaminants could have interfered with the outcome of these studies. (EFSA, 2011b)

There was no association between high fish consumption and breast cancer and levels of PBDEs in breast cancer tissues. No associations were found in case-control studies of testicular and pancreatic cancer. However, the small sample size and confounding by other contaminants and/or lifestyle factors limit the interpretation of these studies. (EFSA, 2011b)

Some studies link diabetes and metabolic syndrome prevalence to serum concentrations of POPs. One cross-sectional study suggests associations of BDE-153 exposure with diabetes and metabolic syndrome. Another study found a non-significant association of PBDEs with diabetes only in subjects with hypothyroid disease. The CONTAM Panel noted that cross-sectional studies may not be the most appropriate study design to investigate the relationship between diabetes and exposure to PBDEs, as they cannot rule out reverse causation in which diabetes may enhance POPs accumulation or inhibit their clearance. (EFSA, 2011b)

Recent studies have reported associations of single PBDE congeners and/or the sum of PBDEs in serum and/or milk with longer time to pregnancy, longer length of average menstrual cycle, shorter pre-pregnancy menstrual cycle length, and delay of age when menstruation periods begin regularly. Impaired birth outcome, particularly for decreased birth weight and height, chest circumference, and BMI of infants were reported in offspring. Inverse correlations were observed between the serum BDE-153 concentration and sperm concentration and testis size. In one study, semen mobility was negatively related to BDE-47 and BDE-100 and to the sum of BDE-47, -99, -100 and -153. PBDE levels in human milk, but not in placenta, showed an association with congenital cryptorchidism. (EFSA, 2011b)

The observed effects on thyroid hormone levels were not always consistent, and exposure to other halogenated contaminants could have confounded the outcome of these studies. (EFSA, 2011b)

EFSA summarises the conclusions reached by the CONTAM Panel's scientific opinions as follows (EFSA, 2012c):

"Eight PBDEs were considered of primary interest and relevant toxicity data were available for four of them (BDE-47, -99, -153 and -209). The risk assessment was limited to these four, for which the margin of exposure (MOE) approach was used. For BDE-99, the MOE indicates a po-

tential health concern with respect to the current dietary exposure. This was notable for young children (aged 1-3 years old), although the presence of one food sample in the category 'Food for infants and small children' with a high concentration of BDE-99 could have led to overestimation of the exposure for this specific age group. For BDE-47, -153 and -209 the current dietary exposure is unlikely to raise a health concern. As numerous products containing PBDEs are still in use, the surveillance of PBDEs should continue."

Being endocrine disruptors, some BFRs can affect neurodevelopment and have been associated with reproductive impairment, but according to Vorkamp (2012), epidemiological evidence and toxicokinetic information are still sparse.

A new report "State of the Science of endocrine disrupting chemicals" from UNEP and WHO (Bergman *et al.*, 2012b) discusses the evidence of links between exposure to PBDEs and endocrine disruption. According to the assessment, it has become apparent that non-descended testes in young boys are linked with exposure to PBDEs and that PBBs are linked to an early age at menarche and pubic hair development.

HBCDD - There are a few available epidemiological studies of HBCDD exposure. No associations were found between bone mineral density or biochemical markers of bone metabolism and HBCDDs in blood serum from an elderly population of Swedish fishermen and their wives (Weiss *et al.*, 2006). In a Norwegian study, no association between HBCDDs in human milk and neonatal thyroid-stimulating hormone (TSH) was observed (Eggesbø *et al.*, 2011).

Exposure of males to HBCDD in house dust was associated with decreased sex hormone binding globulin (SHBG) and increased free androgen index (FAI) (Johnson *et al.*, 2013). The latter association is illustrated in Figure 5, adapted from Johnson *et al.* (2013).

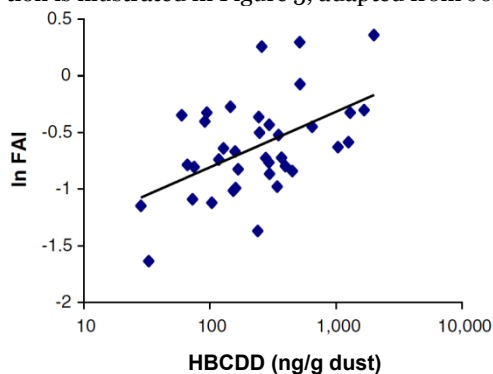


FIGURE 5
SCATTERPLOT OF HBCDD IN HOUSE DUST AND LN-TRANSFORMED FREE ANDROGEN INDEX (FAI) (JOHNSON *ET AL.*, 2013).

EFSA summarises the conclusions reached by the CONTAM Panel's scientific opinions as follows (EFSA, 2012c):

"Current dietary exposure to HBCDDs in the EU does not raise a health concern. Furthermore, additional exposure, particularly of young children, to HBCDDs from house dust is unlikely to raise a health concern."

TBBPA - No human health impacts of concern have been identified for TBBPA (ECB, 2006).

EFSA summarises the conclusions reached by the CONTAM Panel's scientific opinions as follows (EFSA, 2012c): *"Current dietary exposure to TBBPA in the EU does not raise a health concern. No*

occurrence data for TBBPA derivatives were submitted to EFSA and no information on their toxicity was identified. Therefore a risk assessment on TBBPA derivatives was not possible.

DBDPE and EBTEBPI - EFSA summarises the conclusions reached by the CONTAM Panel's scientific opinions as follows (EFSA, 2012c): "*Based on the limited experimental data on environmental behaviour, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and hexabromobenzene (HBB) were identified as compounds that could raise a concern as reports indicate that they can accumulate in the body over time.*"

No data on health impacts of EBTEBPI have been identified.

Other BFRs - EFSA summarises the conclusions reached by the CONTAM Panel's scientific opinions as follows (EFSA, 2012c):

"Brominated phenols and their derivatives (other than TBBPA or its derivatives) – due to the lack of occurrence data and toxicity studies, the risk assessment focused on 2,4,6-tribromophenol (2,4,6-TBP) only. It is unlikely that current dietary exposure to 2,4,6-TBP in the EU would raise a health concern. Also exposure of infants to 2,4,6-TBP via breast feeding is unlikely to raise a health concern. Due to lack of data a risk assessment of the other brominated phenols or their derivatives was not possible."

"Emerging and Novel BFRs – this opinion looks at lesser-known BFRs not covered in the five other scientific opinions. Whereas 'emerging' BFRs have been identified in materials and/or goods and in wildlife, food or humans, 'novel' BFRs have been identified only in materials and/or goods but not in wildlife, food or humans. Limited and widely varying data on 17 emerging and 10 novel BFRs were collected. Due to the lack of data and limited information on occurrence, exposure and toxicity for all these BFRs, a risk characterisation was not possible. Using available information and a modeling exercise, the CONTAM Panel identified some emerging and novel BFRs that could be a potential health concern and should be considered first for future investigations. There is convincing evidence (including more extensive toxicity data) that the emerging BFR tris(2,3-dibromopropyl) phosphate (TDBPP) and the novel BFR 2,2-Bis(bromomethyl)-1,3-propanediol (DBNPG) are genotoxic and carcinogenic, warranting further surveillance of their occurrence in the environment and in food. Based on the limited experimental data on environmental behaviour, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and hexabromobenzene (HBB) were identified as compounds that could raise a concern as reports indicate that they can accumulate in the body over time."

Assessment of the risk of flame retardants to consumers

In a study for the European Commission, Health and Consumers DG, Arcadis (2011) have performed an assessment of the risk to consumers from flame retardants in consumer products. A consumer risk assessment using a REACH first tier approach was undertaken for 24 flame retardants, including 5 BFRs. Furthermore, 20 of the flame retardants were selected for an assessment of the risk to the environment; however, due to the lack of data about the use volume, even a first tier risk assessment could not be carried out.

The consumer risk assessment was based on an assessment of human health effects and an assessment of the exposure of consumers. The exposure to consumers was estimated as direct dermal and inhalation exposure to the substances during the consumer use of the articles, and the oral exposure which mainly consisted of exposure to the substances in food and dust. The flame retardants, based on the risk assessment, were grouped into the following classes (only grouping of the BFRs is shown here):

- Group: "no need for immediate risk management, based on the approach of this study"

- DPDPE
- TBBPA
- Group: "no need for immediate risk management, based on the approach of this study, but with concerns"
 - DecaBDE
 - HBCDD
- Group: "inconclusive"
 - TBBPA-BDBPE
- Group: "risk"
 - None of the BFRs (only FR in this groups was isodecyl diphenyl phosphate).

6.5 Summary and conclusions

Human hazards

The discussed brominated flame retardants cover a broad spectrum of chemicals with both related and dissimilar properties. It is therefore difficult to generalize.

Brominated flame retardants (BFRs) such as PBDEs, PBBPA, HBCDD and others do have bromine content in common, and the carbon-bromine bond is stronger than the carbon-hydrogen bond, which makes these substances more thermodynamically stable and more resistant to biodegradation. Generally, the persistence increases with increasing numbers of bromine atoms in a molecule.

These molecules are insoluble in water and hydrophobic, but are rather lipophilic, accumulating in fats. Since the degradation of these chemicals is slower than the fats they are contained in, levels in body fats will increase over time, age and size of the organism and will biomagnify in food chains.

Some BFRs are POPs, which accumulate mainly in adipose tissues in humans; at steady-state (constant in- and output), the measured concentrations of these chemicals in the various body compartments depends on the fat content. An exception is the brain and foetus, for which there are partially effective barriers diminishing the transfer and the levels, especially for high molecular congeners. Measurements of concentrations of BFRs in blood, adipose tissue and breast milk calculated on a fat basis are used in biological monitoring. Among the HBCDD isomers, the α -isomer is the most persistent and bioaccumulative in human adipose tissues, and has highest transfer to the foetus.

The absorption of these BFRs after oral intake of the main sources, foods and indoor dust, is extensive and mostly >80%. An exception is decaBDE, having many bromine atoms and a high molecular weight and an absorption in rats of about 25%. Although BFRs are highly stable chemicals, in the body some minor substance-specific metabolic degradation processes by debromination and hydroxylation occur.

The body half-lives in humans are often several weeks or months. Hydroxylated metabolites are conjugated and excreted as glucuronide in the bile/faeces. Elimination via the urine is insignificant. The major excretion pathway in females is lactation because of the relatively high fat content of breast milk.

All BFRs have low acute toxicity and no specific irritation or skin sensitization. After long-term exposure, induction of liver enzymes is the most significant effect. Some BFRs have the potential to disrupt endocrine systems at multiple target sites. While the thyroid hormone system appears to be the main target, experiencing the most significant effects of these compounds, recent studies demonstrated *in vivo* effects on both the estrogen- and androgen-mediated processes as well.

Developmental neurotoxic effects of some BFRs have also been reported. These BFRs may decrease levels of total and free T4 following developmental exposure. Thyroid hormones are known to play an important role in brain development and hypothyroidism has been associated with a large number of neuroanatomical and behavioural effects.

A large study from Belgium found neurobehavioral effects associated with PBDE congeners BDE-47, BDE-99, BDE-100, BDE-153, and BDE-209 but not with HBCDD and TBBPA in humans. Consistent with experimental animal data, PBDE exposure was associated with changes in the motor function and the serum levels of the thyroid hormones.

High PBDE levels in breast milk have been associated with effects on newborns regarding lower weight and smaller size, cryptorchidism and delayed mental development. HBCDD in breast milk was associated with decreased sex hormone binding globulin (SHBG) and increased free androgen index (FAI).

BFRs do not appear to be genotoxic or to present a carcinogenic risk to humans.

Some emerging BFRs have not been studied in much detail, but appear to have similar effects. One of these is HBB, which may be more persistent and toxic and therefore hazardous than the PBDEs etc. Since the toxicological mechanisms seem to be related, mixtures of BFRs may have additive and synergistic effects.

Human exposure and health impact

Human exposure to BFRs and potential health impact has recently been reviewed by EFSA Panel on Contaminants in the Food Chain (CONTAM) in six assessment reports.

According to the EFSA reviews, for the general population, food is the major source of exposure to BFRs. The food categories that contribute most to the exposure to decaBDE are animal and vegetable fats and oils, and milk and dairy products, with relative contributions of 43.5 % and 41.7 %, respectively. The contribution of "Fish meat and products" to the median intake of HBCDDs across European dietary surveys vary from 83 to 88.2 % for the different age classes.

The CONTAM panel concludes that the current dietary exposure to BDE-47, -153 and -209 (decaBDE), HBCDD, TBBPA and TBP is unlikely to raise a health concern, whereas the available data indicate a potential health concern for dietary exposure of young children (1-3 years) to BDE-99.

A positive correlation between the levels of PBDEs in house dust and various biological matrices indicated that house dust was a significant source of PBDE exposure in Denmark. EFSA's CONTAM panel concluded that the available exposure estimates indicate that house and car dust can be important routes of exposure especially for children to decaBDE, but also noted that exposure from dust is of no health concern. According to the COMTAM panel, the available studies indicate that the daily non-dietary exposure, mainly through dust in homes, offices, schools, cars and public environment can substantially contribute, and in some cases even dominate the total human exposure to HBCDDs, especially for toddlers and children. Taking into account the uncertainties in the dust exposure estimates, and considering the use of UB dietary intake estimates, the CONTAM Panel, however, concluded that the available information indicates that it is unlikely that additional exposure to HBCDDs and TBBPA from dust raises a health concern.

Several studies have shown the presence of BFRs in umbilical cord blood and have documented that placental transfer does take place and that the foetus is exposed to BFRs.

A large number of epidemiological studies on the effects of PBDEs on thyroid and endocrine disruption, cancer, diabetes and metabolic syndrome, effects on fertility and offspring and neurodevelop-

ment effects have been reviewed by EFSA (2011b). According to the CONTAM panel, most epidemiological studies suggested an association between PBDEs and (sub)clinical hyperthyroidism (overactive thyroid), and with neuropsychological functioning (motor, cognitive and behavioural performance, and mental and physical development in children). The CONTAM Panel noted, however, that the observed effects on thyroid hormone levels were not always consistent, and that exposure to other halogenated contaminants could have confounded the outcome of these studies. In three human studies, effects on neuropsychological functioning were associated with exposure to PBDEs, but these results were heterogeneous. Recent studies have reported associations of single PBDE congeners and/or the sum of PBDEs in serum and/or milk with longer time to pregnancy, longer length of average menstrual cycle, shorter pre-pregnancy menstrual cycle length and delay of age when menstruation periods begin regularly.

There are a few available epidemiological studies of HBCDD exposure. Exposure of males to HBCDD in house dust was associated with decreased sex hormone binding globulin (SHBG) and increased free androgen index (FAI).

Due to lack of data, a risk assessment of the TBBPA derivatives, brominated phenols or their derivatives (except for TBB), emerging and novel BFRs was not possible. Using available information and a modelling exercise, EFSA's CONTAM Panel identified some emerging and novel BFRs that could be of potential health concern and should be considered as priorities for future investigations. There is convincing evidence (including more extensive toxicity data) that TDBPP and DBNPG are genotoxic and carcinogenic, warranting further surveillance of their occurrence in the environment and in food. Based on the limited experimental data on environmental behaviour, BTBPE and HBB were identified as compounds that could raise a concern, as reports indicate that they can accumulate in the body over time.

Biomonitoring and trends

The PBDE level in Swedish human milk almost doubled every four years for the period 1972-1997 and peaked around at the end of the 1990s. Pooled human milk samples from Stockholm (Sweden) showed a clear upward trend for the period 1980-2010, whereas the HBCDD level in blood serum from mothers pregnant for the first time from Uppsala (Sweden) decreased during the period 1996-2010. An increasing trend of HBCDD in human milk has also been demonstrated in Japan. In a Norwegian study, TBBPA was detected for the first time in samples from 1986 and increased slightly up to 1999. For all other BFRs, there is a lack of basic information on their occurrence in human samples, including human milk.

7. Information on alternatives

7.1 Identification of possible alternatives

A large number of studies on alternatives to BFRs have been undertaken, from the early 1990s to present. The first studies on alternatives to brominated and other halogenated flame retardants in EE equipment was published by the German Electrotechnical and Electronic Association (ZVEI) in 1992 and by the OECD in 1994 (as cited in Lassen *et al.*, 1999). The Danish survey of BFRs from 1999 included an evaluation of alternatives as well. For many of the studies it has been a major constraint that environmental and health data for alternatives are scarce.

There are ways that adequate fire performance can be achieved which is relevant when considering alternative solutions. These include (UK, 2012):

- Use of alternative chemical flame retardants
- Use of intrinsically or inherently flame retardant materials
- Product design – achieved by the selection and use of materials alongside other components such as physical and thermal barriers, coatings and layer technologies, heat sinks, etc. How components are physically placed relative to one another can achieve enhanced fire performance in relation to the expected types of ignition source and flame and fire exposure.

All of these approaches are potential alternatives to the use of BFRs. The solutions that are adopted for individual articles are likely to be dependent on what the article is, how and where it is used, and the materials that have been used to manufacture the article.

When replacing a chemical flame retardant with another chemical flame retardant it may be necessary to simultaneously replace the base polymer(s) in order to obtain the desired properties of the final material.

The replacement of a BFR/polymer system by another chemical flame retardant system needs to take into account (UK, 2012):

- The cost of the substitute or alternative (per unit cost and required loadings to achieve the required fire performance);
- The compatibility of the substitute or alternative with the material it is being used to treat;
- The complexity of processes (for instance, the introduction of an alternative may require changes in the processing equipment used by a company);
- The environmental and human health effects of the substitute or alternative (including the energy requirements for production and processing);
- The capability of the substitute or alternative to meet the required safety standards;
- The fire behaviour of the substitute or alternative, including its mechanism of flame retardant action and the composition and quantity of smoke and fumes generated during a fire, and
- The availability of sufficient supplies of alternatives.

In the following, the most recent alternatives assessments for decaBDE, HBCDD and TBBPA are reviewed. The assessments typically include information on both brominated and non-brominated alternatives; the assessments thus also include information of possible non-brominated alternatives to other BFRs than the three substances to some extent, i.e. the assessment of alternatives to decaBDE also includes a comparison of non-halogenated alternatives and DBDPE and EBTEBPE.

Alternative assessments for PBBs, pentaBDE and octaBDE are not reviewed as these substances have already been replaced by other flame retardants.

Furthermore, a short review of surveys of articles manufactured without BFRs is provided. These surveys do often not provide information on the alternatives used, but demonstrate that articles made without BFRs are available in the market, thus illustrating that cost-efficient solutions are available.

For the reviews, data have been sought in the public literature. Furthermore, a request has been addressed to the contact point of a recently finalised European Commission-funded project, ENFIRO, which has undertaken case studies on substitution options for specific BFRs. The project, with €3.1 million of EU funding, should deliver a comprehensive dataset on viability of production and application, environmental safety, as well as a life cycle assessment of the alternative flame retardants (FRs). The project outcome is briefly discussed by Leonards *et al.* (2013), who report that ENFIRO showed that viable alternative flame retardants are available. Very recently, a review of persistence, bioaccumulation, and toxicity of non-halogenated FRs, one of the outcomes of the ENFIRO project, was published (Waaaijers *et al.*, 2013). Other results of the project are, however, not yet publicly available.

7.1.1 DecaBDE Chemical alternatives

A technical review of alternatives to decaBDE in electrical and electronic equipment (EEE) was undertaken by the Danish EPA in 2006 (Lassen *et al.*, 2007), supplemented by a health and environmental assessment for some of the alternatives (Stuer-Lauridsen *et al.*, 2007). The studies demonstrated that alternatives were available for all applications of decaBDE in EEE and none of the six substances selected for a health and environmental assessment appear to have more negative impacts on the environmental, health and/or consumer safety than decaBDE. For the purpose of the studies, it was sufficient to conclude that the alternatives did not have more negative impact than decaBDE. Due to lack of data, it was difficult to evaluate to what extent the alternatives were “better”.

More recently, comprehensive assessments were undertaken by the US EPA (2012), Defra (Stevens *et al.*, 2010) and the Illinois Environmental Protection Agency (IEPA, 2007); furthermore, the available assessments have been reviewed in the Annex XV SVHC dossier for decaBDE (UK, 2012). The Defra study “Fire Retardant Technologies: safe products with optimised environmental hazard and risk performance” (Stevens *et al.*, 2010) more broadly addresses alternatives to problematic flame retardants and offers, in particular, a comprehensive assessment of fire retardants technologies for textiles and furniture, which is described later in this section.

The Annex XV dossier for decaBDE states that stakeholders expect that substitution with other brominated flame retardants will have the least impact on the technical properties of plastics/polymers and require the fewest modifications to formulations and adaptations to processing. Greater modifications and adaptations will be required to move to halogen free systems e.g. aluminium trihydrate and ammonium polyphosphate based systems. Non-halogenated systems have an advantage over halogenated systems in that they have a lower potential to generate toxic combustion products during a fire. However, much higher loadings, up to 60%, may be required to meet fire performance standards; this factor has a negative impact on processability, reduces the strength of the plastic/polymer and increases weight (UK, 2012).

US EPA’s Design for the Environment (DfE) Program has initiated a multi-stakeholder partnership alternatives assessment: “Flame Retardant Alternatives for Decabromodiphenyl Ether (decaBDE)”. A draft assessment report was published in 2012 (US EPA, 2012). DecaBDE is a flame retardant used in a variety of applications, including textiles, plastics, wiring insulation (restricted in the EU),

and building and construction materials. The report is a draft for public comment and the front page of the report states ****Do not cite or quote****. The presented data may be subject to some mistakes and errors which will be corrected later in the process, and the US EPA does not take any responsibility for the correctness of the data. The data in the report should therefore be interpreted with caution and evaluations are indicative only. However, the report includes an environmental and health screening of alternatives not found elsewhere. [intern note til udkastet – disse rapporter udkommer ofte aldrig i endelige versioner]

The summary of human health effects, aquatic toxicity and environmental fate of the evaluated flame retardants is shown in Table 44. The assessment did not include TBBPA because it had been evaluated in another DfE project (US EPA, 2008).

For most of substances, empirical data were only available for a limited number of endpoints and for most endpoints, values were assigned using predictive models and/or professional judgment (shown in black italics).

The summary data does not include some of the parameters which may be relevant when comparing the environmental and health risk related to the use of the different flame retardants, namely:

- Formation of hazardous degradation products, and
- Formation of hazardous substances (mainly brominated dioxins and furans) by fire, uncontrolled combustion or incineration).

The formation of hazardous degradation products of decaBDE by debromination is discussed in the report, but in general, limited information is available on hazardous degradation products of other of the evaluated flame retardants, and the flame retardants are not compared using this parameter.

The report lists known uses of the different flame retardants by polymer and end-use applications, but the study does not include a full assessment of the technical and economic feasibility of the substitution.

As concerns the brominated alternatives, Appendix 5 (Table A5-2) provides some information of the application spectra of the substances from one company, which demonstrates that both non-polymeric and polymeric BFRs are available for all the same applications as decaBDE.

As mentioned before, DBDPE and EBTEBPI have similar application spectra as decaBDE and, in addition, a number of other non-polymeric BFRs can be used for specific polymers; for example, TTBP-TAZ is suitable as an alternative to decaBDE in HIPS. Both DBDPE and TTBP-TAZ have been registered for a total import and manufacture in the EU in the 1,000-10,000 t/y range while the consumption of EBTEBPI appears to be significantly lower. DBDPE, TTBP-TAZ and EBTEBPI have better scores on developmental and neurological effects, eye irritation and dermal irritation and no lesser scores on any of the evaluated parameters, as shown in Table 44. TTBP-TAZ furthermore scores better than decaBDE and the other two alternatives on carcinogenicity.

A number of polymeric BFRs can be used as alternatives to decaBDE for specific applications, while some are marketed as alternatives for the full range of decaBDE alternatives. The polymeric BFR GreenArmor™, shown in Table 44 which is marketed as a general purpose alternative to decaBDE, was not included in the US EPA assessment because the substance had at the time of the assessment not yet completed the Premanufacture Notice (PMN) process at US EPA. The evaluated polymeric BFRs, of which some are applied for many of the same polymer uses as decaBDE, generally score better than the non-polymeric BFR substances, and are assigned low effects. An exception is the persistence which is very high (as most of the non-polymeric BFRs), but the bioaccumulation potential of the polymeric BFRs is low. From the screening data, it appears unlikely that the poly-

meric BFRs themselves should be CMR or PBT substances. The polymeric BFRs also generally score better than the non-brominated FRs. Based on the evaluated parameters, there is no basis for considering non-brominated alternatives as better alternatives from an environmental/health perspective than the polymeric BFRs.

A number of organic phosphorus or nitrogen FRs (PFRs or NFRs), as well as inorganic FRs, are marketed for a variety of applications. For many of the applications, the non-halogenated FRs have been the flame retardants of choice for many years as they provide the best performance for these applications. As such, they are not manufactured and marketed as alternatives, but may be used as alternatives for specific applications. A few of the substances, e.g. aluminium diethylphosphinate, have been developed more specifically for substitution of regulated BFRs.

For some of the non-brominated flame retardants with promising scores, data on their use spectra are shown in Table 45. For the other flame retardants, please see the details in the US EPA report. From the table it is evident that these flame retardants may be used for most of the traditional applications of decaBDE, but as summarised in the Annex XV report (UK, 2012), higher loadings of up to 60% may be required to meet fire performance standards. This has a negative impact on processability, reduces the strength of the plastic/polymer and increases weight. The Annex XV report provides more detailed information on the technical feasibility of these non-halogenated alternatives.

As mentioned, the screening assessment does not indicate that the non-halogenated alternatives are better from an environmental and health perspective than the polymeric BFRs, of which some by the manufacturers are marketed as "green" alternatives.

According to Leonards *et al.* (2013), the LCA study of the ENFIRO project showed that the waste phase was the most important difference between the selected BFRs and non-halogenated FRs. Especially the formation of brominated dioxins during improper electronics waste treatment had a strong negative impact on the LCA scores. Overall, the life cycle environmental performance of the non-halogenated FR scenario was better than for the BFR scenario. As mentioned, the detailed results of the ENFIRO project are still not available. The formation of toxic products is not addressed in detail in any of the available assessments of alternatives.

The Annex XV report states (UK, 2012), without reference, that non-halogenated systems have an advantage over halogenated systems in that they have a lower potential to generate toxic combustion products during a fire. The "San Antonio Statement on Brominated and Chlorinated Flame Retardants" signed by nearly 150 scientists from 22 countries (Birnbaum and Bergman, 2010) states, with a reference to Weber and Kuch (2003), that uncontrolled burning and dismantling/recycling of electronic and electric waste in developing countries results in contamination and formation of brominated and chlorinated dioxins and furans.

Weber and Kuch (2003) have studied the effect of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. The results are discussed in section 4.1 on waste disposal. According to the results, under insufficient combustion conditions, as are present in e.g. accidental fires and uncontrolled burning as well as gasification/pyrolysis processes, considerable amounts of PBDDs/PBDFs (brominated dioxins and furans) can be formed from BFRs, preferentially via the precursor pathway. The precursor pathway is relevant for BFRs which may act as precursors, in particular the PBDEs and PBBs, but possibly also other BFRs. For BFRs, which are not precursors or may act as bromine donors for the "de novo" synthesis of PBDDs/PBDFs, the significance of the formation of the hazardous substances is less clear. It is not clear to what extent it makes a difference whether or not the polymeric BFRs contain brominated aromatic moieties. Gouteux *et al.* (2013) has recently demonstrated that upon application of thermal stress to samples of polymeric BFRs with brominated aromatic moieties, a drastic

increase of the release of brominated compounds was observed. A variety of substituted alkyl benzenes or phenols with two to six bromine atoms were formed. The paper deals with the potential environmental effects of the formed substances, and does not discuss the significance of the releases of the substances to the potential formation of hazardous PBDDs/PBDFs by combustion of the products.

The available assessments indicate that alternatives with better environmental and health profiles than decaBDE exist, but for many of the substances most endpoint values were assigned using predictive models and/or professional judgment. The screening undertaken by US EPA indicates that for the evaluated environmental and health parameters, polymeric BFRs perform as well as non-halogenated FRs. The main outstanding question in the comparison of the environmental and health performance of the halogenated vs. non-halogenated FRs appears to be the significance of the formation of hazardous degradation products and formation of hazardous substances during fire and uncontrolled burning.

TABLE 44

SCREENING LEVEL HAZARD SUMMARY FOR decaBDE AND BROMINATED FLAME RETARDANT ALTERNATIVES (US EPA, 2012) *1

THIS TABLE ONLY CONTAINS INFORMATION REGARDING THE INHERENT HAZARDS OF FLAME RETARDANT CHEMICALS. EVALUATION OF RISK CONSIDERS BOTH THE HAZARD AND EXPOSURE ASSOCIATED WITH SUBSTANCE INCLUDING COMBUSTION AND DEGRADATION BYPRODUCTS. THE CAVEATS LISTED IN THE LEGEND AND FOOTNOTE SECTIONS MUST BE TAKEN INTO ACCOUNT WHEN INTERPRETING THE HAZARD INFORMATION IN THE TABLE.

Chemical	CAS No	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
DecaBDE and discrete BFR alternatives																
Decabromodiphenyl ether, decaBDE	1163-19-5	L	M	L	L	H	H	M	L		L	L	L	L	VH	H
Bis(hexachlorocyclopentadieno) cyclooctane,	13560-89-9	L	M ^s	M ^s	VL	VL	L	M	L		VL	L	L	L	VH	H
Decabromodiphenyl ethane, DBDPE	84852-53-9	L	M ^s	L	L	VL	H ^s	L	L		VL	VL	L	L	VH	H
Ethylene (bistetra bromophthalimide), EBTEBPI	32588-76-4	L	M ^s	L	L	L	M ^s	L	L		VL	VL	L	L	VH	H
Tetrabromobisphenol A bis (2,3-dibromopropyl) ether, TBBPA-BDBPE	21850-44-2	L	M	M	M	M	L	M	M		L	L	L	L	VH	H
Tris(tribromoneopentyl) phosphate, TTBNPP	19186-97-1	L	M	M	L	H	H	M	H		L	L	L	L	H	M
Tris(tribromophenoxy) triazine, TTBP-TAZ	25713-60-4	L	L	L	L	L	L	L	L		L	VL	L	L	VH	H
Polymeric BFRs																
Brominated epoxy resin end-capped with tribromophenol	135229-48-0	H	L	L	L	L	L	M ^d	L		L	VL	L	L	VH	L
Brominated polyacrylate	59447-57-3	L	L	L	L	L	L	M ^d	L		L	L	L	L	VH	L
Brominated polystyrene	88497-56-7	L	L	L	L	L	L	M ^d	L		L	L	L	L	VH	L
Confidential brominated epoxy polymer #1	Confidential	L	L	L	L	L	L	M ^d	L		L	L	L	L	VH	L
Confidential brominated epoxy polymer #2	Confidential	L	L [♦]	L [♦]	L [♦]	L [♦]	L	M ^{♦d}	L [♦]	♦	L	L	L [♦]	L [♦]	VH	L [♦]
Confidential brominated epoxy polymer Mixture	Confidential	L	L [♦]	L [♦]	L [♦]	L [♦]	L	M ^{♦d}	L [♦]	♦	L	L	L [♦]	L [♦]	VH	L [♦]

Chemical	CAS No	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Confidential brominated epoxy polymer Mixture	Confidential	L	L [♦]	L [♦]	L [♦]	L [♦]	L	M ^{♦d}	L [♦]	♦	L	L	L [♦]	L [♦]	VH	L [♦]
Confidential brominated polymer	Confidential	L	L [✕]	L	L [✕]	L [✕]	L [✕]	L [✕]	L	L	L	VL	L	M ^{T✕}	VH ^T	M ^{T✕}
TBBPA glycidyl ether, TBBPA polymer	68928-70-1	L	L [♦]	L [♦]	L [♦]	L [♦]	L	M ^{♦d}	L	♦	L	L	L [♦]	L [♦]	VH	L [♦]
Organic phosphorus or nitrogen flame retardants (PFRs or NFRs) alternatives																
Substituted amine phosphate mixture	Confidential	H	M	M	M	M	L	M	M	M ^s	M ^s	VH	M	L	H	L
Triphenyl phosphate	115-86-6	L	M	L	L	L	L	M	L		L	VL	VH	VH	L	M
Bisphenol A bis-(diphenyl phosphate), BAPP	181028-79-5	L	L	L	L	L ^s	L	L	L		L	L	L	L	H	H ^o
Melamine cyanurate	37640-57-6	L	M	M	M ^s	M ^s	L	H	L		L	L	L	L	VH	L
Melamine polyphosphate	15541-60-3	L	M	M	L ^s	L	L ^s	M	L		L	VL	L	L	H	L
N-alkoxy hindered amine reaction products	191680-81-6	L	M	L	H	H	L	H	L		L	VL	H	H	H	H [†]
Phosphonate oligomer	68664-06-2	L	M	L ^s	L [‡]	L [‡]	M [†]	L ^{*s}	L ^{*s}		M ^{s†}	M [†]	L [‡]	H [†]	VH	H [†]
Polyphosphonate	68664-06-2	L	✕	L	L	L	L	M ^d	L		L	L	L	L	VH	L
Poly[phosphonate-co-carbonate]	77226-90-5	L	L	L	L	L	L	M ^d	L		L	L	L	L	VH	L
Resorcinol bis-diphenylphosphate	125997-21-9	L	M ^s	L	L	VL	M ^s	M	L		L	VL	VH	H [†]	M	H [†]
Inorganic flame retardant alternatives																
Aluminium diethylphosphinate	225789-38-8	L	L	L	L	M	M	L	L		L	VL	M	M	H ^R	L
Aluminium hydroxide	21645-51-2	L	L	L	L	L	M	L	L		VL	VL	M	M	H ^R	L
Ammonium polyphosphate	68333-79-9	L	L	L	L	L	L	M ^d	L		VL	L	L	L	VH	L
Antimony trioxide ¹	1309-64-4	L	L [*]	L	L	L	L	M	L		L	M	M	M	H ^R	L

Chemical	CAS No	Human Health Effects											Aquatic Toxicity		Environmental Fate	
		Acute toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Magnesium hydroxide	1309-42-8	L	L	L	L	L	L	L	L		M	M	L	L	H^R	L
Red phosphorus	7723-14-0	VH	L	M	L	L	L	L	L		M	H	L	L	H	L
Zinc borate	1332-07-6	L	L	H	M	M	H	L	L		L	L	H	H	H^R	L

*1 The cited report is a draft for public comment and the front page says "**Do not cite or quote**".

*2 Copied from US EPA, 2008

Notes from the cited report:

VL = Very Low hazard **L** = Low hazard **M** = Moderate hazard **H** = High hazard **VH** = Very High hazard –

Endpoints in coloured text (**VL**, **L**, **M**, **H**, and **VH**) were assigned based on empirical data.

Endpoints in black italics (*VL*, *L*, *M*, *H*, and *VH*) were assigned using values from predictive models and/or professional judgment.

§ Based on analogy to experimental data for a structurally similar compound.

d This hazard designation is driven by potential for lung overloading as a result of dust forming operations.

♦ Different formulations of the commercial product are available. One of these many formulations has an average MW of ~1,600 and contains significant amounts of lower MW components. These lower MW components are primarily unchanged starting materials that have hazard potentials different than the polymeric flame retardant, as follows: VERY HIGH- Estimated potential for bioaccumulation; HIGH-Experimental concern for acute aquatic toxicity; HIGH-Estimated potential for chronic aquatic toxicity; MODERATE Experimental concern for developmental; and MODERATE-Estimated potential for carcinogenicity, genotoxicity, repeated dose, reproductive, and skin and respiratory sensitization toxicity

✕ This alternative may contain impurities. These impurities have hazard designations that differ from the flame retardant alternative, Confidential Brominated Polymer, as follows, based on experimental data: HIGH for human health, HIGH for aquatic toxicity, VERY HIGH for bioaccumulation, and VERY HIGH for persistence

T This chemical is subject to testing in an EPA consent order.

‡ The highest hazard designation of any of the oligomers with MW <1,000. ○ The highest hazard designation of a representative component of the oligomeric mixture with MWs <1,000.

¥ Phosphonate Oligomer, with a MW range of 1,000 to 5,000, may contain significant amounts of an impurity, depending on the final product preparation. This impurity has hazard designations that differ from the polymeric flame retardant, as follows: MODERATE-Experimental concern for repeated dose, skin sensitization and eye irritation; and HIGH-Experimental concern for reproductive, developmental, acute aquatic toxicity.

R Recalcitrant: Substance is comprised of metallic species that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions.

* Ongoing studies may result in a change in this endpoint

TABLE 45
 USE OF DECAHDE AND SELECTED NON-BROMINATED FLAME RETARDANTS BY POLYMER AND END-USE APPLICATION (BASED ON US EPA, 2012) *1

Polymer applications	Electronics	Wire and cable	Public buildings	Construction materials	Automotive	Aviation	Storage and distribution products	Textiles	Waterborne emulsions & coatings
DecaBDE, CAS No 1163-19-5									
Chlorinated polyethylene (CPE)	✓	✓							
Elastomers	✓	✓	✓	✓	✓	✓		✓	✓
Emulsions									✓
Engineering thermoplastic (PBT,PET; PA;PC)	✓				✓				
High-impact polystyrene (HIPS)	✓								
Polyethylene (PE)	✓	✓	✓	✓	✓	✓	✓		
Polypropylene (PP)	✓	✓	✓		✓		✓		
Thermosets	✓			✓					
Ammonium polyphosphate, CAS No 68333-79-9; 14728-39-3									
Elastomers		✓							
Emulsions								✓	✓
Polyethylene (PE)		✓	✓	✓	✓		✓		
Polypropylene (PP)	✓	✓	✓	✓			✓		
Thermosets			✓	✓		✓	✓		
Aluminium diethylphosphinate CAS No 225789-38-8									
Elastomers	✓	✓			✓	✓			
Epoxy resins	✓				✓	✓			
Polyamide (PA)	✓				✓	✓		✓	
Polybutylene terephthalate (PBT)	✓				✓	✓			
Polyethylene terephthalate (PET)	✓				✓	✓		✓	
Thermoplastic polyurethane (TPU)		✓							
Aluminium hydroxide, CAS 21645-51-2									
Elastomers		✓	✓	✓	✓	✓			
Emulsions								✓	
Ethylene vinyl acetate (EVA)		✓	✓	✓	✓	✓			
Polyethylene (PE)		✓	✓	✓	✓	✓			

Polymer applications	Electronics	Wire and cable	Public buildings	Construction materials	Automotive	Aviation	Storage and distribution products	Textiles	Waterborne emulsions & coatings
Thermosets	✓		✓	✓	✓	✓			
Magnesium hydroxide, CAS 1309-42-8									
Elastomers		✓	✓	✓	✓	✓			
Ethylene vinyl acetate (EVA)		✓	✓	✓	✓	✓			
Polyamide (PA)	✓								
Polyethylene (PE)		✓	✓	✓	✓	✓	✓		
Polypropylene (PP)		✓	✓	✓	✓	✓			✓
Polyphosphonate, CAS 68664-06-2									
Elastomers	✓	✓	✓	✓	✓	✓			
Engineering thermoplastic	✓		✓	✓	✓	✓		✓	

*1 The cited report is a draft for public comment and the front page says **Do not cite or quote**.

ENFIRO project assessment - Very recently a review of persistence, bioaccumulation, and toxicity of non-halogenated FRs was published, as one of the outcomes of the ENFIRO project (Waijers *et al.*, 2013). The review is based on an inventory of the available data that exists (up to September 2011) on the physico-chemical properties, production volumes, persistence, bioaccumulation, and toxicity (PBT) of a selection of non-halogenated FRs that are potential replacements for BFRs in polymers.

An overview of the classification of the selected compounds, based on the REACH criteria for PBT and vPvB chemicals, is given in Table 46. According to the authors, it is important to realize, however, that these assessments are truncated (figuratively meant), and data presented in the relevant sections should be consulted for the detailed data. In particular, bioaccumulation and toxicity are species-dependent, and even variations among individuals within the same species are not uncommon. Therefore, it is not surprising that high as well as low classifications sometimes were reported for the same parameter. Furthermore, bioaccumulation was a more challenging parameter to assess, because many studies did not consider depuration (~loss) times of the chemical. (Waijers *et al.*, 2013)

The authors conclude that large data gaps were identified for the physico-chemical and the PBT properties of the reviewed non-halogenated FRs. TPP has been studied extensively and it is clearly persistent, bioaccumulative, and toxic (PBT). So far, RDP and BDP have demonstrated low to high ecotoxicity and persistence. The compounds ATH and ZB exerted high toxicity on some species and ALPI appeared to be persistent, with low to moderate reported ecotoxicity. DOPO and MPP may be persistent, but this view is based merely on one or two studies, clearly indicating a lack of information. Many degradation studies have been performed on PER and show low persistence, with a few exceptions. Additionally, there is too little information on the bioaccumulation potential of PER. APP has mostly low PBT properties; however, moderate ecotoxicity was reported in two studies. Mg(OH)₂, ZHS, and ZS do not show such remarkably high bioaccumulation or toxicity, but large data gaps exist for these compounds also. Nevertheless, the authors consider the latter compounds to be the most promising among alternative non-halogenated FRs. To assess whether the presently

reviewed non-halogenated FRs are truly suitable alternatives, each compound should be examined individually by comparing its PBT values with those of the relevant halogenated flame retardant. Until more data are available, it remains impossible to accurately evaluate the risk of each of these compounds, including the ones that are already extensively marketed.

TABLE 46
OVERVIEW OF PBT PROPERTIES FOR SELECTED HALOGEN-FREE FLAME RETARDANTS (WAAIJERS *ET AL.*, 2013)*1

Compound	Persistence	Bioaccumulation	vPvB?	Toxicity		
				Ecotoxicity	In Vivo toxicity	In vitro toxicity
TPP	Low to high	Low to high	(Yes)	Low to high	Low	Low to high
RDP	Low to high	Low to high	No	Low to high	Low (to moderate)	(Low)
BDP	Low to high	(Low to high)	(No)	Low to high	(Low)	(Low)
ATH	–	(Low)	(no)	Low to high	(Low)	(Low)
ZB	–	n.d.	n.d.	High	Low to high	(Low)
ALPI	Moderate to high	(Low, not specified)	(No)	Low to moderate	Low	Low
PER	Low to high	(Low)	(No)	Low	Low	Low
DOPO	(Low to high)	(Low)	(No)	Low to moderate	n.d.	(Low)
MPP	(High)	(Low)	(No)	Low	Low	n.d.
APP	–	(Low, not specified)	(No)	Low (to moderate)	(Low)	(Low)
ZHS	–	(Low, not specified)	(No)	Low	Low (to moderate)	(Low)
Mg(OH) ₂	–	n.d.	n.d.	n.d.	(Low)	n.d.
ZS	–	(Low, not specified)	(low)	(low)	(Low)	n.d.

*1 Note by the authors of the paper: Please note that this table gives an overview of the data found in literature and it is not an assessment. (Bracketed) = based on two or less studies, n.d. = no data

Availability and costs of alternatives - The assessments of alternatives provide some information on availability and costs of alternatives, but no comprehensive summary. Table 47 provides a summary of availability and cost difference between BFRs and non-halogenated alternatives for applications in electrical and electronic equipment, as presented by PINFA (2010) which represents the European manufacturers of non-halogenated phosphorous, inorganic and nitrogen (PIN) flame retardants. The materials with non-halogenated FRs are generally 10-30% more expensive than materials with brominated flame retardants.

TABLE 47
 AVAILABILITY, RELIABILITY AND COST OF PIN FLAME RETARDANTS FOR ELECTRICAL (PINFA, 2010)

Component categories	Availability		Health and environment	Cost differential		Technology
	Do products exist?	Meet fire safety standard)		on material level	in finished product	Remaining issues to be resolved for shift (e.g.)
Wire and cable	✓	✓	Nordic and German government studies concluded there are sufficient PIN FRs of a good health & env. profile to provide replacements; REACH registrations	~20%	Represents 1-5% of the retail price of end products (fridge, TV...)	Some cable standards geared to certain materials
Enclosures	✓	✓		~20%		Need to shift from HIPS and ABS to polymer blends (e.g. PC-ABS)
Components	✓	✓		10-20%		Some technical challenges, e.g. very thin parts, glow wire test
Wiring	✓	✓		10-30%		Capacity build up for alternatives; tests for long-term reliability

Material alternatives

For applications in enclosures such as TV housings, less flammable copolymers like PC/ABS, PS/PPE or PPE/HIPS either without FRs, or with non-halogenated FRs, have been marketed and widely applied as substitutes for brominated HIPS and ABS resins. (Lassen *et al.*, 2006) The flame retardants used in these co-polymers have typically been organophosphorous flame retardants such as resorcinol bis(diphenylphosphate) (RDP), bisphenol A bis(diphenylphosphate) (BDP) and triphenyl phosphate (TPP). These substances are included in the assessment of chemical alternatives above. The alternative materials are generally more expensive than HIPS and ABS with BFRs. In 2006, the price of the HIPS/PPE with halogen-free FRs was approximately 158% that of deca-BDE HIPS, corresponding to a cost increase of 0.95 €/kg. The price PC/ABS with halogen-free FRs was approximately the same as the price of the HIPS/PPE.

Material alternatives for decaBDE use in textiles are addressed in section 7.1.4.

Non-plastic alternatives may in principle be used for some applications, but the available assessments do not address non-plastic alternatives and apparently only other polymers are marketed as material alternatives.

7.1.2 HBCDD

Several assessments of chemical alternatives to HBCDD in different applications, as well as an assessment of material alternatives to EPS flame retardant with HBCDD, are available.

Chemical alternatives

Overview tables on chemical alternatives to HBCDD in EPS/XPS as well as on alternatives to HBCDD in HIPS (high impact polystyrene) and textiles have been prepared by the POPs Review Committee under the Stockholm Convention (POPRC, 2012). The summary data are shown in Table 48.

Several chemical alternatives to HBCDD for expanded polystyrene (EPS), extruded polystyrene (XPS), high impact polystyrene (HIPS) and textile applications were identified in the responses from Parties and Observers. Information has been presented approximately as received and separately checked by the POPs Review Committee to the extent possible. According to the POPs Review Committee, the health and safety information available for some of the alternatives below is limited.

Some chemical alternatives to HBCDD have recently been developed, including drop-in alternatives for one-step EPS and XPS production, shown as the first two substances in Table 48. The polymeric BFRs are offered only for providing flame retardancy in PS foams (90% of total HBCDD consumption), not for other HBCDD uses.

According to newer information than provided in the table, supply of the first of the polymeric flame retardants has been realized. Licensees have confirmed that commercial production capacity of 20,000 metric tons will be available by the 2nd half of 2014, ahead of the REACH-sunset date of HBCDD (Azom, 2013). To date, 10,000 tonnes is commercially available already. All licensees made recent announcements about the availability of their new flame retardants containing the Polymeric FR technology.

The FR-122P is described as a block copolymer of polystyrene and brominated polybutadiene (ICL, 2013). The CAS No is 1195978-93-8, Benzene, ethenyl-, polymer with 1,3-butadiene, brominated. The structural formula is shown in Chapter 1.

According to the POPRC (2012) some Parties indicated in their responses that higher costs were associated with the polymeric FR as compared to HBCDD. However, no financial values were included to support this. According to one producer of the Polymeric FR, manufacturing flame retardant products with the alternative to HBCDD is not anticipated to have any significant impact on the cost competitiveness of EPS or XPS. It remains unclear whether the flame retardant represents a significant factor in the price of the final product (EPS/XPS insulation board). More precise cost estimates will not be available until the polymeric FR is fully commercialized. (POPRC, 2012) According to the MSDS information and the industry hazard assessment, polymeric FR is potentially persistent, but not bioaccumulative or toxic. However, there are no independent reviews about its properties as yet (POPRC, 2012).

Non-brominated chemical alternatives to HBCDD appear to be missing for most applications. According to Babrauskas *et al.* (2012) the new polymeric flame retardants rely on the same chemical mechanism as HBCDD to achieve flame-retardant properties during combustion, so they are likely to increase fire toxicity in the same way as has been demonstrated by Babrauskas (1992, as cited by Babrauskas *et al.*, 2012) by increasing the generation of smoke, carbon monoxide and soot. Furthermore, according to the authors, polymers are by nature a heterogeneous mixture in which different sized particles can exhibit different properties. When evaluating the pre-manufacture notice for Emerald 3000, the US EPA (2011) predicted potential toxicity from inhalation of some particle sizes, as well as the potential for smaller polymers to be persistent, bioaccumulative and toxic, if the PMN substance were manufactured where the average number molecular weight is less than 1,000 daltons (see the notice for further details about particles sizes). No data on the actual size distribution of the polymeric BFRs have been identified.

In any case, the environmental and health profile of the polymeric BFRs seems to be better than the profile of HBCDD, and in the absence of other viable alternatives, they will likely be the first alternatives to be introduced for replacement of HBCDD in EPS/XPS.

TABLE 48
CHEMICAL ALTERNATIVES TO HBCDD IN DIFFERENT APPLICATIONS (POPRC, 2012)*

Chemical	Benzene, ethenyl-, polymer with 1,3-butadiene, brominated (brominated co-polymer of styrene and butadiene) Synonym: Polymeric FR CAS No: 1195978-93-8
Trade names	Emerald 3000, FR122P
Claimed suitability	EPS via one-step process, likely also suitable in two-step process And XPS
Availability	Currently pilot scale quantities are being submitted to downstream users for testing. Plant scale production trials successfully run. Commercially available in 2012 from Great Lakes Solutions-Chemtura Corporation. ICL-Industrial Products recently announced they are aiming for commercial production by 2014 (10 000 tonne). Albe-marle (US) will have the chemical commercially available in 2014. Anticipated to be sufficient capacity to replace HBCDD within 3-5 years. See also para 6.
HSE properties	No independent evaluation of properties is available. According to industry information: Potentially persistent (not biodegradable) but low potential for bioaccumulation and low potential for toxicity. Not classified for carcinogenicity due to lack of data. No data available on toxicity to fish. See also para 7.
Costs	Diverging information received (see para 17). Responses reported: According to a manufacturer, cost of manufacturing EPS products containing Emerald 3000 is not anticipated to have significant impact on cost competitiveness with other products. Some Parties expect higher costs than HBCDD. One Party suggests the costs of using the alternative are 90 % (EPS) to 120% (XPS) higher than when using HBCDD. Separately to any cost differences between the FRs are the costs to re- certify flame retardant EPS resins/products for all of the foam applications. Canada has estimated this at a few million dollars.
Efficacy	Pilot tests conducted by customers of one of the manufacturers have reportedly confirmed that FR122P delivers the required level of fire safety to their products. Emerald 3000 is reported to have essentially equivalent flame retardant efficiency to HBCDD when used at equivalent bromine content. XPS producers report efficacy is 83% of HBCDD. Good thermal stability and compatibility with polystyrene. In higher temperature processing conditions Polymeric FR needs to be stabilized, similar to HBCDD. [Copied from body text of the report]: Polymeric FR is reported to have essentially equivalent flame retardant efficiency to HBCDD when used at equivalent bromine content. According to Great Lakes Solutions, 1.7% of Emerald 3000 (trade name) is required to pass the EN Class E flammability test. The required load is thus comparable to that of HBCDD (0.5-2.5% HBCDD w/w) in PS foams.
Chemical	Benzene, ethenyl-, polymer with 1,3-butadiene, brominated (brominated co-polymer of styrene and butadiene) Synonym: Polymeric FR CAS No: 1195978-93-8
Trade names	Pyroguard SR-130 SR-130
Claimed suitability	EPS XPS
Availability	Not available in the USA
HSE properties	See para 7.
Costs	No data
Efficacy	No data
Chemical	Tetrabromobisphenol A bis (allyl ether) CAS No: 25327- 89-3

Trade names	BE 51, FG 3200, Fire Guard 3200, Flame Cut 122K, Pyroguard SR 319, SR 319
Claimed suitability	Two-step EPS process
Availability	Used in the two-step EPS process only
HSE properties	Substance is a derivative of TBBPA (ECB 2006). Little information is available on HSE properties. According to the information reviewed in KLIF (2009) it can be characterised with low toxicity, potential immunotoxin, not easily hydrolysed, may be resistant to environmental degradation (see KLIF 2009 for details).
Costs	No data
Efficacy	No data
Chemical	1,2,5,6- tetrabromocyclo-octane (TBCO) CAS No: 3194-57-8
Trade names	Saytex BC- 48 (Albemarle Corporation)
Claimed suitability	Two-step EPS process Additive FR
Availability	Used in the two-step process only This substance may no longer be commercially available. No information is available on production volumes in the US or in the EU. TBCO is also on the Canadian Non-Domestic Substances List with as much as 10 tons/year reported as being imported into Canada.
HSE properties	A report by the UK Environment Agency (Fisk <i>et al.</i> 2003) indicates that TBCO is hazardous to the aquatic environment (i.e. chronic NOEC < 0.1 mg/l or acute L(E)C50s < 10 mg/l), and potentially PBT/vPvB. Due to poor availability of HSE information further analysis could not be carried out.
Costs	No data
Efficacy	No data
Chemical	2,4,6- tribromophenyl allyl ether CAS No: 3278-89-5
Trade names	Pyroguard FR 100, Great Lakes PHE-65, Bromkal 64-3AE
Claimed suitability	Two-step EPS process
Availability	No data
HSE properties	Proposed as one of the 120 HPV chemicals structurally similar to known Arctic contaminants (Brown & Wania 2008). Likely bioaccumulative and subject to long range transport since the substance is found in Arctic seals in both blubber and brain (Von der Recke & Vetter 2007)
Costs	No data
Efficacy	No data
Chemical	Tetrabromobisphenol A bis(2,3- di-bromopropyl ether) (TBBPA- DBPE), CAS No: 21850-44-2 with dicumene for XPS and dicumyl peroxide for EPS, as usual synergists
Trade names	STARFLA ME PS SAM 54: masterbatch for XPS STARFLA ME PO SAM 55: masterbatch for XPS GC SAM 55 E: powder blend for EPS

Claimed suitability	EPS XPS
Availability	For EPS only laboratory scale experience, not yet in wide use. All raw materials, however, are worldwide commodities and thus GC SAM 55 E is reported to be immediately available for up-scaling on a commercial scale. For XPS the alternative is already in use in commercial scale.
HSE properties	According to the KLIF (2009) review, TBBPA- DBPE has low toxicity. No endocrine effects have been observed, but it has a high potential to inhibit estradiol sulfotransferase and have a moderate competition with the thyroxine for the binding to the plasma protein transthyretin. TBBPA-DBPE is poorly absorbed through the gastrointestinal tract in rats, but the absorbed quantities accumulate in liver and slowly metabolize. The available information does not allow assessing the environmental persistence (Washington State 2006). According to KLIF (2009) and the information from the manufacturer, TBBPA- DBPE has low biodegradability but appears to be susceptible to hydrolysis. Contradicting conclusions on bioaccumulation are reported in Washington State (2006) and KLIF (2009). According to the manufacturer bioaccumulation is not expected. The National Toxicology Program (NTP) believes that the substance might have a carcinogenic potential. Positive for mutagenic activity with and without metabolic activation in Salmonella typhimurium strains (NIEHS 2002). TBBPA-DBPE has also been found in house dust in Belgium and UK (Ali <i>et al.</i> 2011).
Costs	According to the manufacturer, comparable to HBCDD solution in EPS (costs around 6.5 €/kg). Slightly more expensive than HBCDD in XPS.
Efficacy	Flame retardant properties, 20- 30% less than HBCDD. Reportedly good thermal stability, easily dispersible and compatible with polystyrene, insoluble in water and soluble in Toluene and Xylene.
Chemical	Ethylenebis (tetrabromo-mophthalimide) (EBTPI) CAS No: 32588-76-4
Trade names	BT93, BT93W, BT93WFG, Citex BT 93, Saytex BT93, Saytex BT93W
Claimed suitability	HIPS Additive FR
Availability	Commercially available and used extensively It is mostly used in HIPS, polyethylene, polypropylene, thermoplastic polyesters, polyamide, EPDM, rubbers, polycarbonate, ethylene co- polymers, ionomer resins, and textiles.
HSE properties	The available data is insufficient for a comprehensive environmental assessment of EBTPI. The few studies reported indicate that EBTPI is not readily biodegradable, does not bioaccumulate and has a low aquatic toxicity (Danish EPA 2007). Indications are that EBTPI is of low mammalian toxicity (KLIF 2009). The EU Technical Committee of New and Existing Chemicals Substances (TCNES) considered EBTPI very persistent. However, the bioaccumulation criterion was not met based on molecular properties of the substance and EBTPI was not listed as a vPvB substance. The only available study of the aquatic toxicity of EBTPI indicates that acute toxic effects occur at levels much higher than the estimated water solubility. Long-term NOEC values are not found in the literature. More ecotoxicology data are required for assessment of the toxicity (T) criterion. (Pakalin <i>et al.</i> 2007).
Costs	No data
Efficacy	Technically feasible and used extensively
Chemical	Decabromodiphenyl ether (DecaBDE) CAS No: 1163-19-5
Trade names	SAYTEX 102E FR-1210 DE-83R
Claimed suitability	HIPS Textiles
Availability	Commercially available and used extensively. Many manufacturers have phased use out since the early 2000's

HSE properties	Decabromodiphenyl ether was considered toxic according to criteria 64 (a) under the <i>Canadian Environmental Protection Act, 1999</i> , along with other PBDEs in this class (tetra to decaBDEs). A State of Science Report for this substance found that this substance transforms to persistent and bioaccumulative substances (Environment Canada 2010). The POPRC has concluded that there is an increasing number of studies related to the potential of highly brominated congeners, including decabromodiphenyl ether, to be reductively debrominated in the environment and thus contribute to the formation of those brominated diphenyl ethers listed in Annex A (Decision POPRC-7/1). In the EU RAR (European Commission 2002) DecaBDE was not expected to degrade biologically, but was not considered bioaccumulative nor toxic. A later review (Pakalin <i>et al.</i> 2007) concluded as well that DecaBDE does not meet the toxicity (T) criterion. However, there is some indication that DecaBDE can cause behavioural disturbances in mice when they are exposed at a sensitive stage of brain development (possibly via a metabolite). This apparent toxicity makes the presence of DecaBDE in the eggs of top predators a serious finding that is relevant in any assessment of long-term risk. Pakalin <i>et al.</i> (2007) also notes that the normal PEC/PNEC comparison methods described in the EU Technical Guidance Document do not apply to this situation. See also para 8.
Costs	No data
Efficacy	Technically feasible and used extensively
Chemical	Decabromodiphenyl ethane (DBDPE) CAS No: 84852-53-9
Trade names	SAYTEX 8010 Firemaster 2100 Planelon BDE S8010
Claimed suitability	HIPS Textiles Additive FR
Availability	Commercially available and used extensively. DBDPE was introduced in the mid-1980s and became commercially important as an alternative to DecaBDE formulations in the early 1990s. Europe does not produce DBDPE, but imports in 2001 were estimated to be between 1000 and 5000 tons, primarily to Germany. DBDPE is the second highest current use additive BFR in China with production increasing at 80% per year (http://www.polymer.cn/). It is produced by at least two Chinese companies: The production volume of DBDPE in China in 2006 was 12,000 tons (Xiao, 2006). In Japan, there has been a clear shift in consumption away from DecaBDE to DBDPE. Agency 2007, Pakalin <i>et al.</i> 2007). DBDPE has a relatively low hazard potential to aquatic organisms due to its low water solubility. It is also of low toxicity to mammals (Environment Agency 2007). DBDPE alters gene expression in chicken embryos (Egloff <i>et al.</i> 2011), is acutely toxic to <i>Daphnia magna</i> , reduces the hatching rates of zebra-fish eggs, and significantly raises the mortality of hatched larvae (Nakari & Huhtala 2010). In the risk assessment made by the UK, conclusions on bioaccumulation were not possible in the absence of reliable data (Environment Agency 2007). Recent information shows that in fish DBDPE bioaccumulates one order of magnitude higher than DecaBDE which indicates it can significantly accumulate in fish (He <i>et al.</i> 2012). DBDPE is found in predator avian species such as falcons and their eggs (Guerra <i>et al.</i> 2012) and in piscivorous water birds (Luo <i>et al.</i> 2009). In a Lake Winnipeg food web DBDPE was found to biomagnify (Law <i>et al.</i> 2009). DBDPE is widely detected in environmental samples; sewage sludge, air, sediments, fish and birds, as well as in house and office dust (La Guardia <i>et al.</i> 2012). In a recent Nordic screening study (NCM 2011), DBDPE was found in 100% of air, 50% of sediment, 100% of sludge and 70% of biota samples. The concentrations were often comparable with BDE-47 and BDE-209 levels found. DBDPE has also been found in house dust in the US (Stapleton <i>et al.</i> 2008), Belgium, UK (Ali <i>et al.</i> 2011) and Sweden (Karlsson <i>et al.</i> 2007). The chemical is the main BFR in human hair in non-e-waste recycling areas in China. Significant correlations were found between hair levels and dust levels (Zheng <i>et al.</i> 2011) suggesting endogenous pathways to hair.
HSE properties	Available evidence indicates Decabromodiphenyl ethane (DBDPE) is potentially persistent. It is not susceptible to abiotic degradation (e.g., hydrolysis) and is not readily biodegradable under aerobic conditions in the aquatic environment (<i>viz.</i> : 2% according to OECD 301C). Persistence is linked to low water solubility (0.72 µg/l). (Environment Agency 2007, Pakalin <i>et al.</i> 2007).

	<p>DBDPE has a relatively low hazard potential to aquatic organisms due to its low water solubility. It is also of low toxicity to mammals (Environment Agency 2007). DBDPE alters gene expression in chicken embryos (Egloff <i>et al.</i> 2011), is acutely toxic to <i>Daphnia magna</i>, reduces the hatching rates of zebra-fish eggs, and significantly raises the mortality of hatched larvae (Nakari & Huhtala 2010).</p> <p>In the risk assessment made by the UK, conclusions on bioaccumulation were not possible in the absence of reliable data (Environment Agency 2007). Recent information shows that in fish DBDPE bioaccumulates one order of magnitude higher than DecaBDE which indicates it can significantly accumulate in fish (He <i>et al.</i> 2012). DBDPE is found in predator avian species such as falcons and their eggs (Guerra <i>et al.</i> 2012) and in piscivorous water birds (Luo <i>et al.</i> 2009). In a Lake Winnipeg food web DBDPE was found to biomagnify (Law <i>et al.</i> 2009). DBDPE is widely detected in environmental samples; sewage sludge, air, sediments, fish and birds, as well as in house and office dust (La Guardia <i>et al.</i> 2012). In a recent Nordic screening study (NCM 2011), DBDPE was found in 100% of air, 50% of sediment, 100% of sludge and 70% of biota samples. The concentrations were often comparable with BDE-47 and BDE-209 levels found.</p>
Costs	According to one Party, DBDPE is commonly used in HIPS and textiles, with better effect than HBCDD and approximately equal price as HBCD, and basically replaced HBCDD in 2011 in this application in China.
Efficacy	Technically feasible and used extensively
Chemical	Triphenyl phosphate CAS No: 115-86-6
Trade names	No data
Claimed suitability	HIPS
Availability	Commercially available and used extensively
HSE properties	<p>According to a review published by the Danish EPA (2007), TPP is highly toxic to algae, invertebrates and fish with typical L(E)C50 values <1 mg/l. Two studies of the chronic toxicity in fish report NOEC values in the range 0.014-0.23 mg/l, however, the validity of the studies are questionable. BCF values >100 have been reported in several long-term studies with different species of fish, and TPP is considered to be potentially bioaccumulative. This is supported by the log Kow value for TPP (range 4.58-4.67). TPP is inherently biodegradable, and is furthermore found to biodegrade under both aerobic and anaerobic conditions in water/sediment and soil systems under various conditions. The log Kow and log Koc values indicate that the availability and the mobility of TPP in the environment is limited. No data was found with respect to acute or repeated human exposure. The only parameter affected in the Danish review in subacute and subchronic dietary studies in rats was retardation in weight gain (Danish EPA 2007). US EPA (2005) reports moderate systemic toxicity and high acute and chronic ecotoxicity of TPP as two characteristics of concern. The US Occupational Safety and Health Administration (OSHA) reports inhibition of cholinesterase as a health effect of triphenyl phosphate exposure (US OSHA 1999). Danish EPA (2007) concluded that triphenyl phosphate (TPP) does not meet the persistency and bioaccumulation criteria in the PBT assessment. Triphenyl phosphate is considered environmentally hazardous in Germany due to its toxicity to aquatic organisms (Leisewitz <i>et al.</i> 2000). In a recent study, triphenyl phosphate was associated with a substantial 19% decrease in sperm concentration in men (Meeker & Stapleton 2010).</p>
Costs	No data
Efficacy	Technically feasible and used extensively
Chemical	Bisphenol A bis (biphenyl phosphate) (BDP) CAS No: 5945-33-5
Trade names	Fyrolflex BDP
Claimed	HIPS Additive FR

suitability	
Availability	Commercially available and used extensively
HSE properties	Bisphenol A bis (biphenyl phosphate) (BDP) is a phosphoric trichloride reaction product with bisphenol A and phenol. It may contain bisphenol A as an impurity. According to Washington State (2006) the results of the industry toxicity studies indicate low toxicity concern for humans, and low to medium toxicity concern for aquatic organisms. There are no animal cancer studies available for this chemical and no information on potential human exposures. The chemical does show a tendency to persist in the environment. Bioaccumulation could not be assessed. One of the BDP degradation products is bisphenol A (Washington State 2006), a substance declared by Canada to meet the criteria for persistence and toxicity concerns regarding permanent alterations in hormonal, developmental or reproductive capacity (Environment Canada 2008). Based on the potential of its degradation product bisphenol A for endocrine disruption, bisphenol A bis (biphenyl phosphate) was scored as high for the endocrine disrupting attribute in an EU assessment draft (JRC 2011). The same assessment found that BDP was highly persistent and moderately to highly bioaccumulative with BCF values ranging from 300 to 3000 and log Kow of 4.5 – 6.
Costs	No data
Efficacy	Technically feasible and used extensively
Chemical	Diphenyl cresyl phosphate CAS No: 26444-49-5
Trade names	No data
Claimed suitability	HIPS
Availability	Commercially available and used extensively
HSE properties	Diphenyl cresyl phosphate is poorly characterized but appears to be toxic to aquatic organisms and not readily biodegradable (OECD SIDS). According to Washington State (2006) half-life in water is 4.86 years, BCF 980 and it has moderate aquatic toxicity, has developmental and reproductive toxicity but is not mutagenic and has low oral toxicity.
Costs	No data
Efficacy	Technically feasible and used extensively
Chemical	Chlorinated paraffins (C10-13) –CAS No: 85535-84-8
Trade names	No data
Claimed suitability	Textiles
Availability	Available and used extensively
HSE properties	Short-chain chlorinated paraffins (Alkanes, C10-13, chloro) with greater than 48% chlorination have been nominated for listing as a POP under the Stockholm Convention and are currently under review of the POPRC. Chlorinated paraffins (C10-13) assessed as short chain chlorinated paraffins (SCCPs) met the definition of toxic under criteria 64 (a) under the Canadian Environmental Protection Act, 1999 and the Persistence and Bioaccumulative criteria and was subject to Virtual Elimination. In Canada, these substances were included in the proposed Prohibition of Certain Toxic Substance Regulations in 2012 (http://www.ec.gc.ca/lcpe-ce-

	pa/eng/regulations/detailreg.cfm?intReg =87).
Costs	Used extensively
Efficacy	Technically feasible and used extensively
Chemical	Ammonium polyphosphate – CAS RN 68333-79-9
Trade names	No data
Claimed suitability	Textiles
Availability	Available and used extensively
HSE properties	Little data is available on properties. There is no data on bioaccumulation. In Canada the chemical is categorized as Persistent and inherently Toxic.
Costs	Used extensively
Efficacy	No data

* The table has here been transposed in order to improve the readability; please find references in original document.

Material alternatives to flame retarded EPS

Material alternatives to EPS flame retarded with HBCDD and used in the building sector have been reviewed in 2011 by the Norwegian Climate and Pollution Agency (Lassen *et al.*, 2011).

The summary results of the comparison of the EPS flame retardant with HBCDD and other insulation materials are shown in Table 49. The overall conclusion of the study was that alternatives are available for all assessed applications of flame retarded EPS. The flame retarded EPS would likely be replaced by different insulation materials depending on the application, as no one alternative assessed would substitute for all EPS applications, if the use of flame retarded EPS is restricted.

The alternatives typically have better fire performance and contain fewer problematic chemical substances. Apart from this, the flame retarded EPS scores well in the comparison with the other materials (provided that the fire performance is acceptable), in particular if the EPS ultimately is disposed of by incinerated with energy recovery.

The price of the cheapest alternatives ranges approximately from the same price as for flame retarded EPS to 30% more. Alternatives of significantly higher prices exist, but these are typically used because they have some desired technical advantages and would, because of the price, probably not be the first choice substitutes for general application. For some applications, where flame resistance is not needed, non-flame retarded EPS would probably be used to the extent national regulation allows.

Material alternatives to the use of HBCDD in textiles are addressed in section 7.1.4.

Formation of fumes during fire - Stec and Hull (2011) have investigated the fire toxicity of six insulation materials (glass wool, stone wool, EPS, phenolic foam, polyurethane foam and polyisocyanurate foam) under a range of fire conditions. It is not indicated whether the EPS contain flame retardants.

Two of the materials, stone wool and glass wool, failed to ignite and gave consistently low yields of all of the toxic products tested for. The toxicities of the effluents, showing the contribution of individual toxic components, were compared using the fractional effective dose (FED) model and LC₅₀ (the mass required per unit volume to generate a lethal atmosphere under specified conditions).

The FED was expressed as the sum of contributions to toxicity from individual species: CO, hydrogen cyanide, nitrogen dioxide, hydrogen chloride, and hydrogen bromide. For polyisocyanurate and polyurethane foam, a significant contribution from hydrogen cyanide was seen, resulting in doubling of the overall toxicity as the fire condition changed from well-ventilated to under-ventilated. These materials showed an order of increasing fire toxicity, from stone wool (least toxic), glass wool, polystyrene, phenolic, polyurethane to polyisocyanurate foam (most toxic). Among the combustible insulation materials, the EPS was the material yielding less toxic fumes. However, the authors conclude that EPS determination should be repeated under non-flaming conditions to confirm the low yields, and identify the volatiles corresponding to the mass loss.

TABLE 49
COMPARISON OF FLAME RETARDED EPS AND SELECTED ALTERNATIVE INSULATION MATERIALS

Technical solution	Technical feasibility		Fire safety	Human health and ecotoxicological impacts		Other environmental impacts and resource consumption			Recyclability	Price of material (normalised to functional unit (FU) with similar insulation capacity)
	Advantages (as compared to EPS)	Disadvantages (as compared to EPS)		Chemicals	Fibres and dust	Non-renewable energy consumption **, MJ/FU	Renewable energy consumption, MJ/FU	Selected impacts (cradle-to-gate) (as compared to EPS) ****		
Flame retarded EPS sheets	-	-	Euroclass E Development of smoke and burning droplets	HBCDD is a PBT and POP substance - released during the use and disposal phase	No major issues	INC: 111 DEP: 185	INC: 1 DEP: 1		Recyclable - recycling increase the releases of HBCDD to the environment	120-180 € per m ³ (excl. VAT)
Non- flame retarded EPS sheets	-	-	Euroclass F Development of smoke and burning droplets	No major issues	No major issues	INC: 111 DEP: 185	INC: 1 DEP: 1		Recyclable – slightly lower value of recycled materials	(≈)
Stone wool	Diffusion-open. Easier to fasten tight in some cases due to flexibility	Similar to or slightly lower insulation efficiency. Higher weight Lower compressive strength than some EPS types	Euroclass, A1,A2	Small releases of formaldehyde (CMR) from some types	Irritating fibres	INC: 139 DEP: 139	INC: 1 DEP: 1	Global warming (+) Acidification (+) Smog (÷)	Recyclable with low value of recycled materials	(≈/+)

Technical solution	Technical feasibility		Fire safety	Human health and ecotoxicological impacts		Other environmental impacts and resource consumption			Recyclability	Price of material (normalised to functional unit (FU) with similar insulation capacity)
	Advantages (as compared to EPS)	Disadvantages (as compared to EPS)		Chemicals	Fibres and dust	Non-renewable energy consumption **, MJ/FU	Renewable energy consumption, MJ/FU	Selected impacts (cradle-to-gate) (as compared to EPS) ****		
Polyisocyanurate (PIR) sheets (flame retardant)	Higher insulation efficiency Higher compressive strength for some types		Euroclass E Development of smoke (less than EPS)	Halogenated phosphorous flame retardants in some types (not PBT or CMR) May be released during use and disposal	No major issues	INC: 119 DEP: 174	INC: 4 DEP: 4	Global warming (+) Acidification (+) Smog (÷)	Recyclable with low value of recycled materials - recycling may increase releases of halogenated phosphorus compounds	(≈/++)
Wood fibre insulation board	Diffusion-open	Slightly lower insulation efficiency. Somewhat vulnerable to moisture. Some qualities relatively heavy	Euroclass E, F Development of smoke	No major issues	No major issues	INC: -1 DEP: 201	INC: 544 DEP: 544	Global warming (÷) Acidification (+) Smog (÷)	Recyclable with low value of recycled materials	(+/++)

Technical solution	Technical feasibility		Fire safety	Human health and ecotoxicological impacts		Other environmental impacts and resource consumption			Recyclability	Price of material (normalised to functional unit (FU) with similar insulation capacity)
	Advantages (as compared to EPS)	Disadvantages (as compared to EPS)		Chemicals	Fibres and dust	Non-renewable energy consumption **, MJ/FU	Renewable energy consumption, MJ/FU	Selected impacts (cradle-to-gate) (as compared to EPS) ****		
Cellular glass	Very high resistance to compression. Can reduce dimensions of a load bearing insulated wall in some cases. Insensitive to moisture and other climate and chemical pressures.	Slightly lower insulation efficiency Relatively heavy - if used for decks, roofs etc. It may in some cases warrant stronger dimensions of load bearing structures	Euroclass A1	No major issues	No major issues	INC: 166 DEP: 166	INC: 100 DEP: 100	Global warming (+) Acidification (+) Smog (±)	Recyclable with low value of recycled materials	(++)

* Notation: (≈) prices typically similar to EPS; (+) 10-30% more than for EPS; (++) >30% more than EPS. Prices comparison based on materials meeting the functional unit.

** Primary energy consumption for the functional unit (FU) of 1 m² and a thermal resistance of 2.857 m²·K/W. Covers manufacturing (cradle-to-gate) and disposal. For disposal two scenarios are assessed: INC, combustible materials are incinerated with energy recovery of 80% efficiency, DEP, all materials are deposited/landfilled.

*** Euroclasses: Range from the best A1:(non-combustible) to F: not tested (combustible)

***** Notation: (+) higher potential than EPS, (±) lower potential than EPS

7.1.3 TBBPA and derivatives

Alternatives to TBBPA have been assessed by the Swedish Chemicals Agency (Posner, 2006), Lowell Center for Sustainable Production (Morose, 2006) and the US EPA's Flame Retardants in Printed Circuit Boards Partnership (US EPA, 2008).

Chemical alternatives

Alternatives to the additive use of TBBPA is similar to alternatives to decaBDE and are covered by section 7.1.1.

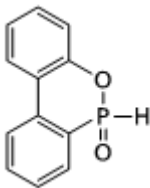
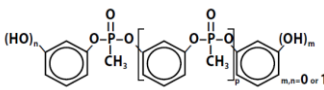
The main application of TBBPA is in printed circuit boards (PCBs) for electronics. Currently, the majority of PCBs produced worldwide meet the V₀ requirements of the UL 94 fire safety standard. This standard is usually achieved through the use of brominated epoxy resins in which the reactive flame retardant tetrabromobisphenol A (TBBPA) forms part of the polymeric backbone of the resin. While alternative flame-retardant materials are used in only a small percentage of FR-4 boards, the use of alternatives has been increasing over the past few years, and additional flame-retardant chemicals and laminate materials are under development.

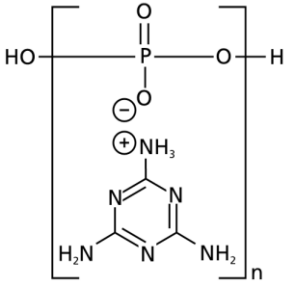
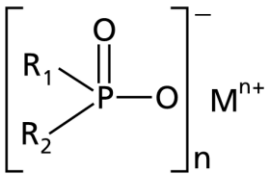
In 2008 most laminate suppliers included halogen-free materials in their portfolio. Pricing for halogen-free laminates were still higher than conventional material by at least 10 %, and often by much more. (US EPA, 2008).

The total market of halogen-free laminates in 2006 totalled \$307 million as compared to a total global laminate market of \$7.7 billion (US EPA, 2008).

A multi-stakeholder partnership alternatives assessment under US EPA's Design for the Environment (DfE) Program has evaluated flame retardants in printed circuit boards (US EPA, 2008). The partnership evaluated eight commercially available flame retardants for FR-4 laminate materials for PCBs: TBBPA, DOPO, Fyrol PMP, aluminium hydroxide, Exolit OP 930, Melapur 200, silicon dioxide, and magnesium hydroxide (Table 50). The reaction products of epoxy resin with TBBPA, DOPO, and Fyrol PMP were also evaluated, because both TBBPA and DOPO undergo chemical reactions during manufacturing. The flame-retardant evaluations in the report are hazard assessments with considerations for exposure, but not full risk assessments.

TABLE 50
NON-BROMINATED FLAME RETARDANTS EVALUATED BY US EPA (2008)

Substance	Chemical formula	Description
DOPO 6H-Dibenz[c,e][1,2] oxaphosphorin, 6- oxide CAS No 35948-25-5	 Pinfa, 2010	DOPO is a hydrogenphosphinate made from o-phenyphenol and phosphorus trichloride. Similar to TBBPA, it can be chemically reacted to become part of the epoxy resin backbone. (US EPA, 2008) In 2010, DOPO was regarded as the major building block used to make phosphorus containing epoxy resins (T _g up to 150 °C). DOPO was commercially available from different suppliers (Pinfa, 2010)
Fyrol PMP Poly-(m-phenylene methylphosphonate) CAS No 63747-58-0	 ICI industrial, 2012	Fyrol PMP is an aromatic phosphonate oligomer with high phosphorus content (17 to 18 percent). Similar to TBBPA and DOPO, Fyrol PMP can be chemically reacted to become part of the epoxy resin backbone. When reacted into a phenol-formaldehyde novolak epoxy, Fyrol PMP provides good flame retardancy at loadings as low as 20 percent (US EPA, 2008)

Substance	Chemical formula	Description
Aluminium Hydroxide CAS No 21645-51-2	Al(OH) ₃	ATH is difficult to use alone to achieve the FR-4 rating of laminates, and as a result, high loadings relative to the epoxy resin, typically up to 60 to 70 % by weight, are needed. ATH is most commonly used in FR-4 PCBs as a flame-retardant filler, in combination with DOPO or other phosphorus-based compounds (US EPA, 2008)
Melamine Polyphosphate CAS No 218768-84-4	 Pinfa, 2010	Melamine polyphosphate, an additive-type flame retardant based on a combination of phosphorous and nitrogen chemistries, is typically used as crystalline powder and in combination with phosphorus-based compounds. Melamine polyphosphate does not negatively impact the performance characteristics of standard epoxy laminates, and functions best when blended with other non-halogen flame retardants (US EPA, 2008)
Phosphoric acid, diethyl-, aluminium salt Exolit OP 930 CAS No 225789-38-8	 General formula for metal phosphinates Pinfa, 2010	Flame retardants based on phosphinate chemistry are a relatively new class of non-halogenated FRs on the market. One such phosphinate-based flame retardant – Exolit OP930, – is a fine-grained powder with high phosphorus content (23 to 24 %) used as a filler in FR-4 laminates. It is designed primarily for use in FR-4 laminate materials with Tg greater than 150°C. Like most phosphorus-based compounds, metal phosphinates achieve flame retardancy by forming a char barrier upon heating, thereby cutting off access to the oxygen needed for the combustion process. It is typically used as a synergist in combination with modified resins and sometimes other filler-type FRs. (US EPA, 2008) In every case the dosage of the metal phosphinate depends on the chemical nature of the varnish backbone. For example, in a combination with a phosphorus modified epoxy resin 15 to 20 phr (parts per hundred resin) of metal phosphinate are recommended. (Pinfa, 2010)
Silica CAS No 7631-86-9, 1317-95-9	SiO ₂	Also known as silicon dioxide (SiO ₂), silica is characterized by its abrasion resistance, electrical insulation, and high thermal stability. Silica is not a flame retardant in the traditional sense. It dilutes the mass of combustible components, thus reducing the amount of FR necessary to pass the flammability test. Silica is most commonly used in combination with novolak-type epoxy resins. (US EPA, 2008)
Magnesium Hydroxide CAS No 1309-42-8	Mg(OH) ₂	Magnesium hydroxide is functionally similar to ATH, in that it endothermically decomposes at high temperatures to produce an oxide (MgO) and water. However, whereas ATH undergoes thermal decomposition at 200-220°C, magnesium hydroxide decomposes at approximately 330°C. This allows manufacturers to use magnesium hydroxide when processing temperatures are too high for ATH (US EPA, 2008)

The summary results of the assessment are shown in Table 51. The level of available human health and environmental information varies widely by flame retardant chemical. Little information exists concerning many of the alternative flame-retardant materials. More established chemicals, including TBBPA and silicon dioxide, are more fully characterized. To help address this discrepancy, and to increase the usefulness of this report, US EPA used the tools and expertise of the New Chemicals Program to estimate the potential impacts of flame retardants when no experimental data were available.

The technical and economic feasibility of the alternatives was not a part of the DfE project, but the performance testing of commercially available non-halogenated FR materials to determine their key electrical and mechanical properties was the focus of a complementary project being conducted by the International Electronics Manufacturing Initiative (iNEMI). iNEMI is a consortium of approximately 100 leading electronics manufacturers, suppliers, associations, government agencies and universities. iNEMI supports the removal of halogenated flame retardants and PVC from electronic equipment (iNEMI, 2011). In the tested non-halogenated FR4 laminates, the resin epoxy backbone was modified - organo-phosphorous or nitrogen compounds substitute for TBBPA and fillers were added - SiO₂, metal hydroxides and/or other compounds (iNEMI, 2011). The changes have some impact on the properties of the laminates; the most critical being that the epoxy backbone change affects the resin electrical properties (Dk and Df) due to moisture absorption, and the addition of fillers increase the dielectric Constant (Dk) of the material, affecting impedance targets, crosstalk and other design considerations. (iNEMI, 2011)

One of the drivers in the shift to BFR-free laminates is the concern about formation of by-products during product use and thermal end-of-life processes.

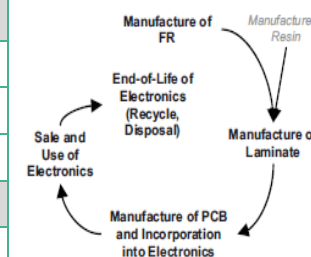
In addition to the hazard assessment of the alternatives, experimental testing was conducted as part of this project to learn more about the combustion by-products released during end-of-life disposal processes of printed circuit boards (US EPA, 2013). Open burning and incineration scenarios were simulated for different combinations of circuit board laminates and components. The laminates tested contained either a brominated flame retardant, a halogen-free flame retardant, or no flame retardant. Halogenated dioxins, halogenated furans, and polyaromatic hydrocarbons emitted during combustion were measured to better understand the risks associated with the combustion of this type of electronic waste. According to US EPA (2013), the partnership report will be updated to reflect findings. The report is still not published.

TABLE 51

THIS TABLE ONLY CONTAINS INFORMATION REGARDING THE INHERENT HAZARDS OF FLAME-RETARDANT (FR) CHEMICALS. EVALUATION OF RISK MUST CONSIDER BOTH THE HAZARD AND EXPOSURE ASSOCIATED WITH FR CHEMICALS, AS WELL AS THE HAZARD AND EXPOSURE ASSOCIATED WITH COMBUSTION AND DEGRADATION BYPRODUCTS. THE CAVEATS LISTED IN THE LEGEND AND FOOTNOTE SECTIONS MUST BE TAKEN INTO ACCOUNT WHEN INTERPRETING THE HAZARD INFORMATION IN THE TABLE BELOW.

Chemical	CAS No	Human Health Effects									Aquatic Toxicity		Environmental		Exposure Considerations	
		Acute toxicity	Skin Sensitizer	Cancer Hazard	Immunotoxicity	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation		
Reactive Flame-Retardant Chemicals ¹																
Tetrabromobisphenol A (TBBPA) (Albemarle, Chemtura, and others) ²																
TBBPA	79-94-7	L	L	L	L	L	M	L	L	L	H	H	M	L		
DOPO (6H-Dibenz[c,e][1,2] oxaphosphorin, 6-oxide) (Sanko Co., Ltd. and others)																
DOPO	35948-25-5	L	L	L	L	L	L	L	L	L	M	M	L	L		
Fyrol PMP (Aryl alkylphosphonate) (Supresta)																
Fyrol PMP	Proprietary	L	L	L	L	L	L	L	L	L	L	L	H	L		
Reactive Flame-Retardant Resins ¹																
Reaction product of TBBPA - D.E.R. 538 (Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with (chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol]]) (Dow Chemical)																
D.E.R. 538	26265-08-7	L	M	M ^o	L	M ^o	M ^o	L	L	M	L	L	M	L		
Reaction Product of DOPO – Dow XZ-92547 (reaction product of an epoxy phenyl novolak with DOPO) (Dow Chemical)																
Dow XZ-92547	Proprietary	L	M	M ^o	L	M ^o	M ^o	L	L	M ^o	L	L	H	L		
Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin (Representative Resin)																
Representative Fyrol PCB Resin	Unknown	L	L	M ^o	L	M ^o	M ^o	L	L	M ^o	L	L	H	L		
Additive Flame Retardants ³																

Chemical	CAS No	Human Health Effects									Aquatic Toxicity		Environmental		Exposure Considerations	
		Acute toxicity	Skin Sensitizer	Cancer Hazard	Immunotoxicity	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation		
Aluminum hydroxide																
Aluminum hydroxide	21645-51-2	<i>L</i>	<i>L</i>	<i>L</i>	<i>M</i>	<i>L</i>	<i>L</i>	<i>M</i>	<i>L</i>	<i>L</i>	H	M	<i>HR</i>	<i>L</i>	Availability of FRs throughout the lifecycle for reactive and additive FR chemicals and resins ²	
Exolit OP 930 (phosphoric acid, diethyl-, aluminum salt) (Clariant)																
Exolit OP 930	225789-38-8	<i>L</i>	<i>L</i>	<i>L</i>	<i>M</i>	<i>L</i>	<i>M</i>	<i>M</i>	<i>L</i>	<i>L</i>	M	<i>M</i>	<i>HR</i>	<i>L</i>		
Melapur 200 (Melamine polyphosphate) (Ciba) ⁴																
Melapur 200	218768-84-4	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>M</i>	<i>M</i>	<i>L</i>	<i>L</i>	<i>M</i>	<i>L</i>		
Polyphosphoric acid	8017-16-1	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>		
Melamine	108-78-1	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	M	M	<i>L</i>	<i>L</i>	M	<i>L</i>		
Silicon dioxide amorphous ⁵																
Silicon dioxide amorphous	7631-86-9	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	H [§]	<i>L</i>	<i>L</i>	<i>L</i>	<i>HR</i>	<i>L</i>		
Silicon dioxide crystalline ⁵																
Silicon dioxide crystalline	1317-95-9	<i>L</i>	<i>L</i>	H [‡]	H [§]	<i>L</i>	<i>L</i>	<i>L</i>	H [§]	H [§]	<i>L</i>	<i>L</i>	<i>HR</i>	<i>L</i>		
Magnesium hydroxide																
Magnesium hydroxide	1309-42-8	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>HR</i>	<i>L</i>		



¹ Reactive FR chemicals and resins may not completely react, and small amounts may be available during other parts of the lifecycle.

² The EU has published a comprehensive risk assessment for TBBPA in reactive applications. This risk assessment is a valuable source of information when choosing flame retardants for printed circuit board applications.

³ Although additive flame retardants are present throughout the lifecycle of the PCB, they are locked into the polymer matrix of the epoxy laminate material.

⁴ Melapur 200 dissociates in water to form polyphosphoric acid and melamine ions. For this reason, Table 4-1 includes both dissociation ions.

⁵ Representative CAS numbers are included in this summary table. Section 4.2.9 includes a full list of CAS numbers.

L = Low hazard **M** = Moderate hazard **H** = High hazard _ Endpoints in colored text (**L**, **M**, and **H**) were assigned based on experimental data.

Endpoints in black italics (**L**, **M**, and **H**) were assigned using estimated values and professional judgment (Structure Activity Relationships).

◇ Hazard designations, which are based on the presence of epoxy groups, arise from the analysis of low molecular weight oligomers (molecular weight <1,000) that may be present

in varying amounts. The estimated human health hazards for higher molecular weight (>1,000) components, which contain epoxy groups, are low for these endpoints.

‡ Concern based on potential inhalation of small particles less than 10 microns in diameter that may be present in varying amounts.

§ Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter.

Δ Persistent degradation products expected (none found in this report).

R Recalcitrant: substance is or contains inorganics, such as metal ions or elemental oxides, that are expected to be found in the environment >60 days after release.

Material alternatives

The use of some of the chemical alternatives mentioned above also includes some modifications of the base polymer. This section concerns possible alternative non-combustible materials or non-flammable resins without flame retardant. The US EPA's Design for the Environment (DfE) Program did not include an assessment of such alternatives.

The assessment of alternatives to TBBPA by the Lowell Center for Sustainable Production (Morose, 2006) mentions polyimide resin as an alternative to epoxy resin for making printed wiring board laminates. Polyimide printed wiring boards are usually inherently flame retardant. The assessment indicates that there are limited data available to estimate the health and environmental effects for these modified resins. Other potential alternatives for high temperature applications are PTFE, other fluoropolymers, cyanates and epoxy-PPE blends, and even ceramics. Cyanates, PTFE, and inorganic substrates are usually inherently flame retardant. The report indicates that the health and environmental performance of the fluoropolymers may be problematic, but does not include a detailed assessment of alternative materials.

7.1.4 Alternatives to BFRs in textiles

Alternatives to BFRs in textiles and/or furniture have been assessed by the Swedish Chemicals Inspectorate (Posner, 2004; Posner, 2006), the Lowell Center for Sustainable Production (Lowell, 2005) and partly included in the quoted assessments by Defra (Stevens *et al.*, 2010) and US EPA (2012). None of these studies include a full assessment of the technical and economic feasibility and an environmental and health assessment.

When incorporating flame retardants into textiles, surface treatment is often used. There are two types of surface treatments: finishes and coatings (Stevens *et al.*, 2010). Finishes are applied by impregnating the fabrics in an aqueous solution of the chemical. Coatings are applied by incorporating a layer of flame retardant to the fabric, generating a heterogeneous fabric/polymer composite.

Typical chemical finishes involve the use of phosphates and polyphosphates, phosphorus amides, phosphonium derivatives, borax and boric acid or halogenated FRs. Typical coatings used are, for instance, natural and synthetic rubbers, poly(vinyl chloride), poly(vinyl alcohols), formaldehyde-based resins, acrylic copolymers, polyurethanes, silicones and fluorocarbons etc. Fire retardants used for coatings include phosphates and phosphonates, e.g. triaryl phosphate, cresyl diphenyl phosphate or phosphinate. Brominated derivatives such as decabromodiphenyl oxide (DBDPO) and hexabromocyclododecane (HBCD) may be applied as a backcoating in the form of a paste or foam. (Stevens *et al.*, 2010). Flame retardants used for finishes include phosphates and polyphosphates, phosphorous amides, phosphonium derivatives, antimony trioxide, borax and boric acid or halogenated flame retardants (Stevens *et al.*, 2010). Modern alternatives to the traditional treatment techniques are being developed. These include adding plasma induced-graft-polymerization and phosphate and phosphinate FRs to the surface and embedding nanoparticles on to textile substrates by a plasma polymerization/co-sputtering process. Neither process is yet commercially available. (Stevens *et al.*, 2010).

For more details on the alternative flame retardants and alternative materials, please consult the mentioned assessments.

The Lowell (2005) report concludes that decaBDE is a low-cost method for treating textiles. There is a multitude of non-halogen replacements on the market, including alternative flame retardants, fibres, fibre blends, barrier layers, nonwovens, and other approaches. These substitutes have their own individual cost, performance, and aesthetic trade-offs. While there is no single replacement for decaBDE for textiles, the multitude of options on the market make it clear that viable market-ready approaches exist.

Posner (2004) concludes that the fact that organic bromine compounds were still used (in 2004) instead of their non-halogenated alternatives was due to a number of factors, only a few of which were technical in nature. Combined with low price, one of the most common reasons why the alternatives do not always make a breakthrough is that the market prefers to use tried-and-tested flame retardants. According to the author, the flame retardants that ultimately are likely to completely replace decaBDE:antimony dioxide are the intumescent systems and those based on phosphorus chemistry. Flame-resistant fibres combined with combustible fibres may also be used successfully in certain applications.

7.1.5 Alternatives to other BFRs

For the BFRs introduced as alternatives to regulated substances, the evaluated alternatives would typically also be potential alternatives for these substances. This survey has not included a review of available alternatives assessments for other BFRs, such as reactive BFRs used in PU foam and other thermosets.

7.2 Historical and future trends

As indicated in the historical use of the BFRs shown in section 3.4, the main trend has so far been the replacement of the PBDEs with other BFRs as a consequence of regulatory action. The BFRs' share of the total market for flame retardants has not changed significantly over the years.

The regulatory pressure on the remaining decaBDE applications and voluntary phase out of the manufacture in the USA by the major manufacturers will likely lead to a continued replacement of decaBDE, mainly with other BFRs, both polymeric and non-polymeric.

In recent years the major manufacturers of BFRs have marketed some polymeric BFRs as "eco-friendly" or "green" alternatives to the traditional non-polymeric BFRs. No data are available to indicate to what extent they have actually replaced the traditional flame retardants.

It is expected that polymeric BFRs will substitute for HBCDD over the coming years; the major manufacturers of BFRs report on expanding the capacity for the specific polymeric BFRs.

Many manufacturers of electronics have moved toward replacement of BFRs – in particular the additive BFRs during the last 10 years. One of the main drivers is Non-Governmental Organization (NGO) pressure to address environmental issues (iNEMI, 2010). Companies who phase out the BFRs typically also intend to phase out chlorinated substances and chlorinated polymers (e.g. PVC); the same is true for halogen-free articles.

According to a ChemSec market review from 2010, particularly the electronics companies in the IT and communications sector are at the forefront when it comes to eliminating the use of brominated flame retardants (ChemSec, 2010). The market overview covers 28 electronic companies. Three out of four companies officially state that by 2014 they will have products totally free from brominated flame retardants and/or PVC on the market (ChemSec, 2010).

The International Electronics Manufacturing Initiative comprising 100 members (among these major electronic companies such as Dell, IBM, HP, Intel, Hitachi and Samsung) supports removal of halogenated flame retardants and has conducted a number of projects under the iNEMI HFR-Free Programs.

7.3 Summary and conclusions

Both brominated and non-halogenated alternatives are available for replacement of the main brominated flame retardants. Though a large number of assessments of alternatives to BFRs have been

undertaken during the last 15 years, comprehensive assessments covering technical and economic feasibility, human health and environmental assessments and an assessment of potential formation of hazardous degradation products are not available.

DecaBDE - Alternatives to decaBDE are readily available, and the substance has already been phased out in most electrical and electronic products as a consequence of the RoHS Directive. The main alternatives are BFRs such as DBDBE, EBTEBPI and TTBP-TAZ. The substances have slightly better scores than decaBDE on the evaluated human health and environmental parameters. Better scores on the evaluated parameters have been found for some polymeric BFRs and some of the non-halogenated FRs. The evaluated polymeric BFRs have scores similar to the less problematic of the non-halogenated FRs. The available assessments do not include an assessment of degradation products and the performance of the flame retarded materials during fire or uncontrolled combustion. The presence of BFRs has been demonstrated to negatively impact e.g. the formation of smoke and result in formation of hazardous substances by thermal stress. Most studies have, however, addressed the PBDEs and other BFRs with high risk of formation of hazardous substances and not e.g. the polymeric BFRs. The significance of formation of hazardous substances and fumes in a life cycle perspective seems to be the main issue when comparing the impact of the non-regulated BFRs and non-halogenated FRs.

HBCDD - Polymeric BFR alternatives to HBCDD have recently been developed and introduced in the market and the main manufacturers of BFRs are currently increasing the production capacity to meet the demand. No independent evaluation of health and environmental properties is available. According to industry information, the polymeric BFRs are potentially persistent (not biodegradable) but with low potential for bioaccumulation and low potential for toxicity. One of the main issues with the polymeric BFRs seems to be the length composition of the oligomers as this parameter highly influences the properties of the substances. As mentioned for decaBDE alternatives, another issue is the possible formation of toxic degradation products and fumes. No non-halogenated chemical alternatives are available for the use in EPS/XPS. For the main application areas, EPS/XPS insulation foams, a number of material alternatives are available. The alternatives have various advantages and disadvantages. The alternative materials typically have better fire performance and contain fewer problematic chemical substances. Among the combustible insulation materials, the EPS was the material yielding fewer toxic fumes. The price of the cheapest alternatives ranges approximately from the same price as for flame retarded EPS to 30% more.

TBBPA - For TBBPA used additively, both BFR and non-halogenated alternatives are available, and they are similar to the evaluated alternatives to decaBDE. For the main application of TBBPA, reactive use in laminates for printed circuit boards, a number of alternatives are marketed and account today for about 5-10% of the market of printed circuit boards. The alternatives score slightly better than TBBPA except for persistence in the environment. Several of the alternatives are more persistent than TBBPA, but none of the alternatives are bioaccumulative. The available assessments do not include the potential for formation of hazardous degradation products and fumes. The phase out of TBBPA in printed circuit boards is often accompanied by the substitution of other BFRs and chlorinated substances and polymers in order to manufacture halogen-free electronic equipment.

Textiles and furniture - Both decaBDE and HBCDD are used as flame retardants in textiles and furniture. There is a multitude of non-halogenated alternatives on the market, including alternative flame retardants, inherently flame retardant fibres, fibre blends, barrier layers, nonwovens, and other approaches. These substitutes have their own individual cost, performance, and aesthetic trade-offs. While there is no single replacement for decaBDE for textiles, the multitude of options on the market makes it clear that viable market-ready approaches exist. The same apply to the use of HBCDD in textiles.

Other BFRs - For the BFRs introduced as alternatives to regulated substances, the evaluated alternatives would typically also be potential alternatives. This survey has not included a review of available alternatives assessments for other BFRs such as reactive BFRs used in PU foam and other thermosets.

Main data gaps.

As mentioned, the available assessments do not include an assessment of degradation products and the performance of the flame retarded materials during fire or uncontrolled combustion. The presence of BFRs has been demonstrated to negatively impact e.g. the formation of smoke and formation of hazardous substances through thermal stress. Most studies have, however, addressed the PBDEs and other BFRs with high risk of formation of hazardous substances and not e.g. the polymeric BFRs. The significance of formation of hazardous substances and fumes in a life-cycle perspective seems to be the main issue when comparing the impact of the non-regulated BFRs and non-halogenated FRs. Data on the effect of non-halogenated FRs on the formation of fumes and hazardous substances are limited and comparative assessments of different types of BFRs and non-halogenated FRs on these parameters are lacking.

The authors of a recent review of persistence, bioaccumulation, and toxicity of non-halogenated FRs, as one of the outcomes of the ENFIRO project, conclude that large data gaps were identified for the physico-chemical properties and the PBT properties of the reviewed non-halogenated FRs. To assess whether the presently reviewed non-halogenated are truly suitable alternatives, each compound should be examined individually by comparing its PBT values with those of the equivalent halogenated flame retardant. Until more data are available, it remains impossible to accurately evaluate the risk of each of these compounds, including the ones that are already extensively marketed.

8. Overall findings and conclusions

The results of the survey is summarised in the "Conclusion and summary" chapter, while this chapter summarises the main findings and issues identified and main data gaps.

8.1 Main findings

PBBs and PBDEs

For the BFRs currently addressed by the POPs Regulation, hexaBB, c-pentaBDE and c-octaBDE, the uses are restricted in the EU except for some exemptions to the RoHS Directive, and the substances are not produced any more according to the available reviews. The remaining issues have been summarised as follows in the Danish national implementation plan for the Stockholm Convention: 1) Validation of destruction of technical pentaBDE (this issue seems to have been solved as mentioned in this report), 2) Possible separation of household waste containing pentaBDE. 3) Guidelines concerning articles which must not be reused and recycled. 4) Examine the possibilities of identifying pentaBDE in shredder waste.

DecaBB, which was the only PBB used in Denmark in 1999, is restricted in EEE, but otherwise not restricted in the EU and not covered by the Stockholm Convention. According to the available information, however, none of the PBBs are produced in any country today.

DecaBDE has been restricted for some years in EEE, but is otherwise not restricted in the EU and it remains one of the main BFRs. DecaBDE have been identified as substances of very high concern (SVHC) and an Annex XV SVHC dossier has been submitted. The dossier suggests that decaBDE meet the definition of a PBT/vPvB-forming substance due to a high probability that decaBDE by debromination is transformed in soil and sediments to form lower brominated substances which either have PBT/vPvB properties, or act as precursors to substances with PBT/vPvB properties. DecaBDE has recently been nominated for the Stockholm Convention on the basis that the substance fulfils the criteria for persistence, bioaccumulation and long-range transport and that decaBDE alone and/or in concert with its debromination products have the potential to damage human health and/or the environment (Norway, 2013). The dossier and the nomination report are currently under review. The production of decaBDE has voluntarily been phased out by the major manufacturers in the USA. In Germany and Denmark the PBDEs were already phased out in the 1990s. The successful replacement of decaBDE in EEE and the voluntary phase out in the USA clearly demonstrate that alternatives are available and decaBDE today is mainly used as a low-cost solution. Drop-in alternatives as DBDPE and EBTEBPI seem to have a better environmental and health profile than decaBDE, but some concern has been raised about their overall environmental performance. Polymeric BFRs and non-halogenated alternatives are marketed as well for the main use areas, but at higher costs (further discussed under the Alternatives chapter). A restriction of decaBDE is not expected to have any negative impact on manufacturers of plastic parts in Denmark.

HBCDD

HBCDD has recently been included in the list of substances subject to authorisation (Annex XIV to REACH) with a sunset date 21 August 2015. It has furthermore been included in the list of restricted substances under the Stockholm Convention with a time-limited exemption for the main application area, EPS/XPS insulation materials. Polymeric BFRs have recently been introduced as drop-in alternatives to HBCDD and the major manufacturers of BFRs are currently increasing the production capacity to meet the expected demand. Non-halogenated alternatives have not been available to the present, but the flame retarded EPS/XPS can be replaced by other insulation materials. Compared to other EU Member States, the use of flame retarded EPS/XPS is limited in Denmark because non-flammable insulation materials have been the preferred option. The use of EPS for building insulation seems to be increasing e.g. for "zero energy" houses. HBCDD is used in limited quantities for production in Denmark. A restriction of HBCDD is not expected to have a significant negative impact on manufacturers of EPS/XPS or users of the materials in Denmark.

TBBPA

TBBPA is mainly used as reactive FR in printed circuit boards. In 1999, TBBPA and its derivatives were the main additive BFRs used for manufacturing in Denmark, but this does not appear to be the general situation at the EU level today, where additive use of TBBPA and derivatives account for a small proportion of the use of additive BFRs. Additive use of TBBPA is mentioned as an example of BFRs included in LOUS. The rationale is that in reactive use of TBBPA, the TBBPA is not present *per se* in the final products, but has rather been built into the polymer structure. The EU Risk Assessment estimated that volatile loss during service life of articles from additive flame retardants use was approximately 15% of the total emissions to the air, whereas other losses from the service-life of articles was considered negligible. However, according to the EU Risk Assessment, the direct consumer exposure to TBBPA is likely to be insignificant and EFSA concludes that current dietary exposure to TBBPA in the EU does not raise a health concern. The substance is classified as toxic in the aquatic environment, but does not meet the REACH PBT criteria based on the currently available data and is furthermore not covered by any pipeline activities under REACH. TBBPA can undergo debromination under anaerobic conditions to form bisphenol-A and is thus linked to the discussion about the potential impact of that substance. The main source of release to the environment was identified to be manufacturing processes in the EU risk assessment. A voluntary program by manufacturers and downstream users of the substance has in recent years significantly reduced total releases. Alternatives to the additive use are similar to alternatives to decaBDE. Alternatives to the reactive use are usually non-halogenated FRs. Replacement of TBBPA in printed circuit boards appears to be part of a process where all halogen containing compounds and plastics are replaced in order to be able to market the equipment as halogen-free. One of the drivers is pressure from international environmental NGOs.

DBDPE and EBTEBPI

The two substances have application spectra quite similar to decaBDE and can be used as drop-in alternatives to decaBDE. In the EU and apparently also in China, DBDPE is used in much larger quantities than EBTEBPI. DBDPE is found in sewage sludge in the Nordic Countries in concentrations of the same magnitude as decaBDE. The available data indicate that contamination of the Swedish environment with DBDPE has already approached that of decaBDE, and that this contamination is primarily occurring via the atmosphere. DBDPE is suggested for further monitoring in the Arctic. Very limited data on EBTEBPI are available as the substance has not been included in screenings of BFRs in the Nordic and Arctic environments. DBDPE is included in the Community Rolling Action Plan under REACH. DBDPE is persistent but does not meet the REACH PBT criteria based on the currently available data; however, there are currently insufficient reliable data. A UK Environment Risk Assessment considered that there was a potential for DBDPE to undergo reductive debromination by analogy with decaBDE and it has recently been shown that DBDPE may have potential to undergo photolytic debromination reactions. However, the environmental significance of such reactions is currently unknown. According to a TC NES sub-group on identification of PBT

and vPvB substances evaluation, EBTEBPI was not considered a PBT substance. Alternatives to DBDPE and EBTEBPI are either polymeric BFRs or non-halogenated FRs, some of which have better environmental and health profiles in screening assessments.

Other BFRs

Data on the consumption of other BFRs are scarce. The public part of the REACH registrations provides some indication on the production and import in the EU in ranges of a factor of 10 of the non-polymeric BFRs, but the polymeric BFRs are not subject to registration and no information on the market volumes of these substances are available. In general, limited data on environmental and human health hazards as well as exposure is available and the PBT status of these substances is currently unknown.

A screening of 16 "new" BFRs in the Nordic environment indicated that the concentrations of the "new" BFRs are, with a few exceptions, on the same order of magnitude or lower compared to the sum of BDE congeners BDE-28, -47, -99, -100, -153 and -154 included as priority substances under the Water Framework Directive.

With the purpose of identifying BFRs for priority for further studies, the following table summarises information on other BFRs demonstrated in the environment, and/or registered under REACH or with statistics on import to the EU.

Of the additive BFRs with registered import or production in the EU (i.e. production and import is above 100 t/y) the following have not been included in the recent screening of BFRs in the Nordic environment, and no data on their occurrence in the Nordic or Arctic environments have been identified: EBTEBPI, TTBP-TAZ, 4'-PeBPOBDE2o8 and TTBNPP. The screening of BFRs in the Nordic environment also identified some reactive BFRs in significant concentrations (DBP and TBP). Four of the registered reactive BFRs have not been included in the screening: DBNPG, HEEHP-TEBP and TEBP-Anh, halogenated polyetherpolyol B and tetrabromophthalic anhydride based diol.

TABLE 52
OTHER BFRS DEMONSTRATED IN THE NORDIC OR ARCTIC ENVIRONMENT, REGISTERED UNDER REACH OR WITH STATISTICS ON IMPORT TO THE EU

Abb.	Common name/description	Man. *2	Registered import /production t/y	Detected in Nordic or Arctic envi- ronment *1	Evaluated by EFSA
Additive BFRs					
4'-PeBPOBDE2o8	Bis(pentabromo-phenoxy) benzene		import: 216 (2011, together with pentaBDE)	Not incl. in Nordic scr.	x
BEH-TEBP	Tetrabromophthalate ester	x	100-1000	Nordic, Arctic	x
BTBPE	Bis (tribromophenoxy) ethane	x	import 82 (average 2006/2007; conf. for 2011)	Nordic, Arctic	x
DBDPE	Decabromodiphenyl ethane	x	1,000 +	Nordic, Arctic	x
DBE-DBCH	1,2-Dibromo-4-(1,2- dibromoethyl)cyclohexane			Nordic, Arctic	x
DPTE	1,3,5-Tribromo-2-(2,3- dibromopropoxy)benzene			Arctic	
EBTEBPI	Ethylenebis(tetrabromophthalimide)	x	100 - 1,000 Imp: 181 (2011)	Not incl. in Nordic scr.	x

Abb.	Common name/description	Man. *2	Registered import /production t/y	Detected in Nordic or Arctic envi- ronment *1	Evaluated by EFSA
EH-TBB	Ethylhexyl tetrabromobenzoate	x		Nordic, Arctic	x
HBB	Hexabromobenzene			Nordic, Arctic	x
PBEB	Pentabromoethylbenzene			Nordic, Arctic	x
PBT	Pentabromotoluene			Nordic, Arctic	x
TBA	Tribromoanisole			Nordic	
TTBNPP	Tris(tribromo-neopentyl)phosphate	x	100-1000	Not incl. in Nordic scr.	x
TTBP-TAZ	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine	x	1,000 - 10,000	Not incl. in Nordic	x
Reactive BFRs					
DBNPG	Dibromoneopentyl glycol		100-1,000	Not incl. in Nordic scr.	x
DBP	2,4-dibromophenol			Nordic, Arctic	x
HEEHP-TEBP	Mixture of the diester/ether diol of tetra- bromophthalic anhydride and phosphate ester.	x	100 - 1,000	Not incl. in Nordic scr.	x
TBP	2,4,6-tribromophenol	x	1,000-10,000	Nordic, Arctic	x
TEBP-Anh	Tetrabromophthalic anhydride	x	100-1,000	Not incl. in Nordic scr.	
-	Halogenated polyetherpolyol B	x	1,000 - 10,000	Not incl. in Nordic	
-	Tetrabromophthalic anhydride based diol	x	1,000 - 10,000		

*1 N: among the BFRs detected in highest concentration in the Nordic Environment. A: detected in Arctic – marked in bold and underline = suggested as particular relevant for monitoring in the Arctic. "Not incl in Nordic scr." indicates that the substance was not been included in the screening of BFRs in the Nordic Environment. It has not been checked if the substance has been included in any of the studies in the Arctic.

*2 Manufactured by major manufacturers of BFRs

The consumption of polymeric BFRs seems to be increasing and some of the polymeric BFRs are marketed as "green" alternatives to some of the regulated BFRs. The polymeric BFRs are persistent, but in general the releases, bioaccumulation and toxicity of the polymeric are relatively low, but dependent on chain length. Concern has been raised on potential degradation products. The polymeric BFRs are not subject to registration under REACH and limited information on consumption volumes, as well as environmental and human health data, is available for the polymeric. The flame retardancy action of the polymeric BFRs is the same as for other BFRs and it has been argued that when under thermal stress, hazardous brominated substances may be formed, but limited data are available as to this process.

8.2 Data gaps

For many of the BFRs, the data gaps far exceed the available information. The following summarises the main data gaps identified in the survey considered to be of importance for the Danish EPA's assessment of the need for further measures.

Consumption of BFRs - Detailed data on the use of BFRs other than the PBDEs, HBCDD and TBBPA globally and in the EU are not available in the public literature. The public part of the REACH registrations provide some indication of the production and import in the EU in ranges of a factor of 10, but the polymeric BFRs are not subject to registration and no information on the market volumes of these substances are available. More detailed information may, however, be available for the authorities in the confidential part of the registrations. The lack of consumption data constrains an assessment of the potential releases and exposure of humans and the environment and thereby also constrains a comprehensive risk assessment of the different BFRs and an assessment of the need for further regulatory action. Furthermore, it constrains an assessment of the trends in the use of the BFRs and the monitoring of the effects of the regulatory actions.

Uncontrolled disposal of WEEE - Updated assessments of the illegal export of WEEE and the legal export of second hand EEE to developing countries from Denmark and the EU and the actual fate of the equipment in the countries are lacking. It constrains an assessment of the need for further measures in order to prevent illegal export and uncontrolled waste disposal and an assessment of the potential efficacy of different measures.

Environmental assessments - Few data are currently available for a large number of other BFRs than the main BFRs; consequently, the PBT status of these substances is currently unknown.

Human health assessment - Few data are currently available for a large number of other BFRs than the main BFRs; consequently, the PBT status of these substances is currently unknown.

Environmental monitoring and exposure - Some monitoring data are available based on a review of the available data on BFRs in Arctic biota and abiotic media combined with information on the substances' potential for bioaccumulation. The Danish Centre for Environment and Climate include five "new" brominated flame retardants in a list of candidates for inclusion in the Arctic monitoring programme: DPTE, BEH-TEBP, TBB, BTBPE, and DBDPE. Of these substances only BEH-TEBP and DBDPE are registered in quantities of more than 100 t/y while the latest import data for BTBPE indicate an average annual import just below 100 t/y.

Human monitoring and exposure – A recent review of BFRs in human biomonitoring (Vor-kamp, 2012) concludes that the majority of studies concern the PBDEs while BB-153, HBCDD and TBBPA have been included only in a few studies. Virtually nothing is known about other BFRs. Furthermore, little information is available on metabolites, although hydroxylated PBDEs have been associated with disruptions of thyroid hormone transport. Analytical efforts will be required to include additional BFRs and potentially toxic metabolites in human biomonitoring.

Assessment of alternatives – The most comprehensive assessment available indicates that brominated alternatives with a better environmental and health profile than the PBBs and the PBDEs are available and have already substituted for nearly all application of PBBs, pentaBDE, octaBDE and decaBDE in electrical and electronic equipment. Recently, polymeric BFR alternatives to the main applications of HBCDD have been developed and marketed. Non-halogenated FRs are the main alternatives to the reactive use of TBBPA. At the moment, there is a strong movement toward non-halogenated FRs in electronic products in particular, with the goal of manufacturing halogen-free articles. The assessments do not clearly indicate major differences between the BFRs with the best environmental and health profiles and the non-halogenated alternatives. As a result of the lack of data, however, the assessment is to a large extent based on model data and expert estimates.

The authors of a recent review of persistence, bioaccumulation, and toxicity of non-halogenated FRs conclude that large data gaps were identified for the physico-chemical and the PBT properties of the reviewed non-halogenated FRs. To assess whether the presently reviewed non-halogenated FRs

are truly suitable alternatives, each compound should be examined individually by comparing its PBT values with those of the halogenated flame retardants that they may substitute for. Until more data are available, it remains impossible to accurately evaluate the risk of each of these compounds, including the ones that are already extensively marketed.

Formation of polybrominated dioxins and furans (PBDD/F) – Knowledge about the significance of the different types of BFRs on the formation of brominated (PBDD/F) and mixed brominated/chlorinated dioxins and furans (PXDD/F) as well as other hazardous substances by different types of thermal processes is limited for most BFRs. Furthermore, quantitative assessments of the contribution of brominated and mixed brominated/chlorinated dioxins and furans from the burning of BFRs to the total dioxins/furan load to the environment are lacking. A wealth of literature on PBDD/F and PXDD/F in articles, food, air, different environmental samples, etc. has been published since the review of the International Program of Chemical Safety was published in 1998.

Formation of hazardous fumes - The available assessments generally do not include an assessment of degradation products and the performance of the flame retardant materials during fire or uncontrolled combustion. The presence of BFRs (or at least some types of BFRs) has been demonstrated to negatively impact e.g. the formation of smoke and result in formation of hazardous fumes through thermal stress. These effects appear to be the main argument for the halogen-free electronics movement. Most studies have addressed the PBDEs and other BFRs with high risk of formation of hazardous substances and not e.g. the polymeric BFRs. The significance of formation of hazardous substances and fumes in a life cycle perspective appears to be the main issue when comparing the impact of non-regulated BFRs and non-halogenated flame retardants. Data on the effect of non-halogenated FRs on the formation of fumes and hazardous substances are limited and comparative assessments of the effects of different types of BFRs and non-halogenated FRs by fire and uncontrolled combustion are lacking.

9. Abbreviations and acronyms

Abbreviations for the individual brominated flame retardants are listed in Appendix 2

ADI	Acceptable daily intake
AMAP	Arctic Monitoring and Assessment Programme
BAPP	Bisphenol A bis-(diphenyl phosphate)
BAT	Best Available Techniques
BCF	Bioconcentration factor
BFR	Brominated flame retardants
BMD	Benchmark dose
BSEF	Bromine Science and Environment Forum
CAS	Chemical Abstract Service
CEFIC	European Chemical Industry Council
CLP	Classification, Labelling and Packaging
CMR	Carcinogenic, mutagenic or reprotoxic
COHIBA	Control of hazardous substances in the Baltic Sea region
CONTAM	EFSA Panel on Contaminants in the Food Chain (under)
CORAP	Community rolling action plan
c-pentaBDE	Commercial pentaBDE (mixture of different PBDEs)
c-octaBDE	Commercial octaBDE (mixture of different PBDEs)
DfE	Design for the Environment
DPA	Danish producer responsibilities system for WEEE
ECB	European Chemicals Bureau
EBFRIP	European Brominated Flame Retardant Industry Panel (EBFRIP) (dissolved in 2011)
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EEE	Electrical and electronic equipment
ENFIRO	EU-funded collaborative research project
E-PRTR	European Pollutant Release and Transfer Register
EQC	Equivalent level of concern
ESIS	European chemical Substances Information System
EU	European Union
FAI	Free androgen index
FR	Flame retardant
FSO	Fugebranchen, Danish trade organisation of the sealant industry
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
iNEMI	International Electronics Manufacturing Initiative
Kow	Octanol/water partitioning coefficient
LCA	Life-cycle assessment
LOAEL	Lowest observed adverse effect level
LOD	Limit of detection
LOUS	List of Undesirable Substances (of the Danish EPA)

LOQ	Limit of quantification
MOE	Margin of exposure
MSWI	Municipal solid waste incinerators
MWWTP	Municipal waste water treatment plant
NOEC	No observable effect concentration
NOAEL	No observable adverse effect level
NOVANA	Danish national monitoring and assessment programme
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PEC	Predicted environmental concentration
PBB	Polybrominated biphenyls
PBDE	Polybrominated diphenyl ethers
PCDD/F	Polychlorinated dibenzo-p-dioxins and dibenzofurans
PBDD/F	Polybrominated dibenzo-p-dioxins and dibenzofurans
PXDD/F	Mixed polybrominated/chlorinated dibenzo-p-dioxins and dibenzofurans
PBT	Persistent, bioaccumulative and toxic
PIN FR	Phosphorus, Inorganic and Nitrogen Flame Retardants
PINFA	Phosphorus, Inorganic and Nitrogen Flame Retardants Association
PNEC	Predicted no-effect concentration
POPRC	POPs Review Committee (under the Stockholm Convention)
PRAB	Practical abbreviations
RDP	Resorcinol bis (diphenyl phosphate)
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RAR	Risk Assessment Report
RoHS	Restriction of the use of certain hazardous substances [in electrical and electronic equipment] (Directive 2011/65/EU)
SHBG	Sex hormone binding globulin
STP	Sewage treatment plant
SVHC	Substance of Very High Concern
TDI	Tolerable daily intake
TPP	Triphenyl phosphate
UB	Upper bound. Data reported to be below the limit of detection (LOD) or limit of quantification (LOQ) is represented by the LOD/LOQ
UK	United Kingdom
US EPA	United States Environmental Protection Agency
UL94	Underwriters Laboratories 94 classification
LB	Lower bound. Data reported to be below the limit of detection (LOD) or limit of quantification (LOQ) is represented by 0.
vBvP	Very bioaccumulative, and very persistent
VECAP	Voluntary Emissions Control Action Programme
V-0; V-2	UL94 classes
WEEE	Waste electrical and electronic equipment

UNITS

bw	Body weight
d.w.	Dry weight
l.w.	Living weight
w.w.	Wet weight
f.w.	Fat weight

Plastics and rubbers

ABS	acrylonitrile butadiene styrene
BMC	Bulk molding compound, polyester resin/glass fibre premix

SBR	Styrene-butadiene rubber
EPDM	Ethylene propylene diene monomer
EPS	Expanded polystyrene
EPDM	Ethylene propylene diene monomer (rubber)
EVA	Ethylene vinyl acetate
HIPS	High-impact polystyrene
HIPS/PPO	High-impact polystyrene/ polyphenylene oxide blend
PA	Polyamide
PAEK	Polyaryletherketone
PBT	Polybutylene terephthalate
PC	Polycarbonate
PC	Polycarbonate
PC/ABS,	Polycarbonate/ acrylonitrile butadiene styrene blend
PE	Polyethylene
PE/EVA	Polyphenylene oxide/ethyl vinyl acetate
PES	Polyethersulfone
PET	Polyethylene terephthalate
PIR	Polyisocyanurate
PK	Polyketone
PP	Polypropylene
PPE	Polyphenylene ether
PPO	Polyphenylene oxide
PS	Polystyrene
PSU	Polysulfone
PU	Polyurethane
PVC	Polyvinylchloride
SMC	Sheet moulding compound (SMC): a flat pre-preg material, comprising thickened resin, glass fibre and fillers, covered on both sides with polyethylene or nylon film, ready for press-moulding
TPU	Thermoplastic polyurethane
UPA; UPS	Unsaturated polyesters
XL PE/EVA	Cross-linked polyethylene/ethyl vinyl acetate
XPS	Extruded polystyrene

PBDE congeners

BDE-47	2,2',4,4'-Tetrabromodiphenyl ether
BDE-99	2,2',4,4',5-Pentabromodiphenyl ether
BDE-100	2,2',4,4',6-Pentabromodiphenyl ether
BDE-153	2,2',4,4',5,5'-Hexabromobiphenyl ether
BDE-154	2,2',4,4',5,6'-Hexabromodiphenyl ether
BDE-209	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether

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Appendix 1: Background information to chapter 2 on legal framework

The following annex provides some background information on subjects addressed in Chapter 2. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 2.

EU and Danish legislation

Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave a margin for manoeuvring as to the form and means of implementation. However, there are great differences in the space for manoeuvring between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently, and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a “comitology procedure” involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabelling criteria for specific product groups.
- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, to some extent Danish legislation regulate chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation

REACH and CLP

The REACH Regulation¹¹ and the CLP Regulation¹² are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP

¹¹ Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

¹² Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration

All manufacturers and importers of chemical substances > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered deadlines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

Evaluation

A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation

Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction

If the authorities assess that there is a risk to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling

The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publishes the classification and labelling inventory based on all notifications

received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 6 to the main report.

Ongoing activities - pipeline

In addition to listing substances already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA website also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)

The EU Member States have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating when and by whom a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV

Before a substance is included in REACH Annex XIV and therefore subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list¹³
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions

When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intentions in relation to Annex XV dossiers divided into:

- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

for the three types of Annex XV dossiers.

International agreements

OSPAR Convention

OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

¹³ It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance;
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out;
- guidelines or guidance setting out the way that any programme or measure should be implemented, and
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

HELCOM - Helsinki Convention

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

CLRTAP - Convention on Long-range Transboundary Air Pollution

Since 1979 the Convention on Long-range Transboundary Air Pollution (CLRTAP) has addressed some of the major environmental problems of the UNECE (United Nations Economic Commission for Europe) region through scientific collaboration and policy negotiation.

The aim of the Convention is that Parties shall endeavour to limit and, as far as possible, gradually reduce and prevent air pollution including long-range transboundary air pollution. Parties develop policies and strategies to combat the discharge of air pollutants through exchanges of information, consultation, research and monitoring.

The Convention has been extended by eight protocols that identify specific measures to be taken by Parties to cut their emissions of air pollutants. Three of the protocols specifically address the emission of hazardous substances of which some are included in LOUS:

- The 1998 Protocol on Persistent Organic Pollutants (POPs); 33 Parties. Entered into force on 23 October 2003.
- The 1998 Protocol on Heavy Metals; 33 Parties. Entered into force on 29 December 2003.
- The 1991 Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes; 24 Parties. Entered into force 29 September 1997.

Stockholm Convention on Persistent Organic Pollutants (POPs)

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention – PIC Convention

The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management, and
- a regulatory system applying to cases where transboundary movements are permissible.

Eco-labels

Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower

The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

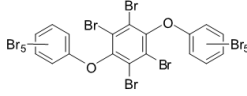
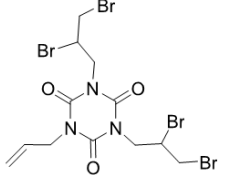
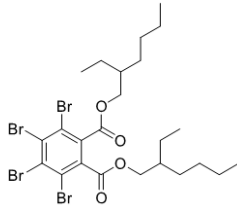
Nordic Swan

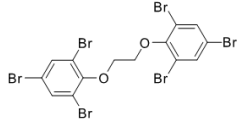
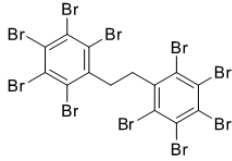
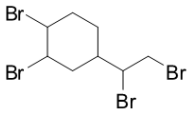
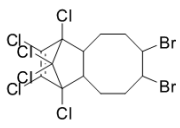
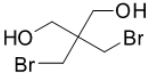
The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" (<http://www.ecolabel.dk/>). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).


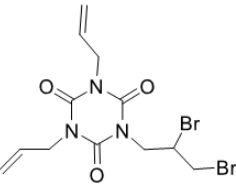
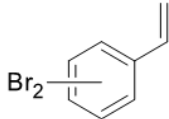

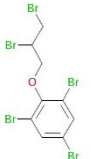
Appendix 2: Physical and chemical properties

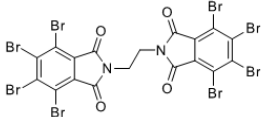
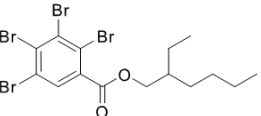
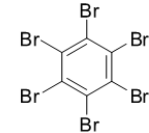
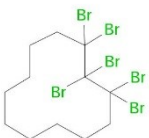
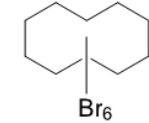
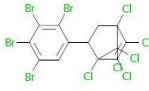
Common names are indicated if a common easily readable name is used e.g. in the description of marketed flame retardants. Bergman *et al.* (2012) lists for each of the substances a number of synonyms a number of common names and trade names. Vapour pressure (Pa), LogK_{ow} and molecular weight is mainly derived from Bergman *et al.* (2012).

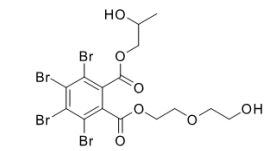
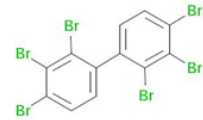
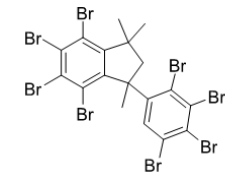
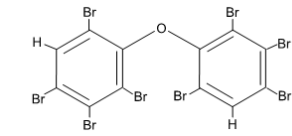
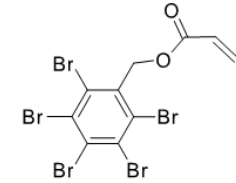
Chemical structures are copied from EFSA reports and ESIS (European chemical Substances Information System). Chemical structures for other substances are shown in Bergman *et al.* (2012).

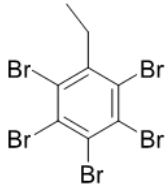
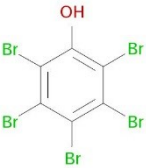

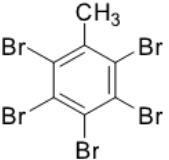
Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
4'-PeBPOB-DE2o8 (DPeTeBrBz)	58965-66-5	1,2,4,5-tetrabromo-3,6-Bis(pentabromophenoxy) benzene	Bis(pentabromophenoxy) benzene	A	C ₁₈ Br ₁₄ O ₂	 EFSA, 2012a	9.17E-17	12.67	1366.85
BDBP-TAZTO	75795-16-3	1,3-Bis(2,3-dibromopropyl)-5-allyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione		A/R	C ₁₂ H ₁₅ Br ₄ N ₃ O ₃	 EFSA, 2012a	8.90E-12	3.55	568.88
BEH-TEBP (BEHTBP)	26040-51-7	Bis(2-ethylhexyl) tetrabromophthalate	Tetrabromophthalate ester	A	C ₂₄ H ₃₄ Br ₄ O ₄	 EFSA, 2012a	1.55E-11	9.34	706.14

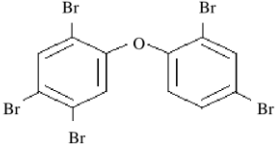
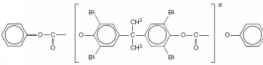
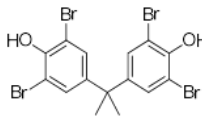
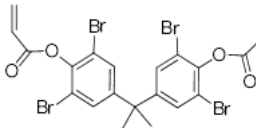
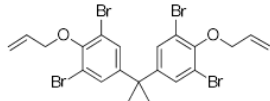
Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
BTBPE	37853-59-1	1,2-Bis(2,4,6-tribromophenoxy) ethan		A	C ₁₄ H ₈ Br ₆ O ₂	 EFSA, 2012a	2.91E-12	8.31	687.64
DBDBE	497107-13-8	Benzene, 1,1'-[oxybis(methylene)]bis[2,3,4,5,6-pentabromo(9Cl)]	Decabromodibenzyl ether	A	C ₁₄ H ₄ Br ₁₀ O		2.31E-16	10.34	987.22
DBDPE	84852-53-9	1,1'-(Ethane-1,2-diyl)bis[pentabromobenzene]	Decabromodiphenyl ethane	A	C ₁₄ H ₄ Br ₁₀	 EFSA, 2012a	6.0E-15	11.1	971.22
DBE-DBCH (TBECH)	3322-93-8	1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane		A	C ₈ H ₁₂ Br ₄	 EFSA, 2012a	2.97E-03	4.82	427.8
DBHCTD	51936-55-1	7,8-Dibromo-1,2,3,4,11,11-hexachloro-1,4,4a,5,6,7,8,9,10,10a-decahydro-1,4-methanobenzocyclooctene		A	C ₁₃ H ₁₂ Br ₂ Cl ₆	 EFSA, 2012a	8.27E-07	7.62	540.76
DBNPG	3296-90-0	2,2-bis(bromomethyl)propane-1,3-diol	Dibromoneopentyl glycol	R	C ₅ H ₁₀ Br ₂ O ₂	 EFSA, 2012a	6.88E-05	0.41	261.94

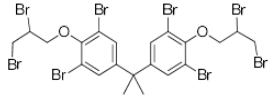
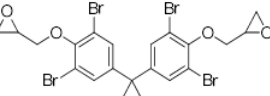
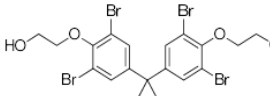
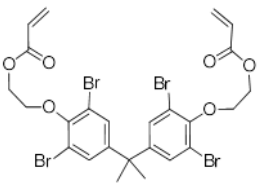
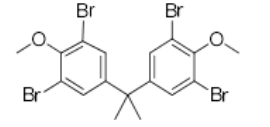

Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
DBP (24DBP ; 2,4-DBP)	615-58-7	2,4-dibromophenol	2,4-dibromophenol	A/R	C ₆ H ₄ Br ₂ O	 ESIS	3.65E+00	3.47	251.9
DBP-TAZTO	57829-89-7	1-(2,3-Dibromopropyl)-3,5-diallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione		A/R	C ₁₂ H ₁₅ Br ₂ N ₃ O ₃	 EFSA, 2012a	2.16E-06	2.66	409.07
DBS	31780-26-4	Dibromostyrene	Dibromostyrene	A/R	C ₈ H ₆ Br ₂	 EFSA, 2012a	na	na	261.94
DecaBB	13654-09-6	Decabromo-1,1'-biphenyl	Decabromobiphenyl	A	C ₁₂ Br ₁₀		< 6E10-6	9.4	943.22
decaBDE	1163-19-5	Bis(pentabromophenyl) ether	Decabromodiphenyl ether	A	C ₁₂ Br ₁₀ O	 ESIS	1.64E-12	na	959.17
DPTE	35109-60-5	1,3,5-tribromo-2-(2,3-dibromopropoxy)benzene		A	C ₉ H ₇ Br ₅ O	 ESIS	6.22 x 10 ⁻⁷ US EPA, 2009	6.3 US EPA, 2009	530.67

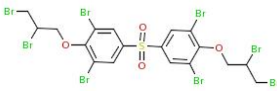
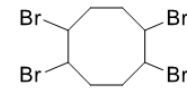
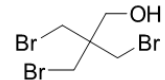
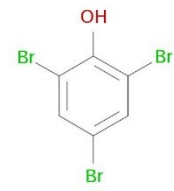
Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
EBTEBPI	32588-76-4	N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide)	Ethylene bis(tetrabromophthalimide)	A	C ₁₈ H ₄ Br ₈ N ₂ O ₄	 <p>EFSA, 2012a</p>	1.97E-25	6.63	951.47
EH-TBB (EHTeBB)	183658-27-7	2-ethylhexyl-2,3,4,5-tetrabromobenzoate		A	C ₁₅ H ₁₈ Br ₄ O ₂	 <p>EFSA, 2012a</p>	3.71E-07	7.73	549.92
HBB (HxBBz)	87-82-1	Hexabromobenzene		A	C ₆ Br ₆	 <p>EFSA, 2012a</p>	1.14E-04	6.11	551.49
HBCDD (HBCD)	25637-99-4 3194-55-6	1,2,5,6,9,10-Hexabromocyclododecane	Hexabromocyclododecane	A	C ₁₂ H ₁₈ Br ₆	 <p>ESIS</p>	1.04E-07	7.92	641.7
HBCYD	25495-98-1	Hexabromocyclodecane	Hexabromocyclodecane	A	C ₁₀ H ₁₄ Br ₆	 <p>EFSA, 2012a</p>	na	na	613.64
HCTBPH	34571-16-9	1,2,3,4,7,7-Hexachloro-5-(tetrabromophenyl)bicyclo[2.2.1]hept-2-ene		A	C ₁₃ H ₄ Br ₄ Cl ₆	 <p>ESIS</p>	1.61E-08	10.24	692.5

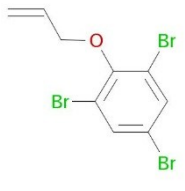
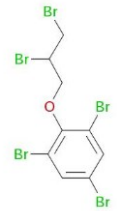
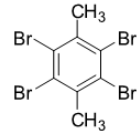
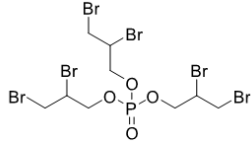
Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
HEEHP-TEBP	20566-35-2	2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	Mixture of the diester/ether diol of tetrabromophthalic anhydride and phosphate ester.	A	C ₁₅ H ₁₆ Br ₄ O ₇	 EFSA, 2012a	4.79E-13	1.04	627.9
HexaBB	36355-01-8	Hexabromo-1,1'-biphenyl	Hexabromobiphenyl	A	C ₁₂ H ₄ Br ₆	 ESIS	6.9 E-6	6.39	627.62
OBTMPI	1084889-51-9 1025956-65-3 893843-07-7 155613-93-7	Octabromotrimethyl-phenyl indane	Octabromotrimethyl-phenyl indane	A	C ₁₈ H ₁₂ Br ₈ (CASno155613-93-7)	 Efsa, 2012a	1.75E-12	15.11	867.52
octaBDE	32536-52-0	Diphenyl ether, octabromo derivative	Octabromodiphenyl ether	A	C ₁₂ H ₂ Br ₈ O	 ECB, 2003	6.59.10-6 ECB, 2003	6.29 ECB, 2003	801.42
PBB-Acr	59447-55-1	(Pentabromophenyl)methyl acrylate	Poly pentabromobenzyl acrylate	R	C ₁₀ H ₅ Br ₅ O ₂	 EFSA, 2012a	3.64E-07	5.6	556.67
PBBB	38521-51-6	Benzene, 1,2,3,4,5-pentabromo 6-(bromomethyl)	Pentabromobenzyl bromide	R	C ₇ H ₂ Br ₆		4.25E-06	6.22	565.51

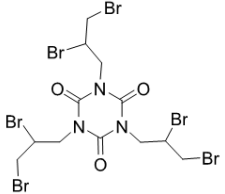
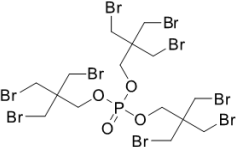
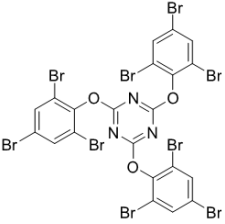
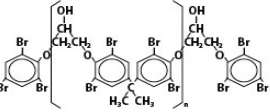
Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
PBBC	58495-09-3	Benzene, 1,2,3,4,5-pentabromo6-(chloromethyl)	Pentabromobenzyl chloride	R	C ₇ H ₂ Br ₅ Cl		8.64E-06	5.95	521.06
PBEB	85-22-3	2,3,4,5,6-Pentabromoethylbenzene	Pentabromoethylbenzene	A	C ₈ H ₅ Br ₅	 EFSA, 2012a	1.56E-04	6.76	500.65
PBP	608-71-9	Pentabromophenol	Pentabromophenol	A/R	C ₆ HBr ₅ O	 ESIS	2.55E-03	5.22	488.59
PBP-AE	3555-11-1	Allyl pentabromophenyl ether	Pentabromophenol allyl ether	A/R	C ₉ H ₅ Br ₅ O	 ESIS	9.21E-05	6.22	528.66
PBT	87-83-2	2,3,4,5,6-Pentabromotoluene	Pentabromotoluene	A/R	C ₇ H ₃ Br ₅	 EFSA, 2012a	6.00E-04	6.25	486.62

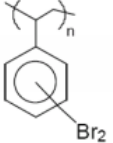
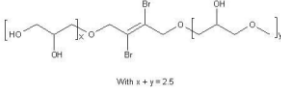
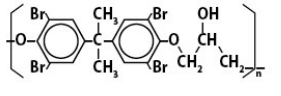
Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
pentaBDE	32534-81-9	Diphenyl ether, pentabromo derivative	Pentabromodiphenyl ether	A	C ₁₂ H ₅ Br ₅ O	 ECB, 2001	4.60 E-5 ECB, 2001	6.57 ECB, 2001	564.72
RDT-7	71342-77-3	Carbonic dichloride, polymer with 4,4'-(1-methylethylidene)bis[2,6-dibromophenol], bis(2,4,6-tribromophenyl) ester	Phenoxy-terminated carbonate oligomer of TBBPA	R	(C ₇ H ₂ Br ₃ O ₂). (C ₁₆ H ₁₀ Br ₄ O ₃) _n . (C ₆ H ₂ Br ₃ O)	 Lassen et al., 2006	na	na	973.59
TBA	607-99-8	2,4,6-tribromoanisole	C ₇ H ₅ Br ₃ O				na	na	344.83
TBBPA (TBBP-A)	79-94-7	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol (tetrabromobisphenol A)	Tetrabromobisphenol A	A/R	C ₁₅ H ₁₂ Br ₄ O ₂	 Efsa, 2011c	1.88E-05	9.69	543.87
TBBPA-BA	55205-38-4	2-Propenoic acid, 1,1'-[(1-methylethylidene)bis(2,6-dibromo-4,1-phenylene)] ester		R	C ₂₁ H ₁₆ Br ₄ O ₄	 EFSA, 2011c	3.84E-11	9.37	651.97
TBBPA-BAE (TBBPA-bAcr)	25327-89-3	1,1'-Isopropylidenebis[4-(allyloxy)-3,5-dibromobenzene]	Tetrabromobisphenol A bis (allyl ether)	A/R	C ₂₁ H ₂₀ Br ₄ O ₂	 EFSA, 2011c	1.83E-08	11.42	642

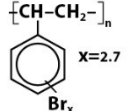
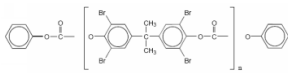
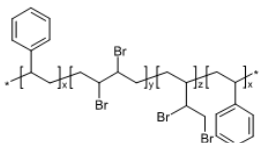
Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
TBBPA-BDBPE (TBBPA-bDiBPrE)	21850-44-2	1,1'-(Isopropylidene) bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene]	Tetrabromo-bisphenol-A, bis (2,3-dibromopropyl ether)	A	C ₂₁ H ₂₀ Br ₈ O ₂	 EFSA, 2011c	2.85E-15	12.99	943.61
TBBPA-BGE	3072-84-2	2,2'-[(1-Methylethylidene)bis[(2,6-dibromo-4,1-phenylene)oxymethylene]]bisoxirane	Brominated epoxy	R	C ₂₁ H ₂₀ Br ₄ O ₄	 EFSA, 2011c	1.64E-10	8.87	656
TBBPA-BHEE (TBBPA-boHEE)	4162-45-2	4,4'-isopropylidenebis(2-(2,6-dibromophenoxy)ethanol)	Tetrabromo-bisphenol A bis(2-hydroxyethyl) ether	A/R	C ₁₉ H ₂₀ Br ₄ O ₄	 EFSA, 2011c	2.89E-12	8.51	631.98
TBBPA-BHEEBA (66710-97-2)	66710-97-2	2-Propenoic acid, 1,1'[(1-methylethylidene)bis[(2,6-dibromo-4,1phenylene)oxy-2,1-ethanediyl]] ester	Tetrabromo-bisphenol A bis(2-hydroxyethyl)ether	R	C ₂₅ H ₂₄ Br ₄ O ₆	 EFSA, 2011c	1.96E-14	10.76	740.07
TBBPA-BME	37853-61-5	Benzene, 1,1'-(1-methylethylidene) bis[3,5-dibromo-4-methoxy	Tetrabromo-bisphenol A bismethyl ether	R	C ₁₇ H ₁₆ Br ₄ O ₂	 EFSA, 2011c	2.25E-06	10.35	571.92
TBBPA-boAc	37853-59-1	4,4'-isopropylidenebis[2,6-dibromophenyl] diacetate	Tetrabromo-bisphenol A bisacetate	A	C ₁₄ H ₈ Br ₆ O ₂		3.28E-09	9.45	627.94

Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
TBBPA-BP	37419-42-4	Phenol, 4,4'-(1-methylethylidene)bis[2,6dibromo-, dipropanoate (9CI)	Tetrabromo-bisphenol A bispropanoate	A	C ₂₁ H ₂₀ Br ₄ O ₄		4.17E-10	10.47	656
TBBPS	39635-79-5	4,4'-sulphonylbis[2,6-dibromophenol]	Tetrabromo-bisphenol S	A/R	C ₁₂ H ₆ Br ₄ O ₄ S		4.03E-10	5.81	565.85
TBBPS-BDBPE	42757-55-1	bis[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl] sulphone	Tetrabromo-bisphenol S bis(2,3-dibromopropyl ether)	A	C ₁₈ H ₁₄ Br ₈ O ₄ S	 ESIS	1.65E-21	8.68	965.6
TBCO	3194-57-8	Cyclooctane, 1,2,5,6-tetrabromo	Tetrabromocyclooctane -	A	C ₈ H ₁₂ Br ₄	 EFSA, 2012a	4.79E-03	5.28	427.8
TBCT	39569-21-6	Benzene, 1,2,3,4-tetrabromo5-chloro-6-methyl		A	C ₇ H ₃ Br ₄ Cl		1.72E-03	6.29	442.17
TBNPA	1522-92-5 36483-57-5	Tribromoneopentyl alcohol [same substance as CAS No 36483-57-5]		R	C ₅ H ₉ Br ₃ O	 EFSA, 2012a	1.60E-03	2.06	324.84
TBP (2,4,6-TBP)	118-79-6	2,4,6-Tribromophenol	2,4,6-Tribromophenol	A/R	C ₆ H ₃ Br ₃ O	 ESIS	2.00E-01	4.4	330.8

Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
TBP-AE (ATE)	3278-89-5	2-(allyloxy)-1,3,5-tribromobenzene	2,4,6-Tribromophenyl allyl ether	A/R	C ₉ H ₇ Br ₃ O	 ESIS	2.40E-02	5.04	370.8
TBP-DBPE (DPTE)	35109-60-5	1,3,5-tribromo-2-(2,3-dibromopropoxy)benzene		A	C ₉ H ₇ Br ₅ O	 ESIS	1.26E-05	5.82	530.67
TBPD-TBP	168434-45-5	Phenol, 2,4,6-tribromo-3-(tetrabromopentadecyl)		A/R	-		na	na	856.78
TBBPS-BME	70156-79-5	Benzene, 1,1'-sulfonylbis[3,5-dibromo-4-methoxy	Tetrabromo-bisphenol S bis-methyl ether	A	C ₁₄ H ₁₀ Br ₄ O ₄ S		3.43E-11	6.05	593.91
TBX	23488-38-2	2,3,5,6-Tetrabromo-p-xylene		A	C ₈ H ₆ Br ₄	 EFSA, 2012a	5.80E-03	6.2	421.75
TDBPP	126-72-7	tris(2,3-dibromopropyl)phosphate		A	C ₉ H ₁₅ Br ₆ O ₄ P	 EFSA, 2012a	3.17E-09	3.71	697.61

Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
TDBP-TAZTO	52434-90-9	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione		A	C ₁₂ H ₁₅ Br ₆ N ₃ O ₃	 <p>EFSA, 2012a</p>	4.09E-13	4.45	728.67
TEBP-Anh	632-79-1	Tetrabromophthalic anhydride	Tetrabromophthalic anhydride	R	C ₈ Br ₄ O ₃		1.27E-09	3.7	463.7
TTBNPP	19186-97-1	Tri[3-bromo-2,2-bis(bromomethyl)propyl]phosphate.	Tris(tribromoneopentyl)phosphate	A	C ₁₅ Br ₉ H ₂₄ PO ₄	 <p>EFSA, 2012a</p>	1.41E-17	7.55	1018.46
TTBP-TAZ	25713-60-4	1,3,5-Triazine, 2,4,6-tris(2,4,6-tribromophenoxy)-		A	C ₂₁ H ₆ Br ₉ N ₃ O ₃	 <p>EFSA, 2012a</p>	2.69E-23	12.97	1067.43
-	135229-48-0	Pratherm EC 20 (as indicated in the pre-registration)	End capped brominated epoxy	A	C ₆ H ₂ OBr ₃ (C ₁₈ H ₁₆ O ₃ Br ₄) _n C ₉ H ₈ O ₂ Br ₃	 <p>ICL, 2013</p>	-	-	15000

Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
-	148993-99-1	Polydibromo-styrene copolymer	Polydibromo-styrene copolymer	A	-	 <p>Lassen et al., 2006</p>	-	-	-
-	158725-44-1	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol, oligomeric reaction products with 1-chloro-2,3-epoxypropane and 2,4,6-tribromophenol	End capped brominated epoxy	A	C ₆ H ₂ OBr ₃ (C ₁₈ H ₁₆ O ₃ Br ₄) _n C ₉ H ₈ O ₂ Br ₃	-	-	-	-
-	68441-62-3	2-butyne-1,4-diol, polymer with 2-(chloromethyl)oxirane, brominated, dehydrochlorinated, methoxylated	Halogenated polyetherpolyol B	R	-	 <p>With x + y = 25</p> <p>Registration</p>	0.0655 Pa	1.29	-
-	68928-70-1	Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with 2,2'-(1-methylethylidene)bis[(2,6-dibromo-4,1-phenylene)oxymethylene]]bis[oxirane]	Brominated Epoxy polymer	A	C ₃ H ₅ O(C ₁₈ H ₁₆ O ₃ Br ₄) _n C ₁₈ H ₁₅ Br ₄ O ₂	 <p>ICL, 2013</p>	-	-	50000

Abbreviation	CAS No	Chemical name	Common name	A/R	Molecular formula	Chemical structure	Vapour pressure (Pa)	LogK _{ow}	Molecular weight
-	88497-56-7	Benzene, ethenyl-, homopolymer, brominated [Brominated Polystyrene]	Brominated Polystyrene	A	(C ₈ H ₈ -xBr _x) _n	 <p>ICL, 2013</p>	-	-	600,000
-	94334-64-2	Carbonic dichloride, polymer with 4,4'-(1-methylethylene)bis[2,6-dibromophenol] and phenol	Phenoxy-terminated carbonate oligomer of TBBPA	A	-	 <p>Lassen et al., 2006</p>	-	-	-
-	1195978-93-8	Benzene, ethenyl-, polymer with 1,3-butadiene, brominated	-	A	-	 <p>US EPA, 2011a</p>	-	-	-

Appendix 3: BFRs marketed by major manufacturers

The following list of brominated flame retardants marketed by the major manufacturers for flame retardants is based on information from the company's websites March 2013. Websites of the following manufacturers have been consulted: Albemarle Corporation, Chemtura, ICL Industrial Products, Tosoh Corporation and Solvay. For each of the substances, examples of product names are provided, but the list of products may not be comprehensive.

CAS No	Substance name (as indicated by manufacturer)	Abb.	Applications (as indicated by manufacturers)	Product name (ex.)	Manufacturer
1163-19-5	Decabromodiphenyl oxide	decaBDE	High bromine content coupled with its exceptional thermal stability makes it the material of choice for a large variety of applications.	FR-1210	ICL
			In elastomers, wire & cable, textile coatings, business machines and television cabinets formulations. SAYTEX 102E flame retardant is particularly effective in polyolefins, styrenic, polyamide and polyester resins.	SAYTEX 102E	Albemarle
			-	Flamecut 110R	Tosoh Corporation
			Additive flame retardant for thermoplastic, elastomeric and thermoset polymer systems, such as HIPS, PBT, nylon, polypropylene, LDPE, EPDM, unsaturated polyester, and epoxy. DE-83R is an excellent flame retardant for coatings and adhesive systems, including backcoatings for fabrics.	DE-83R	Chemtura
118-79-6	2,4,6-tribromophenol	TBP	Reactive flame retardant with a high content of aromatic bromine, used mainly as an intermediate for high molecular weight flame retardants, low MW proprietary flame retardant, including end-capping of brominated epoxies. It is also an effective fungicide and wood preservative	FR-613	ICL
			Flame retardant, antifungal agent (with FIFRA approval) or chemical intermediate in a convenient non-caking briquette form	PH-73FF	Chemtura
12124-97-9	Ammonium Bromide	-	Flame retardant used mainly for chipboard. It can be easily introduced in the early stage of the process to prepare the wet mat which will feed the press	FR-11	ICL

CAS No	Substance name (as indicated by manufacturer)	Abb.	Applications (as indicated by manufacturers)	Product name (ex.)	Manufacturer
135229-48-0	End capped brominated epoxy	-	HIPS, ABS; styrenic copolymers	F-3020	ICL
148993-99-1	Polydibromo-styrene copolymer	-	Designed for polyamides and thermoplastic polyesters (PBT and PET).I has low molecular weight and preferred for applications where improved flow is a requirement.	Firemaster CP-44HF	Chemtura
158725-44-1	End capped brominated epoxy	-	Suitable for use in HIPS and ABS including electronics applications. Exhibits high thermal and UV stability, good low metal adhesion, and excellent flow properties. Is non-blooming.	F-3516	ICL
19186-97-1	Tris(tribromoneopentyl)phosphate	TTBNPP	Additive flame retardant developed for applications such as PP and HIPS to reach class V-2 according to the UL 94 standard, with outstanding UV and light stability.	FR-370	ICL
20566-35-2	Mixture of the diester/ether diol of tetrabromophthalic anhydride and phosphate ester.	HEEHP-TEBP	Reactive diol for rigid polyurethane and polyisocyanurate foams, urethane elastomers and coatings	SAYTEX RB-7950	Albemarle
21850-44-2	Tetrabromobisphenol-A, bis (2,3-dibromopropyl ether)	TBBPA-BDBPE	Suitable for polyolefin and styrenic resins and it is especially recommended for UL-94 class V-2. It is also applicable in class V-0 polypropylene	FR-720	ICL
			PE-68 has excellent thermal stability and melts during processing for uniform dispersion	PE-68	Chemtura
25327-89-3	Tetrabromobisphenol A bis (allyl ether)	TBBPA-bAE	Additive flame retardant for EPS and in foam polystyrene. The unsaturated end groups provide the unique function of initiating FR performance.	BE-51	Chemtura
25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine	TTBP-TAZ	Major use of FR-245 is in ABS and HIPS	FR-245	ICL
26040-51-7	Tetrabromophthalate ester	BEH-TEBP	Flame retardant plasticizer for PVC applications such as wire and cable insulation, coated fabrics, film and sheeting. It is proven to be extremely effective in PVC jacketing for wire and cable meeting the plenum (UL910) standards.	DP-45	Chemtura

CAS No	Substance name (as indicated by manufacturer)	Abb.	Applications (as indicated by manufacturers)	Product name (ex.)	Manufacturer
			Flame retardant for flexible polyurethane foam and can be used in a wide variety of applications, in particular where low fogging is critical.	Firemaster® BZ-54	Chemtura
3072-84-2	Brominated epoxy	TBBPA-BGE	Used to stabilize plastic compositions containing active halogen atoms such as flame retardant Poly styrene foam (XPS). It can also be used as a FR in epoxy formulation	F-2200 HM	ICL
3194-55-6	1,2,5,6,9,10-Hexabromocyclododecane	HBCDD	Recommended for styrene based systems such as expanded and extruded polystyrene foams	FR-1206	ICL
			Recommended as an additive flame retardant for thermoplastic and thermosetting polymers.	CD-75P	Chemtura
			Used in polystyrene and polypropylene resins. It can also be used in textile treatments, adhesives and coating applications.	SAYTEX HP-900	Albemarle
	Stabilized hexabromocyclododecane	HBCDD	Additive flame retardant for critical thermoplastic and thermosetting polymer applications and product of choice for EPS (expanded polystyrene foam) and other styrene based resin systems where improved melt viscosity stability is needed in processing.	SP-75	Chemtura
32588-76-4	Ethylenebistetra-bromophthalimide	EBTEBPI	Used in polyolefins, high-impact polystyrene (HIPS), thermoplastic polyesters (PBT, PET, etc.), polycarbonate and elastomers.	SAYTEX BT-93	Albemarle
3278-89-5	Tribromophenyl allyl ether	TBP-AE	Additive flame retardant for EPS and foamed polystyrene. PHE-65 may also be used as a synergist for aromatic bromine containing flame retardants in applications where maximum process temperatures do not exceed 150°C.	PHE-65	Chemtura
3296-90-0	Dibromoneopentyl glycol	DBNPG	Used in CFC-free foam systems designed to meet more stringent standards of flame retardancy.	FR-522	ICL
36483-57-5	Tribromoneopentyl alcohol	TBNPA	Used as a reactive intermediate for high molecular weight flame retardants, particularly in the production of phosphorus and bromine containing FRs	FR-513	ICL

CAS No	Substance name (as indicated by manufacturer)	Abb.	Applications (as indicated by manufacturers)	Product name (ex.)	Manufacturer
37853-59-1	Bis (tribromophenoxy) ethane	BTBPE	Flame retardant for HIPS, ABS, polycarbonate, thermoplastic, elastomers, unsaturated polyesters, adhesives, coatings, and textiles	FF-680	Chemtura
59447-55-1	Brominated acrylate monomer	PBB-Acr	Latex, rubbers. Reactive monomer, thermal stability, improves compatibility in polymer matrix	FR-1025M	ICL
59447-57-3	Poly pentabromobenzyl acrylate	-	Especially suitable for engineering thermoplastics, PET, PBT, nylon and styrenic copolymers	FR-1025	ICL
632-79-1	Tetrabromophthalic anhydride	TEBP-Anh	SAYTEX RB-49 flame retardant is designed as a reactive intermediate for use in unsaturated or saturated polyesters, polyols, esters and imides	SAYTEX RB-49	Albemarle
			Primarily been used as a flame retardant in the production of unsaturated polyester resins. Its derivatives have been used as flame retardants in applications as diverse as rigid polyurethane polyols, wire coatings and wool	PHT-4	Chemtura
68441-62-3	Halogenated polyetherpolyol B	-	Particularly well suited for the production of rigid polyurethane foams.	IXOL® B 251	Solvay
68928-70-1	Brominated Epoxy polymer	-	For PC/ABS and PBT	F-2100L	ICL
			Used in unsaturated polyester and vinyl ester resins.	F-2001	ICL
			ABS	F-2016	ICL
71342-77-3	Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A	RDT-7	Flame retardant for thermoplastic resin systems	BC-58	Chemtura
79-94-7	Tetrabromobisphenol A	TBBPA	Used as a reactive flame retardant in the manufacture of epoxy, phenolic and polycarbonate resins	FR-1524	ICL
				Flamecut 120G	Tosoh Corporation

CAS No	Substance name (as indicated by manufacturer)	Abb.	Applications (as indicated by manufacturers)	Product name (ex.)	Manufacturer
			As a reactive flame retardant, SAYTEX CP-2000 flame retardant finds particular application in epoxy, vinyl esters and polycarbonate systems. As an additive flame retardant, SAYTEX CP-2000 flame retardant is widely used in ABS	SAYTEX CP-2000	Albemarle
			Used as a reactive flame retardant for polycarbonates and as an additive for styrenic thermoplastics such as ABS and high impact polystyrene.	BA-59P	Chemtura
84852-53-9	Ethane-1,2-bis(pentabromophenyl) Decabromodiphenyl ethane	DBDPE	Major application areas include HIPS, Low-Density Polyethylene, Polypropylene (Homopolymers and Copolymers), Elastomers, PBT, Polyamides, UPE and Epoxy.	FR-1410	ICL
			Used in styrenic polymers, engineering resins, wire & cable and elastomers.	Saytex 8010	Albemarle
			Additive flame retardant for thermoplastic, elastomeric and thermoset polymer systems, such as HIPS, PBT, polypropylene, LDPE, EPDM, unsaturated polyester, and epoxy.	Firemaster 2100R	Chemtura
88497-56-7	Brominated Polystyrene	-	Especially suitable for engineering thermoplastics such as: Nylon, PET and PBT	FR-803P	ICL
			It is particularly suitable for engineering plastic applications such as polyesters (PET, PBT, PCT) and polyamides (nylons).	SAYTEX HP-7010	Albemarle
94334-64-2	Phenoxy-terminated carbonate oligomer of TBBPA	-	For thermoplastic resin systems	BC-52	Chemtura
1195978-93-8	Benzene, ethenyl-, polymer with 1,3-butadiene, brominated [Brominated Butadiene/Styrene Block Copolymer]	-	For expanded polystyrene (EPS/XPS) for thermal insulation applications. R-122P is an alternative product to FR-1206 (HBCD).	FR-122P	ICL
			A stable, high molecular weight polymeric flame retardant designed to gradually replace Hexabromocyclododecane (HBCD) for use in extruded (XPS) and expanded (EPS) polystyrene applications.	Green-Crest™	Albemarle
			Sustainable, Innovative, High-Performance, Brominated Polymeric Flame Retardant for Polystyrene Foams	Emerald Innovation™ 3000	Chemtura

CAS No	Substance name (as indicated by manufacturer)	Abb.	Applications (as indicated by manufacturers)	Product name (ex.)	Manufacturer
Proprietary	Physical blend of brominated polystyrene and a polyester resin	-	Designed specifically for injection-molding grades of polybutylene terephthalate (PBT). Additive that works well in unfilled, fiberglass and fiberglass/mineral-reinforced PBT composites	SAYTEX 621	Albemarle
Proprietary	Reactive diol blend	-	For rigid polyurethane and polyisocyanurate foams, urethane elastomers and coatings	SAYTEX RB-7001	Albemarle
Proprietary	Aromatic reactive diol	-	For rigid polyurethane and polyisocyanurate foams, urethane elastomers and coatings	SAYTEX RB-9170	Albemarle
Proprietary	Brominated polymer	-	For styrenic polymers especially for HIPS and ABS, engineering resins and polyolefins for wire and cable and elastomers.	Green-Armor	Albemarle
Proprietary	Tetrabromophthalic anhydride based diol	-	Uses include rigid foam, polyurethane RIM, elastomers, coatings, adhesives, and unsaturated polyesters.	Firemaster 520	Chemtura
Proprietary CAS No 183658-27-7 and 26040-51-7 (CECBP, 2008)	Chemtura	-	For PU foams and other applications which require a liquid product	Firemaster 550	Chemtura
Proprietary	Phosphorus-bromine flame retardant	-	For polyurethane foams which is recommended for mechanically cooled foams	Firemaster552	Chemtura
Proprietary	Phosphorus-bromine flame retardant	-	For polyurethane foams and other applications	Firemaster 600	Chemtura
Proprietary	Phosphorus-bromine flame retardant	-	For flexible polyurethane foams and is recommended for mechanically cooled foams.	Firemaster 602	Chemtura

*1 Chemical name according to ESIS ([HTTP://esis.jrc.ec.europa.eu](http://esis.jrc.ec.europa.eu))

Appendix 4: Substance flow diagram for decaBDE and HBCDD

Substance flow diagrams for decaBDE and HBCDD for the Baltic Sea region from the COHIBA (2012) project are found below (see text in Chapter 4 in main report).

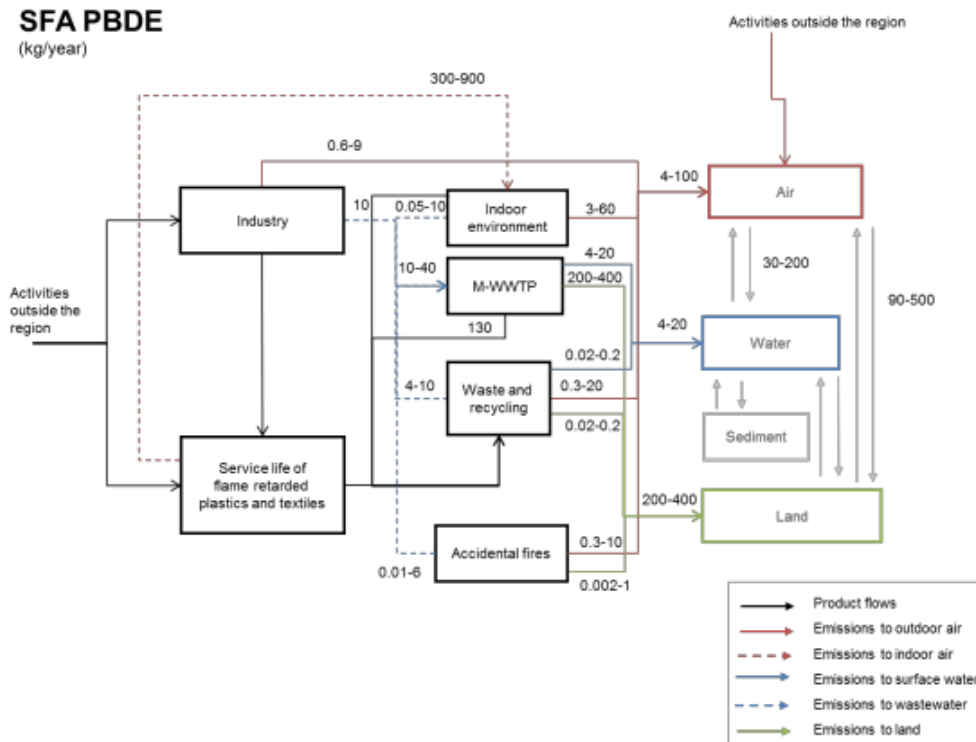


Figure 6: Simplified substance flow analysis (SFA) for PBDE in the Baltic Sea Region (c. 2008-c. 2011).

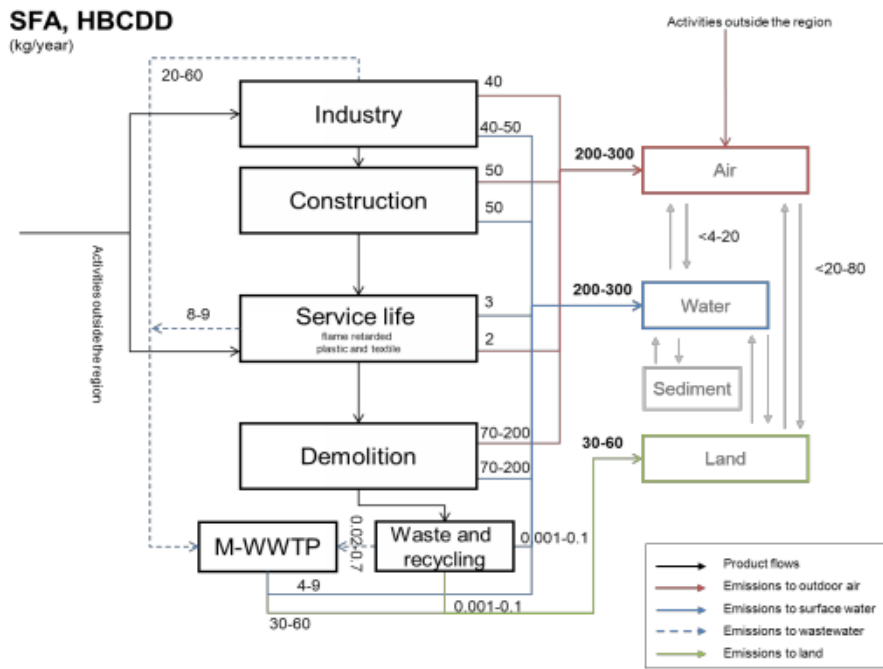


Figure 10: Simplified substance flow analysis (SFA) for Hexabromocyclododecane (HBCDD) in the Baltic Sea Region (c. 2008- c.2011). Numbers are rounded to one significant digit.

Appendix 5: Supplemental data on the applications of the BFRs

The following appendix includes information supplemental to the description in Chapter 3 – please see chapter four for further description.

TABLE A5-2
APPLICATIONS OF DECABDE (BSEF, 2006)

Electrical and electronic (E&E) equipment

- housings and internal components of TVs
- mobile phones and fax machines
- audio and video equipment
- remote controls
- communications cables
- capacitor films
- building cables
- wire and cables, e.g., heat shrinkable tubes
- connectors in E&E equipment
- circuit breakers
- coils of bobbins
- printing and photocopy machine components - toner
- cartridges and connectors
- scanner components

Ships, boats, airplanes

- electrical wiring and cables
- electric & Electronic equipment
 - navigation and telecommunications equipment
 - computers and computer devices
 - audio and video equipment
 - electrical connectors
 - appliances
 - housings and internal components of TVs
 - fax machines
 - remote controls
 - communications cables
 - capacitor films
 - cables
 - circuit breakers
 - printing and photocopy machine components - toner
 - cartridges and connectors
 - scanner components
 - air ducts for ventilation systems
 - electrical ducts and fittings
 - switches and connectors
 - components in fans, heating fans and hair dryers

Textiles and furniture

- households/furniture appliances
 - upholstery textiles e.g. sofas, offices chairs
 - PU flexible foam
- army tents

Automobiles/mass transportation

- fabric (where Deca-BDE is encapsulated in backcoating of article)
- rear deck
- upholstery
- headliner
- sun visor
- head rest
- trim panel
- reinforced plastics
- instrument panel
- interior trim
- under the hood or dash
- terminal /fuse block
- higher amperage wire & cable jacketing (sparkplug wire)
- Electric & Electronic equipment
- battery case and battery tray
- engine control
- electrical connectors
- components of radio disk, GPS and computer systems

Household

- lamp sockets
- kitchen hoods
- electrical kitchen appliances
- curtains and hanging drapes
- components of water heating device
- components of electrical appliances such as
- transformers and switches
- components in fans, heating fans and hair dryers

Public, private and industrial buildings/construction applications

- pipes
- lamp holders
- stadium seats
- reinforced plastics
- switches and connectors
- facing laminates for insulation panel
- film for use under the roof and to protect building areas
- electrical ducts and fittings
- components in analytical equipment in industrial and
- medical laboratories
- air ducts for ventilation systems
- pillars for telephone and communication cables

TABLE A5-2
APPLICATION SPECTRA OF BFRS FROM ALBEMARLE (ALBEMARLE, 2013)

Application	DecaBDE	DBDPE	EBTEBPI	HBCDD	TBBPA	TEBP-Anh	Tetrabromophthalic anhydride diester/etheriol	Proprietary polymeric BFR GreenArmor	Proprietary polymeric BFR GreenCrest	Brominated polystyrene *1
Solid thermoplastics										
ABS	✓	✓	✓		✓			✓		
HIPS	✓	✓	✓	✓				✓		
Polyamide	✓	✓						✓		✓
High temperature polyamide										✓
Polyester	✓	✓	✓					✓		✓
Polycarbonate	✓	✓	✓		•			✓		✓
Polypropylene	✓	✓	✓					✓		
Polyethylene/copolymers	✓	✓	✓					✓		
SAN	✓	✓	✓					✓		
Alloys (PC/ABS, HIPS/PPO)	✓	✓	✓					✓		✓
Elastomers	✓	✓	✓					✓		
PVC	✓	✓	✓					✓		
Foams										
Extruded Polystyrene				✓					✓	
Expanded Polystyrene				✓					✓	

Application	DecaBDE	DBDPE	EBTEBPI	HBCDD	TBBPA	TEBP-Anh	Tetrabromophthalic anhydride diester/etheriol	Proprietary polymeric BFR GreenArmor	Proprietary polymeric BFR GreenCrest	Brominated polystyrene *1
Rigid polyurethane										
Flexible polyurethane							•			
Polyolefins	✓	✓	✓					✓		
PVC/nitrile	✓	✓	✓					✓		
Elastomers	✓	✓	✓					✓		
Wire and cable										
Silicone	✓	✓	✓							
EPDM	✓	✓	✓							
Polypropylene	✓	✓	✓							
PE/EVA	✓	✓	✓							
PVC	✓	✓	✓							
XL PE/EVA	✓	✓	✓							
TPU	✓	✓								
PVC	✓	✓	✓							
Thermosets										
Epoxy	✓	✓	✓		•	•				
Phenolic	✓	✓	✓		✓	•				
Unsaturated polyester	✓	✓	✓		•	•				
Vinyl esters	✓	✓	✓		•	•				

Application	DecaBDE	DBDPE	EBTEBPI	HBCDD	TBBPA	TEBP-Anh	Tetrabromophthalic anhydride diester/etheriol	Proprietary polymeric BFR GreenArmor	Proprietary polymeric BFR GreenCrest	Brominated polystyrene *1
Acrylic resins		√								
SMC/BMC	√		√			•				
PU/CASE	√	√	√				•			
Polyurea		√	√				•			
Latex	√	√	√	√						
Textiles and coatings										
Backcoating	√	√	√							
Paints	√	√	√		•			√		
Hot Melts		√						√		
Fibres		√						√		√

√: additive, •: reactive

*1: Four products with brominated polystyrene are merged here.

Concentrations of BFRs in materials

The concentration of BFRs added to the different polymers depends on:

- The efficacy of the BFR (e.g. determined by the bromine content of the BFR) and synergists;
- The desired level of flame retardancy (tested by different flammability tests), and
- The flammability of the base resin (expressed by the "limiting oxygen index" of base resin).

With a bromine content of 84% decaBDE has the highest specific bromine content among the commercial BFRs. By the substitution of regulated BFRs by other BFRs, the efficacy of the BFRs will influence the loading necessary to obtain a similar level of flame retardancy, as further discussed in chapter 7.

The limiting oxygen index indicates the minimum percentage of oxygen required in the combustion atmosphere to sustain ignition and combustion. If the limiting oxygen index is 20% (atmospheric concentration) or lower, the resin will continue burning when ignited in the normal atmosphere. The oxygen index gives a broad indication of the flammability performance of the material.

Oxygen indices of a number of resins are shown in Table 5A-3. The oxygen index of the resins may vary somewhat, and slightly different values may be found in different information sources. The oxygen index is also dependent on the addition of reinforcement materials. The addition of glass fibres, for instance, lowers the oxygen index of the plastic material, and requires a higher flame retardant loading to obtain a desired FR classification.

Resins with a limiting oxygen index of more than about 30% are self-extinguishing, i.e. they can achieve a flame retardant grade without addition of flame retardant substances. Three of the resins included in the table - polysulfone, polyaryletherketone and polyethersulfone - have such high oxygen indices that relevant flame retardant grades are achieved without addition of flame retardants.

By mixing a resin with a low limiting oxygen index, e.g. polystyrene, with a resin with a higher index, e.g. polyphenylene, a copolymer with a higher limiting oxygen index than the pure polystyrene can be obtained. With a higher limiting oxygen index, the copolymer can meet a desired FR classification at lower FR loading, or with the use of less efficient flame retardants. The use of co-polymers with a higher LOI has been used as an approach in the substitution of regulated BFRs as further discussed in Chapter 7.

TABLE 5A-3
LIMITING OXYGEN INDEX (LOI) OF BASE RESINS (LASSEN *ET AL.*, 2006)

Base polymer	Abbreviation	Limiting oxygen index of base polymer * (%)
Polystyrene	PS	18
Polyketone	PK	20
Polybutylene terephthalate	PBT	22
Polyamide	PA	24.5
Polyphenylene ether	PPE	28
Polycarbonate	PC	29
Polysulfone	PSU	29.5
Polyaryletherketone	PAEK	37
Polyethersulfone	PES	38

* See Lassen *et al.*, 2006 for original references

The desired level of flame retardancy is generally determined by the standards the articles, components or materials have to meet.

In the description of the efficacy of BFRs and the necessary loadings in order to obtain a certain level of flame retardancy, it is common to refer to the material classification of the UL94 classification of the American Underwriters Laboratories (UL, 2013). There are 12 flame classifications specified in UL 94 that are assigned to materials based on the results of small-scale flame tests. These classifications listed in descending order for each of the following three groupings are used to distinguish a material's burning characteristics after test specimens have been exposed to a specified test flame under controlled laboratory conditions.

- Six of the classifications relate to materials commonly used in manufacturing enclosures, structural parts and insulators found in consumer electronic products (5VA, 5VB, V-0, V-1, V-2, HB).
- Three of the classifications relate to low-density foam materials commonly used in fabricating speaker grills and sound-deadening material (HF-1, HF-2, HBF).
- The last three classifications are assigned to very thin films, generally not capable of supporting themselves in a horizontal position (VTM-0, VTM-1, VTM-2). These are usually assigned to substrates on flexible printed circuit boards.

For electronic products the UL 94 material flammability classifications range from HB (the lowest standard) to successively more stringent vertical burning tests (Class UL 94 V-2, V-1, V-0 and 5V) and higher loadings or higher LOI of base resin are needed to meet the classification. Plastic parts in contact with electrical bearing parts should typically meet the V-0 classification, whereas casing and other structural parts would typically only need to meet a V-2 classification.

Examples of loadings of BFRs needed for V-0 grade HIPS, PBT and PA are shown in Table 5A-4. As indicated in the table, higher LOI of the base resin does not necessarily result in lower loading, as the highest loadings are recommended for PA with the highest LOI.

TABLE 5A-4
 EXAMPLES OF COMMERCIALY AVAILABLE BFRS FOR V-0 GRADE HIPS, PBT AND PA (BASED ON LASSEN *ET AL.*,
 2006)

Substance	HIPS (LOI=18)		PBT (LOI=22)		PA (LOI 24.5)	
	Loading for V-0 grade	Synergist ATO	Loading for V-0 grade	Synergist ATO	Loading for V-0 grade	Synergist ATO
DecaBDE	12-13%	4-5%	10.4%	4%	16-18 %	6-7 %
DBDPE	12-13%	4-5%	10.4 %	4%	16-18 %	6-7 %
EBTEBPI	12-13%	4-5%	12-14 %	5%	n.a.	n.a.
Brominated epoxy polymer**	n.a	n.a	15.8 %	4%	n.a.	n.a.
TBBPA	14-20%	4%	n.a.	n.a.	n.a.	n.a.
Phenoxy-terminated carbonate oligomer of TBBPA	n.a.	n.a.	14.5 %	4%	n.a.	n.a.
TBBPA-BDBPE	5% (in "styrenic based resins") *1	5%	n.a.	n.a.	n.a.	n.a.
Brominated polystyrene	n.a.	n.a.	12.1 %	4%	19-21 %	6-7%
Poly(dibromostyrene	n.a.	n.a.	14.5 %	4.4%		
4'-PeBPOBDE2o8	12%	4%	12-14 %	5%	16-18 %	6-7 %
TTBP-TAZ	14.3%	6%	n.a.	n.a.	n.a.	n.a.

*1 The low loadings indicate that the "styrenic based resins" may be styrenic based copolymers.

n.a. Not available.

*2 See Lassen *et al.* (2006) for original references.

Appendix 6: Self classification of selected brominated flame retardants

The Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA) contains classification and labelling information on notified and registered substances received from manufacturers and importers. The database includes the harmonised classification as well. Companies have provided this information in their C&L notifications or registration dossiers (ECHA, 2013d). ECHA maintains the Inventory, but does not verify the accuracy of the information.

The C&L database has been searched for all BFRs listed in Table 1 and 2 of the main report. Classification of the BFRs listed in the C&L database is shown in the table below.

Please note that in many instances, the substances are not classified because data are lacking. The absence of a classification e.g. for environmental hazards, does not necessarily mean that the substances are not hazardous. Reference is made to the C&L inventory for more information on the self-classification of each of the substances.

TABLE A3
CLASSIFICATION INFORMATION ON NOTIFIED AND REGISTERED SUBSTANCES RECEIVED FROM MANUFACTURERS AND IMPORTERS (C&L LIST)

CAS No	Substance name (as indicated in pre-registration)	Abbrev.	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
1163-19-5	Bis(pentabromophenyl) ether	DecaBDE	Total Acute Tox. 4 Acute Tox. 4 Eye Irrit. 2 Acute Tox. 4 Muta. 2 STOT RE 2 Aquatic Chronic 4	H302 H312 H319 H332 H341 H373 H413	255 49 48 27 23 15 14 22
118-79-6	2,4,6-Tribromophenol	TBP	Total Acute Tox. 3 Acute Tox. 4 Skin Sens. 1 Eye Irrit. 2 STOT SE 3 Repr. 2 STOT SE 2 STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1	H301 H302 H315 H317 H319 H335 H361 H371 H373 H400 H410	111 2 24 23 82 105 23 1 1 1 82 2
12124-97-9	Ammonium bromide		Total Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	H315 H319 H335	456 60 452 60

CAS No	Substance name (as indicated in pre-registration)	Abbrev.	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
126-72-7	Tris(2,3-dibromopropyl) phosphate	TDBPP	Total Acute Tox. 4 Skin Irrit. 2 Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H302 H315 H350 H400 H410	26 26 23 23 23 23
1522-92-5	3-Bromo-2,2-bis(bromomethyl)-1-propanol Pentaerythritol Tri-bromide	TBNPA	Total Eye Irrit. 2 Acute Tox. 4 Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4	H319 H302 H312 H315 H319 H332	25 24 1 1 1 1 1
158725-44-1	2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol, oligomeric reaction products with 1-chloro-2,3-epoxypropane and 2,4,6-tribromophenol	OBTMPI	Total Not classified (no information provided)		4 4
20566-35-2	2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	HEEHP-TEBP	Total Aquatic Chronic 3	H412	94 71
21850-44-2	1,1'-(Isopropylidene) bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene]	TBBPA-BDBPE	Total Not classified (no information provided)		44 43
23488-38-2	2,3,5,6-Tetrabromo-p-xylene	TBX	Total Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	H315 H319 H335	23 23 23 23
25327-89-3	1,1'-Isopropylidenebis[4-(allyloxy)-3,5-dibromobenzene]	TBBPA-bAE	Total Eye Irrit. 2 Aquatic Chronic 4	H319 H413	33 3 20
25637-99-4	Hexabromocyclodecane	HBCDD	Total Repr. 2 Lact. Aquatic Acute 1 Aquatic Chronic 1	H361 H362 H400 H410	193 9 9 10 190

CAS No	Substance name (as indicated in pre-registration)	Abbrev.	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
26040-51-7	Bis(2-ethylhexyl) tetrabromophthalate	BEH-TEBP	Total Eye Irrit. 2	H319	23 22
3072-84-2	2,2'-[(1- Methylethylide- ne)bis[(2,6-dibromo- 4,1- phenyle- le- ne)oxymethylene]]bis oxirane	TBBPA-BGE	Total Skin sens. 1	H317	36 2
31780-26-4	Dibromostyrene	DBS	Total Not classified (no infor- mation provided)		1 1
32534-81-9*	Diphenyl ether, pen- tabromo derivative	pentaBDE	STOT RE 2 Lact. Aquatic Acute 1 Aquatic Chronic 1	H373 H362 H400 H410	
32536-52-0*	Diphenyl ether, oc- tabromo derivative	octaBDE	Repr. 1B	H360Df	
32588-76-4	N,N'- ethylenebis(3,4,5,6- tetrabromoph- thalimide)	EBTEBPI	Total Not classified (data lacking)		116 53
3278-89-5	2-(allyloxy)-1,3,5- tribromobenzene	TBP-AE	Total Not classified (no infor- mation provided)		20 20
3296-90-0	2,2- bis(bromomethyl)prop ane-1,3-diol	DBNPG	Total Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 STOT SE 3 Muta. 1B Carc. 1B Carc. 2 STOT RE 2 Aquatic Chronic 4	H302 H315 H319 H335 H340 H350 H351 H373 H413	116 26 26 111 25 85 85 30 81 81
3322-93-8	1,2-Dibromo-4-(1,2- dibromoeth- yl)cyclohexane	DBE-DBCH	Total Eye Irrit. 2	H319	23 23
3555-11-1	Allyl pentabromo- phenyl ether)	PBPAAE	Total Aquatic Chronic 4	H413	23 23
36355-01-8	Hexabromo-1,1'- biphenyl	HexaBB	Total No indication		1

CAS No	Substance name (as indicated in pre-registration)	Abbrev.	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
36483-57-5	2,2-dimethylpropan-1-ol, tribromo derivative	TBNPA	Total Acute Tox. 4 Eye Irrit. 2 Muta. 2 Aquatic Chronic 3	H302 H319 H341 H412	121 20 4 20 93
37853-59-1	1,1'-[ethane-1,2-diylbis(oxy)]bis[2,4,6-tribromobenzene]	BTBPE	Total Not classified (no information provided)		29 29
4162-45-2	4,4'-isopropylidenebis(2-(2,6-dibromophenoxy)ethanol)	TBBPA-BHEE	Total Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	H315 H319 H335	27 24 24 23
52434-90-9	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	TDBP-TAZTO	Total Skin Irrit. 2 Eye Irrit. 2 STOT SE 3 Aquatic Chronic 4	H315 H319 H335 H413	59 57 57 53 2
58965-66-5	1,2,4,5-tetrabromo-3,6-Bis(pentabromophenoxy) benzene	4'-PeBPOB-DE2o8	Total No classification indicated		34
59447-55-1	(Pentabromophenyl)methyl acrylate	PBB-Acr	Total Skin Sens. 1 Eye Irrit. 2 Aquatic Chronic 4	H317 H319 H413	25 2 25 23
608-71-9	Pentabromophenol	PBP	Total Acute Tox. 3 Acute Tox. 3 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 3 STOT SE 3 Aquatic Acute 1	H301 H311 H315 H319 H331 H335 H400	25 23 23 23 23 23 23 23
615-58-7	2,4-dibromophenol	DBP	Total Acute Tox. 2 Acute Tox. 4 Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 STOT SE 3 Aquatic Chronic 3	H300 H302 H312 H315 H319 H332 H335 H412	30 25 3 3 25 25 3 23 2

CAS No	Substance name (as indicated in pre-registration)	Abbrev.	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
632-79-1	Tetrabromophthalic anhydride	TEBP-Anh	Total Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2 STOT SE 3	H315 H317 H319 H335	74 24 48 24 23
68441-62-3	2-butyne-1,4-diol, polymer with 2- (chlorome- thyl)oxirane, bromin- ated, dehydrochlorin- ated, methoxylated		Total Acute Tox. 4 Eye Irrit. 2	H302 H319	165 165 165
68928-70-1	Phenol, 4,4'-(1- methylethyl- dene)bis[2,6-dibromo- , polymer with 2,2'-[(1- methylethyl- dene)bis[(2,6- dibromo-4,1- phe- nylene)oxymethylene]]bis[oxirane]		Total Skin Irrit. 2 Eye Irrit. 2 Not classified	H315 H319	73 23 23 2
79-94-7*	2,2',6,6'-Tetrabromo- 4,4'- isopropylidenediphe- nol	TBBPA	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	
84852-53-9	1,1'-(Ethane-1,2- diyl)bis[pentabromo- benzene]	DBDPE	Total Aquatic Chronic 4	H413	439 302
85-22-3	2,3,4,5,6- Pentabromoethylben- zene	PBEB	Total Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	H315 H319 H335	26 26 26 23
87-82-1	Hexabromobenzene	HBB	Total Acute Tox. 4 Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 STOT SE 3	H302 H312 H315 H319 H332 H335	26 23 23 24 24 23 23
87-83-2	2,3,4,5,6- Pentabromotoluene	PBT	Total Skin Irrit. 2 Eye Irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H315 H319 H335 H400 H410	24 24 24 23 1 1

CAS No	Substance name (as indicated in pre-registration)	Abbrev.	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
88497-56-7	Benzene, ethenyl-, homopolymer, bro- minated [Brominated Polysty- rene]		Total No hazard statement Eye Irrit. 2 Not classified	H319	35 28 1 6

* Harmonised classification

Survey of brominated flame retardants

This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The report presents information on the use and occurrence of the brominated flame retardants, internationally and in Denmark, information on environmental and health effects, releases and fate, exposure and presence in humans and the environment, on alternatives to the substances, on existing regulation, waste management and information regarding ongoing activities under REACH, among others. The survey in particular focuses on the three main brominated flame retardants: decaBDE, TBBPA og HBCDD and alternatives to these flame retardants.

Kortlægning af bromerede flammehæmmere

Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Rapporten indeholder blandt andet en beskrivelse af brugen og forekomsten af bromerede flammehæmmere, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, udslip o skæbne, eksponering og forekomst i mennesker og miljø, viden om alternativer, eksisterende regulering, affaldsbehandling og igangværende aktiviteter under REACH. Kortlægningen fokuserer i særlig grad på de tre vigtigste bromerede flammehæmmere: decaBDE, TBBPA og HBCDD og alternativer til disse flammehæmmere.



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