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**Consideration of draft risk management evaluations:
octabromodiphenyl ether**

Additional information related to the commercial octabromodiphenyl ether risk management evaluation

Note by the Secretariat

A draft risk management evaluation on commercial octabromodiphenyl ether (UNEP/POPS/POPRC.4/6) was prepared during the intersessional period by the working group established by the Committee for that purpose. Annex I to the present note contains additional information related to that risk management evaluation, while annex II contains additional information submitted by the International POPs Elimination Network on debromination and alternatives to commercial decabromodiphenyl ether. The annexes are presented as received and have not been formally edited by the Secretariat.

* UNEP/POPS/POPRC.4/1.

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Annex I

Additional information related to the risk management statement for commercial octabromodiphenyl ether

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1. Status of the chemical under American States legislation

- California: Bill, enacted in August 2003, prohibits a person from manufacturing, processing, or distributing in commerce a product, or a flame-retarded part of a product, containing more than 0.1% OctaBDE, by January 1, 2008; in September 2004 this phase out date was moved to June 1, 2006.
- Hawaii: Law enacted June 2004 (same terms as California), effective January 1, 2006.
- Illinois: Law enacted July 2005 (same terms as California), effective January 1, 2006. Certain exemptions exist. *[The law requires the Illinois Environmental Protection Agency to submit to the General Assembly and the Governor a report that reviews the latest available scientific research related to the effects of decaBDE. The Agency released the report 20 March 2007 concluding that from the available science, decaBDE can and should be eliminated¹.]*
- Maryland: Law enacted June 2005 (same terms as California), effective October 1, 2008. *[It requires the Department of Environment to report on the use of DecaBDE and recommend restrictions on its use and sale.]*
- Maine: Law enacted April 2004 prohibits sale and distribution of new products containing OctaBDE, effective January 1, 2006. *[The law states that Maine will ban deca-BDE if a “safer, nationally available alternative is identified” as of January 1, 2008 and required The Department of Environmental Protection and the Department of Human Services, Bureau of Health to annually submit a report regarding the regulation and dangers of brominated flame retardants, including the availability of safer alternatives to deca-BDE. A second law enacted June 2007 bans new uses of DecaBDE in mattresses and upholstered furniture effective 1 January 2008 and phases out existing uses of Deca in televisions and computer housings by 1 January 2010. The law also authorizes the state to adopt rules to ban other harmful alternative flame retardants for these same products, if there are safer alternatives that meet fire safety standards; requires product manufacturers to notify sellers if these products contain DecaBDE, effective 1 January 2008, and for the state to assist retailers; Authorizes participation in an interstate clearinghouse on PBDEs and BFRs; Adds state authority to require compliance certification; and Requires continued reporting to the Legislature every two years on hazard and risk assessments and alternatives to the use of all brominated flame retardants.]*
- Michigan: Law enacted January 2005 (same terms as California), effective October 1, 2008. New York: Law enacted August 2004, (same terms as California), effective January 1, 2006.
- Minnesota: Bans octa-BDE in products effective 1 January 2008. *[The law requires a study of deca-BDE to be reported to the legislature by 15 January 2008.² The report notes that deca-BDE has been determined to break down into more toxic PBDE congeners including Hexa-, Hepta-, Octa-, and Nona-BDES. By 1 January 2008, the state shall make available for purchase and use by all state agencies equipment, supplies, and other products that do not contain polybrominated diphenyl ethers, unless exempted.]*
- New York: Law enacted August 2004 (same terms as California), effective January 2008. *[The law establishes a Task Force on Flame Retardant Safety to study the risks associated with deca-BDE and the availability, safety and effectiveness of alternatives to such flame retardant.]*
- Oregon: Law enacted July 2005 prohibits the introduction or delivery for introduction into commerce of any product containing more than 1/10 of 1% by mass of OctaBDE, effective January 1, 2006. Certain exemptions. *[The law requires the state to track all brominated flame retardants and report to the legislature on a summary review of relevant new studies on brominated flame retardants and recent findings and rulings by the US EPA and the EU; Recommendations regarding restrictions on the disposal of products containing brominated flame retardants; and any other recommendations to protect public health and the environment from brominated flame retardants.]*

¹ <http://www.epa.state.il.us/reports/decabde-study/index.html>

² Minnesota Pollution Control Agency (2008) Decabromodiphenyl ether (Deca-BDE)
<http://proteus.pca.state.mn.us/publications/reports/lrp-ei-2sy08.pdf>

- Rhode Island: Law enacted July 2006 prohibits manufacture and sale of products containing OctaBDE, effective January 2007. [*The law requires a study of decaBDE to be reported to the legislature.*]
- Washington³: Bill passed April 2007 bans OctaBDE, effective January 2008. [The law bans the use of decaBDE in mattresses by 2008; and bans the use of the decaBDE in televisions, computers, and residential upholstered furniture by 2011.]

2. Production, use and releases

2.1 Levels and trends of production

2.1.1 Overall demand and production

The annual world-wide production of all commercial polybrominated diphenyl ethers was in 1994 estimated as 40,000 tonnes/year, which was broken down as 30,000 tonnes/year (i.e. 75%) of c-decaBDE, 6,000 tonnes/year (i.e. 15%) of c-OctaBDE and 4,000 tonnes/year (i.e. 10%) of c-PentaBDE (WHO 1994). The production volumes of c-OctaBDE have since decreased to about 3,800 tonnes/year in 2001. More up to date figures are available for use volumes (see chapter 2.2).

Information on production of PBDEs in general is given in the Environmental Health Criteria document on PBDEs (WHO 1994). In this report it is stated that in the early 1990s there were eight producers of PBDEs (commercial penta-, octa- or deca-) in the world, with one in the Netherlands, one in France, two in the United States, three in Japan and one in the United Kingdom. The same total number of manufacturers was reported by KEMI (1994), but production was also reported to occur in Israel as well.

According to the Bromine Science and Environmental Forum, c-OctaBDE is no longer produced in the EU, USA and Japan. Information about production in developing countries is sparse. Until 2004, production was situated in the Netherlands, France, USA, Japan, UK and Israel (UNEP 2007c, BSEF). Investigations showed that it is at present essentially impossible to buy c-OctaBDE at global level (Canada Gazette, 2006a).

Within the European Union, there were two reported producers of c-OctaBDEs in the EU IUCLID database in 1994. However, both companies stopped production within the EU (1996/1998).

The amount imported into the EU in 1999 was estimated as 450 tonnes/year as the substance itself, with around 1,350 tonnes/year imported in finished articles (European Commission 2003a). In the light of the legislative restrictions that are in place in the EU, import of c-OctaBDE as such or in articles is prohibited, since "import" is also considered as "placing on the market" in the EU legislation.

In the USA c-OctaBDE is subject to EPA's TSCA Inventory Update Reporting Rule, under which production and import information is periodically collected. For the 2002 reporting year, U.S. production of c-OctaBDE was estimated in the range of 450 to 4,500 tonnes (UNEP 2007c, USA). Production in the USA has since ceased. A voluntary phase out was complete before the end of 2004 (UNECE survey 2007, BSEF).

c-OctaBDE has never been produced in Canada (UNECE survey 2007, Canada). A mandatory industry survey conducted by Environment Canada in the year 2000 confirmed that c-OctaBDE is not manufactured in Canada. The survey also indicated that approximately 1300 tonnes of PBDEs (including c-OctaBDE) were imported into Canada in that year. (UNEP, 2007c Canada 2).

2.2 Use of c-OctaBDE

2.2.1 Use volumes

Arias (2001) reported that worldwide demand for c-OctaBDE was 3,825 tonnes/year in 1999. According to BSEF, the market demand for c-OctaBDE in 2001 was a comparable amount with 3,790 tonnes/year (UNEP, 2007c Canada 1) of which 40% are used in the Americas⁴, 16% in Europe⁵, 40% in Asia⁶ and 4% in the rest of the world.

³ Comment made by Canada (e-mail by Maya Berci from 25 May 2007): "This information is out of date, legislation that sets a North American precedent was recently passed in Washington State. House Bill 1024 was passed April 19, 2007 which prohibits manufacture, sale or distribution of most items containing PBDE as long as a safer alternative exists. The legislation calls for a ban on the manufacture and sale of mattresses containing PBDE effective January 1, 2008, and the manufacture and sale of televisions, computers and residential upholstered furniture containing PBDE by January 1, 2011, if a safer and technically feasible alternative is found. Wording to be checked with Washington State."

⁴ All countries in North, South and Central America

Within the EU, the placing on the market and use of c-OctaBDE was totally banned in 2003 (European Union, 2003). Before the ban, the combined import and production figure for the EU (i.e. the total EU consumption) of all PBDE flame retardants was 10,946 tonnes/year (in 1989) (WHO 1994).

In addition, it is possible that c-OctaBDE has been imported into or exported from the EU as a component of finished articles or master batch (polymer pellets containing additives). Reliable figures for likely quantities involved are not available. Manufacturers estimate that a figure of around 1,350 tonnes/year was realistic for the imports of c-OctaBDE into the EU in finished articles or master batch in 1999 (this figure then means that around 33% of the global amount of c-OctaBDE produced entered the EU either as c-OctaBDE itself or in finished or semifinished articles) (European Commission 2003a). Since the ban of c-OctaBDE in 2004 the import of articles containing c-OctaBDE into the EU is prohibited.

The UNECE survey (2007) has led to the following information on the use of c-OctaBDE in EU Member States:

- Belgium: the use of c-Octa-BDE has stopped; no information when;
- Czech Republic: c-OctaBDE has never been used;
- Cyprus: c-OctaBDE is not imported in Cyprus; no data is available on c-OctaBDE in imported products;
- Italy: according to industry statements use of c-OctaBDE has stopped since the 1980;
- Netherlands: use stopped in 2004;
- France: goods containing PBDEs imported to France in 2004 cause imports of 133 tonnes of PBDEs (including c-OctaBDE) to France. Volumes of exported PBDE were negligible;
- United Kingdom: use of c-OctaBDE as flame retardant in polymer pellets and as flame retardant in finished products (wearing apparel, textiles, rubber and plastic products and furniture) stopped since 1997.

In Norway, a prohibition against production, import, export and the use of c-OctaBDE has been in place since 2004. It is also prohibited to produce, import, export or use products or flame retardant parts of products with over 0.1 % of BDE-196 by weight. An exception for use in evacuation equipment in aeroplanes ended 21 March 2006. Waste with a content of BDE-196 of 0.25 % or greater is treated as hazardous waste; for OctaBDE this means destruction. Recycling of articles containing banned BFRs (Brominated Flame Retardants) is therefore only accepted if the producers of the new product can guarantee that it will not contain BFRs (UNEP, 2008 Norway). [*In 2008, Norway prohibited a ban on new products containing decaBDE leaving the transport sector as the only exemption.*]

For Switzerland figures are available on the amount of c-OctaBDE still in use in plastics in electrical and electronic appliances but the use was declining. Since 2005 marketing and use of c-OctaBDE is prohibited. According to a substance flow analyses on the end of the 1990s approximately 5.2 tonnes of c-OctaBDE have been imported for the use in domestic production of electric and electronic goods and approximately 36 tonnes have been imported in finished products. Consumption of c-OctaBDE in finished products is estimated to be 22 tonnes/y. Preparations of c-OctaBDE are not used in Switzerland. About 60% of the 22 tonnes c-OctaBDE which are used per year in consumer goods are used in electric and electronic goods, 40% in cars. During the past two decades a stock of 680 tonnes of OctaBDE in products has been accumulated in Switzerland. Currently this stock is reduced by 40 tonnes/year. About 70% of the total c-OctaBDE stock of 680 tonnes can be found in electric and electronic goods. The most important products for stocks and emissions are TVs (40%), cars (20%) and building materials such as plastic foils (10%; these do, however, not contain c-OctaBDE anymore). Exports were around 19 tonnes in finished products and 62 tonnes in solid waste (UNEP 2007c Switzerland; SAEFL 2002).

According to Environment Canada (2006b), no ABS (main use type of c-OctaBDE flame retardant) is produced in Canada. According to the Annex E response of Canada on c-OctaBDE (UNEP, 2007c Canada), a very small amount of c-OctaBDE was imported and used in Canada in 2000. The volumes reported do not include quantities imported in finished articles. Significant reformulation activity has occurred in recent years. All companies that reported use of c-OctaBDE in 2000 reported minor remaining uses in 2005, and complete phase-out by 2006 (UNECE survey 2007, Canada).

According to BSEF, the use of c-OctaBDE as flame retardant in polymer pellets in the USA stopped in 2004 (UNECE survey 2007, BSEF). According to the US-EPA, production, not use, was voluntarily phased out in the USA. However US-EPA expects, that levels of the stockpiles will decrease over time (UNECE survey 2007, USA).

No use is reported from Turkey and Mauritius (UNEP, 2007c).

Watanabe and Tatsukawa (1990) reported that around 1 000 tonnes of c-OctaBDE were used in Japan in 1987. Use in Japan has declined from 1,100 tonnes in 1992 to 3 tonnes in 2002 (UNEP, 2007c Japan).

⁵ All countries in Eastern and Western Europe

⁶ Australia, New Zealand and the Indian subcontinent

All importation of c-OctaBDE into Australia ceased prior to 2005.

2.2.2 Use types

Polybrominated diphenyl ethers in general are used as flame retardants. They are mostly used in applications in the plastics and textile industries. Historically about 70 per cent of c-OctaBDE had been used in ABS polymers. Other minor uses included HIPS, PBT and polyamide polymers. c-OctaBDE was mainly used as flame retardant in ABS type plastics which were used in consumer and commercial electronics and office equipment (UNEP, 2008 BSEF). As is common with BFRs in general, a synergist is also added (frequently antimony trioxide) to increase the overall effectiveness of the flame retardant treatment. PBDEs are flame retardants of the additive type, i.e. they are physically combined with the material being treated rather than chemically combined (as in reactive flame retardants). This means that there is the likely possibility that the flame retardant may diffuse out of the treated material to some extent.

The amount of flame retardant used in any given application depends on a number of factors such as the flame retardancy required of the finished product, the effectiveness of the flame retardant, and synergist within a given polymer, the physical properties of the end product (e.g. colour, density, stability) and the use to which the end product will be put. Typically, the flame retardants are added at concentrations between 5 and 30% by weight (WHO 1994). Further information provided by industry indicates that c-OctaBDE is always used in conjunction with antimony trioxide. In the EU, it was primarily used in ABS polymers at 12-18% weight loadings in the final product (European Commission, 2003a). Globally, 70% of c-OctaBDE has been added to ABS polymers (Environment Canada, 2006b).

The main type of use indicated in the Annex E responses in 2007 is the use in ABS polymers. According to the European Union Risk Assessment Report (European Commission, 2003a), around 95% of the total c-OctaBDE supplied in the EU was used in ABS. Other minor uses, accounting for the remaining 5% use, included HIPS, PBT and polyamide polymers, at typical loadings of 12-15% weight in the final product. In some applications, the flame retardant is compounded with the polymer to produce pellets (masterbatch) with slightly higher loadings of flame retardant. These are then used in the polymer processing step to produce products with similar loadings as given above.

The flame retarded polymer products are typically used for the housings of office equipment and business machines. Other uses that have been reported for c-OctaBDE include nylon and low density polyethylene (WHO, 1994), polycarbonate, phenol-formaldehyde resins and unsaturated polyesters (OECD, 1994) and in adhesives and coatings (WHO, 1994).

2.3 Global demand in the future

The annual world-wide production of c-OctaBDE was about 6,000 tonnes/year in 1994. As of the year 2001, production volumes decreased to about 3,800 tonnes/year. Considering a value of 3.6 €/kg this corresponded to a global market value of 13.7 m€. Due to the phase out of production in the USA, first voluntary phase out activities in Asia (Japan) and marketing and use restrictions in the EU, Norway and Switzerland and an already significantly increased use of alternatives (UBA, 2003b) it can be assumed that the demand has already further decreased and will continue to do so.

2.4 Emissions from production and processing

The European Union Risk Assessment on c-OctaBDE (European Commission, 2003a) contains release estimates from production, handling, compounding and conversion (processing), use of products, disposal and recycling and dismantling. Table 1 and Table 2 give an overview on estimated releases of c-OctaBDE based on the European Union Risk Assessment for 1994 and 1999 use volumes respectively. Due to the ban of c-Octa BDE in the EU the actual releases from production, handling, compounding and conversion are considered to be zero in the EU.

Table 1: Overview on estimated releases of c-OctaBDE based on the European Union Risk Assessment (European Commission, 2003a) for 1994 use volumes⁷

Emissions/releases from	1994 (tonnes/year)				
	to air	to water	to wastewater	to waste	to soil
Production					
Handling				5.4	
compounding and conversion	1.28		1.28		
use of products	0.0557	13.9			41.8
Disposal				2480	

⁷ Note: The figures diverge from the summary figures in the European Union Risk Assessment (see European Commission, 2003a, Table 3.1, Summary of estimated releases of c-OctaBDE to the environment) as the release is indicated for the EU as a total and not for the continental model. To present results for the continental model figures would have to be reduced by 10%.

Recycling and dismantling					
EU total per medium	1.3357	13.9	1.28	2485.4	41.8
EU total	2543.7157				

Table 2: Overview on estimated releases of c-OctaBDE based on the European Union Risk Assessment (European Commission, 2003a) for 1999 use volumes.

	1999 (tonnes/year)				
Emissions/releases from	to air	to water	to wastewater	to waste	to soil
Production					
Handling				0.945	
compounding and conversion	0.225		0.225		
use of products	0.0269	6.69			20.2
Disposal				1316	
Recycling and dismantling					
EU total per medium	0.2519	6.69	0.225	1316.945	20.2
EU total	1344.3119				

As there is no production of c-Octa BDE in the EU, Switzerland, Norway, Canada and the USA, releases from production are considered as zero for the Europe and North America. Information about c-OctaBDE production from developing countries is sparse.

Releases from polymer processing sites may arise during handling and compounding and conversion. Due to marketing and use restrictions, there is currently no compounding and conversion of c-Octa BDE in the EU.

In Canada releases have been estimated for historic polymer processing in the year 2000. Releases of c-OctaBDE to solid waste/water and air were estimated to be very low, at 0.03 tons/year and 0.01 tons/year respectively from compounding and conversion processes (unpublished internal report, Environment Canada, 2003). Processing of c-OctaBDE has stopped in Canada since 2006 (UNECE survey 2007, Canada).

Table 3: Estimated releases from historic use in 2000 (UNEP, 2008 Canada)

Source of Release	Release (ton/year)	Compartment of release (air, water, soil)
Materials Handling - removal from drums/sacks, pouring etc.	0.4	liquid waste
Compounding -formulation into resin, simple mixing; and Conversion – open process: foam articles	0.03 (0.023 from compounding + 0.010 from conversion)	Solid waste/water
Compounding - formulation into resin, simple mixing; and Conversion – open process: foam articles	(0.002 from compounding; + 0.010 from conversion)	Air
Emissions from c-OctaBDE from plastic products in service	0.7	Air
Emissions from c-OctaBDE from ABS products at disposal	>3.09 tons/year, with >150.97 tons per year remaining in the disposed products	solid waste/water

Releases from current processing are considered zero in the EU and Canada.

As in the USA, although production of c-OctaBDE (not use) was phased out there may still some releases be expected from processing. It is assumed that levels of any existing stockpiles will decrease over time and it can be expected that releases from processing will correspondingly decrease.

In France OctaBDE was measured in waste waters of seven out of 667 so called "classified plants for environment protection". Five out of these seven plants dealt with textile treatment (UNECE survey 2007, INERIS 2006).

The commercial octaBDE mixture, DE79 also contains both polybrominated biphenyls (PBB) and polybrominated dibenzofurans (PBDF) which are also present in other commercial PBDE mixtures such as DE-71 and DE-83 (Hanari *et al.* 2006). Using production / usage estimates of commercial PBDE mixtures in 2001, potential global annual emissions of PBB and PBDF resulting from the use of PBDEs were calculated to be 40 kg and 2300 kg respectively.

General process and release descriptions, and exposure estimates for c-OctaBDE are available in an April 2003 risk assessment conducted by an industry sponsor under US EPA's Voluntary Children's Chemical Evaluation Program (US EPA, 2003b; UNECE survey 2007, USA). The study contains no information on amounts released from production, handling, use, waste or recycling/recovery.

2.5 Emissions from handling and transport

Releases from polymer processing sites may arise during handling of c-OctaBDE containing polymer raw material. Losses of powders (as dust) during the handling of raw materials have been estimated as 0.21% for powders of particle size >40 µm. It is expected that the dust will rapidly settle and so losses will be mainly to solid waste, which may be recycled or disposed of, or washed to wastewater (European Commission, 2003a).

In the EU and Canada handling of polymer pellets containing c-OctaBDE does not occur at present.

In Canada the release estimate for the year 2000 from historic handling (materials handling - removal from drums/sacks, pouring etc.) was 0.36 tonnes/year to liquid waste. Processing of c-OctaBDE has stopped in Canada since 2006 (UNECE survey 2007, Canada).

Although processing and use of existing stock is not regulated, there is no information on the USA handling of polymer pellets containing c-OctaBDE. It is expected this operation has already ceased or is very limited and should decrease over time.

2.6 Emissions from the use of products containing c-OctaBDE

In the light of the ban and phase out of c-OctaBDE, it is important to focus on the fate in products (ECE EB, 2006). Emissions of c-OctaBDE occur from volatile and leaching losses over the service life of polymers, and also particulate losses over their service life and at disposal. In practise it is expected that total emissions will be dominated by volatile losses from polymers over their service life (e.g. >91% of the total emission of c-OctaBDE to air).

2.6.1 Volatilisation

According to the European Union Risk Assessment (European Commission, 2003a) the loss during the service life of a product are estimated be 0.54% (assuming a life of 10 years). The available information for 1999 indicates that the amount of c-OctaBDE present in finished articles in the EU could be around 1,350 tonnes/year (the estimate includes

both articles manufactured in the EU and imported articles containing c-OctaBDE). This corresponds to a loss of 0.73 tonnes/year in the EU, based on the 1999 EU consumption figure of 1,350 tonnes/year. These figures overestimate the current EU usage of c-OctaBDE but, as a result, may account to some extent for the (unquantifiable) amount of c-OctaBDE that may be imported into (or exported from) the EU in finished articles or masterbatch. The losses will initially enter the atmosphere. It should be born in mind that since the products may be used over a 10 year lifetime or longer, and that each year new products containing c-OctaBDE are likely to enter into use during this time, the actual amount of c-OctaBDE present in plastic products, and hence potentially released, could be around 10 times the amount estimated above. The estimated amount of volatile losses in the EU from products in service life is therefore 7.29 tonnes/year using the 1999 data.

According to estimations for Canada the estimated amount of volatile losses from products in service life is 0.6 tonnes⁸ per year for the year 2000 (UNECE survey 2007, Canada). Extrapolating the Canadian estimation in an analogous way to the use figures for all countries in North, South and Central America for 2001 result in an estimated amount of volatile losses from products in service life of 0.86 tonnes per year for this region in 2001.

2.6.2 “Waste remaining in the environment”

“Waste remaining in the environment” can be considered to be particles (or dust) of polymer product, or dust generated from polymer products that contain c-OctaBDE. These particles are primarily released to the urban/industrial soil compartment, but may also end up in sediment or air. End-products with outdoor uses are most likely to be sources of this type of waste, where releases can occur over the lifetime of the product due to weathering and wear.

Increasing attention has focused on the release of OctaBDE and other PBDEs to dust in the indoor environment (Wilford *et al.*, 2005; Blake *et al.*, 2004; Santillo *et al.*, 2003; Stapleton *et al.*, 2006; Betts, 2008; Allen *et al.*, 2007; Allen *et al.* 2008). Keeping consumer products containing octaBDE and other PBDEs for many years in the home and office has the potential to be a long-term exposure source and human body burdens of PBDEs have been associated with house dust concentrations (Wu *et al.*, 2007). Recent research indicates that hexaBDE and other BDEs in dust are available and biologically active (Huwe *et al.*, 2008).

In addition, releases of this type can occur from disposal processes, particularly where articles are dismantled or subject to other mechanical processes, regardless of the method of ultimate disposal (or recycling/recovery). Air and dust monitoring data at dismantling plants confirm that this is a source of release of polybrominated diphenyl ethers (European Commission, 2003a).

At present there is no agreed methodology given in the Technical Guidance Document (European Commission 2003b) for assessing the risks from this type of waste. However, a methodology was outlined in the draft risk assessment report for di-(2-ethylhexyl)phthalate (DEHP) (European Commission, 2000) and a similar approach is taken in the European Union Risk Assessment (European Commission, 2003a). The release estimates obtained show a high degree of uncertainty.

According to this approach the amount of “waste remaining in the environment” for the EU in 1999 can therefore tentatively be estimated as indicated in Table 4:

⁸ Estimated based on an emission factor of 0.054% per annum, and a vapour pressure of 4.9×10^{-8} mm Hg at 20°C, and 1223.22 tons estimated market demand for OctaBDE in plastics in Canada in 2000

Table 4: Release estimates during service life and disposal of products containing c-OctaBDE for the EU in 1999

	1999 data
Total amount of octabromodiphenyl ether present in polymers	1,350 tonnes/year
Amount lost through volatilisation over the service life	7.29 tonnes/year
Total amount remaining in plastics	1,343 tonnes/year
Estimated fraction of plastic used for outdoor applications	0.1%
Amount of in plastic used for outdoor applications	1.34 tonnes/year
Estimated loss as “waste remaining in the environment”	2% over lifetime
Emission as “waste remaining in the environment” over lifetime	0.027 tonnes/year
Total amount remaining in plastics at disposal	1,343 tonnes/year
Estimated loss as “waste remaining in the environment” at disposal	2%
Emission at disposal	26.86 tonnes/year
Amount remaining in plastics for disposal (or recycling)	1,316 tonnes/year

As indicated in the table the estimated amount of “waste remaining in the environment” in the EU, which is particularly related to waste treatment at disposal, is 26.9 tonnes/year (26.86 tonnes per year from disposal + 0.027 tonnes per year from product lifetime) for the EU in 1999. According to the European Union Risk Assessment it has been assumed that these releases enter industrial/urban soil (~75%), air (~0.1%) and surface water (~24.9%).

For Canada releases have been estimated for the year 2000. The estimated amount of emissions of c-OctaBDE from ABS products at disposal will exceed 2.8 tonnes per year⁹, with >137 tonnes per year remaining in the disposed products (UNECE survey 2007, Canada).

Extrapolating the Canadian estimation in an analogous way to the use figures for all countries in North, South and Central America for 2001 i.e. approximately 1,500 tonnes per year this would result in an amount of waste remaining in the environment of approximately 3.5 tonnes per year from disposal.

Consequently as current products reach the end of their service life, proper management of this waste will eliminate service life losses to the indoor and outdoor environments over the coming years.

2.7 Emissions from waste containing c-OctaBDE

2.7.1 Emissions at disposal

In addition to the “waste remaining in the environment” during the service life of a product a second fraction of “waste remaining in the environment” occurs at disposal. These emissions at disposal are already covered in the release estimates during the service life of a product.

2.7.2 Emissions after disposal

According to the European Union Risk Assessment (European Commission, 2003a), emission of c-OctaBDE also occurs after disposal.

In a Swiss study (SAEFL 2002) a substance flow analysis of c-OctaBDE has been performed for Switzerland. During the past two decades a stock of 680 tonnes of c-OctaBDE in products has been accumulated in Switzerland. Currently this stock is reduced by 40 tonnes/year. With respect to the fate of c-OctaBDE in waste the study shows that c-OctaBDE usually enters the solid waste stream. Common pathways for disposal and elimination are incineration, landfilling and export (which amounted in Switzerland according to the study to approximately 86%, 10% and 4% respectively). Comparable pathways and possibly also relations might be extrapolated to other countries in the UNECE region as well. Assuming that an amount of 1,350 tonnes of c-OctaBDE is placed on the EU market in products each year and an average product lifetime of 10 years leads to a rough estimation of a stock of c-OctaBDE of 13,500 tonnes in products in the EU. Assuming that since 2005 no more c-OctaBDE containing products entered the market, the current stock can be roughly estimated to amount to approximately 9,450 tonnes (in 2007).

Plastics containing c-OctaBDE will usually be disposed of either to landfill or by incineration. It is expected that emissions of PBDEs from state of the art incineration processes will be near zero, although the question of formation of brominated dibenzofurans and dibenzo-p-dioxins (PBDD/F) has been raised as a potential problem (European Commission, 2002). According to SAEFL 2002 the destruction efficiency of c-OctaBDE in incineration was estimated 99.9% with the remainder of 0.1% being mainly disposed of to landfill.

⁹ Estimated based on a loss to the environment of approx 2% of the quantity disposed

When plastic containing c-OctaBDE is disposed of to landfill, in theory it could volatilise to the atmosphere or leach out of the plastic and groundwater.

Using the assumption that the amount of plastic containing c-OctaBDE produced each year replaces that disposed of each year the amount of c-OctaBDE disposed of in plastic articles could be around 1,316 tonnes/year for the EU based on the 1999 consumption data.

PBDEs are released to water from raw landfill leachate and leaching is enhanced by humic acid (Osako *et al.*, 2004; Kim *et al.*, 2006). Analysis of a landfill in Japan revealed significant PBDE concentrations below heptaBDE in the leachate (Kim *et al.*, 2006). PBDEs were also detected in an analysis of landfill leachates in South Africa and the authors expressed concern that the compounds could infiltrate groundwater around the sites since the landfills were not adequately lined (Odusanya *et al.*, 2008). A study by the Minnesota Pollution Control Agency (USA) revealed pentaBDE, hexaBDE, nonaBDE and decaBDE accumulation in landfill leachate from five landfills including municipal, industrial, and demolition landfills with decaBDE accounting for the highest percentage of total PBDE concentrations (Fardin, 2005).

No experiments appear to have been carried out on the leachability of c-OctaBDE from polymers in landfills, but, by comparison with the decaBDE (see the risk assessment report of decaBDE (European Commission, 2002)), it would not be expected to leach to a significant extent from polymers, unless the polymer itself undergoes some form of degradation. It should be noted that the lower brominated components of c-OctaBDE would be expected to leach more than the decaBDE congener. In addition, c-OctaBDE is likely to adsorb strongly onto soil which will significantly lower its leaching potential from landfills into groundwater. Similarly, the low vapour pressure of the substance would limit its volatility from landfills. In addition, release to the environment of volatilised c-OctaBDE is very limited due to the coverage of landfills and the capture and treatment of waste gas from landfills.

To conclude, releases after disposal, if handled correctly and by applying BAT and BEP, may be considered to be low, however, due to conditions in different countries and the current lack of knowledge, the possible long-term increase in levels as a result of releases from waste sites may need to be considered further (European Commission 2003a).

2.7.3 Emissions from sewage sludge

C-OctaBDE and other PBDEs are released from waste water treatment facilities and can be measured in aquatic organisms (Gevao *et al.*, 2008; Wang *et al.*, 2007a; Wang *et al.*, 2007b; Knoth *et al.*, 2007; Hale *et al.*, 2006; North, 2004). Land application of sewage sludge contaminated with c-octaBDE and other PBDEs leads to their release into soils and subsequent uptake by earthworms presenting an exposure pathway into the terrestrial food chain (Eljarrat *et al.*, 2008; Sellstrom *et al.*, 2005).

2.7.4 Emissions from recycling and dismantling

Volatile and/or particulate emissions of c-OctaBDE occur during recycling/recovery and dismantling, particularly where articles are dismantled or subject to other mechanical processes, regardless of the method of ultimate disposal (or recycling). These emissions can be allocated to emissions at disposal and are already covered in the release estimates during the service life of a product.

Air and dust monitoring data at dismantling plants confirm that this is a source of release of polybrominated diphenyl ethers (European Commission, 2003a). According to the European Union Risk Assessment the estimated loss as “waste remaining in the environment” at disposal is estimated to be 2% of the total amount of c-OctaBDE that is contained in products at the end of their service life. In addition the formation of brominated dibenzofurans and dibenzo-p-dioxins (PBDD/F) has been raised as a potential problem at dismantling plants. Severe PBDD/F and PCDD/F emissions have been observed in air near electronic waste dismantling areas in China (Li *et al.*, 2007). Surface soils near dismantling and recycling sites have also been found to contain octaBDE, PCDD/Fs, and other PBDEs (Leung *et al.*, 2007).

In the European Union Risk Assessment (European Commission, 2003) it has been assumed that this release is distributed to industrial/urban soil (75%), air (0.01%) and surface water (24.9%).

3. Information on alternatives (products and processes) to c-octaBDE

Environmental Health Criteria 192 on Flame Retardants (WHO, 1997) provides a general review of all flame retardants and their effects to the human health and the environment. Alternatives to C-OctaBDE include substitute chemicals and alternative techniques including non-chemical alternatives such as design changes. These are described in several governmental reports (Environment Canada, 2006a; Leisewitz *et al.*, 2000; Washington State, 2005; RPA, 2002; Danish Environmental Protection Agency, 1999). The German Environmental Protection Agency has published a guidance document for the application of environmentally safe substances which focuses on substitution of PBDEs. The study focuses on substitution of c-decaBDE but it is stated that the results can be used for the substitution of other additive type flame retardants (UBA, 2003b).

Among the countries that responded to the UNECE survey 2007 Belgium, Czech Republic, Cyprus, Germany, the UK, Switzerland and the USA indicated to have no information on possible substitutes of c-OctaBDE (Italy did not respond to the relevant question). France refers to the RPA Risk reduction strategy (RPA, 2002) and analysis of advantages and drawbacks for c-OctaBDE and states that, instead of looking for a chemical substitution, it may be worth investigating possibilities of eco-design that lower risks of ignition of products c-OctaBDE was used to prevent.

3.1 Design changes to address c-OctaBDE

Design changes can eliminate the need for flame retardants by using alternative materials or designs that eliminate the need for chemical flame retardants. These include shielding the plastic outer casing of components with metal or making the entire case of metal (RPA, 2002; Danish Environmental Protection Agency, 1999). Whilst there is inadequate data to estimate the likely costs of such techniques, it is considered that they are likely to be more expensive than using c-OctaBDE in most cases, at least in the short-term.

According to the RPA report (RPA, 2002), there are also other options for replacing c-OctaBDE, without utilising a substitute flame retardant. These include re-design of the electrical or electronic products or use of polymers with lower rates of combustion. Other options described in the RPA report include maintaining certain distances between high voltage parts and the outer casings and using polymers with low rates of combustion such as amino-, phenol-, fluoro-, and silicone-based polymers.

In some cases design changes can occur by utilizing plastics or blends of polymers that contain different substances for flame retardation (RPA, 2002). The RPA report mentions use of polycarbonate / ABS blends (PC/ABS) and polypropylene / polystyrene (PPE/PS) blends.

Two flame retardants used in the polymer blends are triphenyl phosphate (TPP) and bis (diphenylphosphate) (RDP). US EPA reports moderate systemic toxicity and high acute and chronic ecotoxicity of TPP as two characteristics of concern.¹⁰ The US Occupational Safety and Health Administration (OSHA) reports inhibition of cholinesterase as a health effect of triphenyl phosphate exposure (US OSHA, 1999). Bioconcentration factors for TPP in several fish species vary from 6 – 18,900 (Danish Environmental Protection Agency, 1999). In addition, triphenyl phosphate is considered environmentally hazardous in Germany due to its toxicity to aquatic organisms (Leisewitz *et al.*, 2000). RDP also appears to be harmful to aquatic organizations and estimates on losses from products to the environment is lacking (RPA, 2002). While TPP and RDP have hazardous properties that must be addressed across their lifecycle, neither is persistent and RDP does not appear to be bioaccumulative.

3.2 Assessing c-OctaBDE alternatives

The RPA report summarizes the alternatives for c-OctaBDE by noting the lack of comprehensive data available for the chemical alternatives and pointing out the viability of non-chemical alternatives such as shielding the plastic outer casing of components with metal or making the entire case of metal, maintaining certain distances between high voltage parts and the outer casings, and using polymers with low rates of combustion such as amino-, phenol-, fluoro-, and silicone-based polymers (RPA, 2002; Danish Environmental Protection Agency, 1999).

Generally it is considered that a substitution by additive type flame retardants that are PBT (i.e. Persistent, Bioaccumulative and Toxic) such as PBDEs, SCCPs (short chain chlorinated paraffin), MCCPs (medium chain chlorinated paraffin) or additive TBBP-A is related to a higher risk of release to the environment during use and disposal of products – irrelevant whether they contain halogens, nitrogen or phosphorus – compared to reactive type flame retardants. Halogenated flame retardants are in addition related to the risk to generate non-desired reaction products in the case of fires (UBA, 2003b).

The use of halogenated flame retardants in the EU is significantly decreasing (with the exception of chlorinated phosphoric esters). Mineral type flame retardants such as Aluminum-tri-hydroxide (ATH) or Magnesium-hydroxide or

¹⁰ USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives
Polyurethane Foam <http://www.epa.gov/dfe/pubs/index.htm#ffr>

Nitrogen containing flame retardants (e.g. melamin derivatives) show significant increases. An important driving force for these market adjustments is the consideration of environmental risks (UBA, 2003b).

Two chemical substitutes are both persistent and bioaccumulative: bis (tribromophenoxy) ethane and hexabromocyclododecane. In addition, dibromostyrene was somewhat persistent and not bioaccumulative based on a low BCF value.

The remaining chemical alternatives, while not both persistent and bioaccumulative, still have characteristics that raise some concerns about human health and the environment. The core substance of the reactive phosphorous constituent, methyl phosphonic acid, is persistent. Triphenyl phosphate is bioaccumulative since bioconcentration factors in several fish species vary from 6 – 18,900 (Danish Environmental Protection Agency, 1999). Resorcinol bis (diphenylphosphate) is neither persistent nor bioaccumulative, however its triphenyl phosphate degradation product has moderate concern for bioaccumulation and it is harmful to aquatic organisms (Washington State, USA, 2005; Rossi and Heine, 2007; RPA, 2002). Information is sparse for three substitutes: triaryl phosphates butylated, bisphosphate, and tribromophenyl allyl ether.

Halogen free flame retardants are suitable substitutes in many relevant cases. In electric and electronic equipment an efficient flame retardancy of used plastics is important. Approximately 25 % of all plastic components in this sector are flame retarded. The main share thereof is thermoplastic housings, followed by thermosetting printed circuit boards and electronic small parts. For thermoplastic housings suitable and efficient substitutes are available. In injection moulding for thermoplastic housings the fluidness is a critical parameter. Therefore mineral type flame retardants are not appropriate substitutes. Suitable alternatives that have to be evaluated in each single case are (according to UBA, 2003b) for example:

- halogen free systems on phosphorus-organic basis (organic triaryl- and biphosphates such as phenylcresylphosphate mixtures, triphenylphosphate, resorcinolbis(diphenylphosphate) or bisphenol-A-diphenylphosphate for PC/ABS and high-impact HIPS housings).
- brominated systems with low dioxin/furan formation potential, in particular with respect to recycling/recovery processes (e.g. 1,2-bis(pentabromophenyl)ethane or ethylenbis(tetra-bromophthalate)).

It has to be noted that the halogen free systems based on organophosphorus compounds cannot be generally considered to be the environmentally preferable substitute. However, the ecologic advantages outweigh the disadvantages at least in comparison with decaBDE or additive TBBP-A if

- substances that have been sufficiently tested for toxicological properties and have proven degradability and low volatility are used as additive type flame retardant in these systems or
- organophosphates that have been sufficiently tested for toxicological properties are used as reactive type flame retardant.

In the guidance document the technical practicality of substitution is demonstrated by means of several examples (UBA, 2003b).

UBA 2003a contains a comparison of 9 typical flame retardants in plastic materials and considerations on possible adverse effects: decaBDE, TBBP-A (additive), hexabromocyclododecane, trischloropropylphosphate, antimony trioxide, aluminum trihydroxide, ammonium polyphosphate, resorcinol bis(diphenylphosphate) and zinc borate. The comparison takes health (mutagenicity, genotoxic carcinogenicity, reprotoxicity, carcinogenicity, and allergic effects) and environmental (persistence, bioaccumulation and aquatic toxicity) aspects into consideration. There is no unambiguous result that enables to determine the most appropriate flame retardant. Ammonium polyphosphate has neither CMR (Carcinogenic, Mutagenic, and Reprotoxic) nor PBT (Persistence, Bioaccumulation, Toxicity) properties but has restricted practicability due to technical reasons. This underlines the need that the evaluation has to be done on a case by case basis. However, CMR and PBT substances should generally not be used.

Identifying alternatives for POPs provokes a deeper question about methods to evaluate and compare the hazards of various substances.

One screening guide focuses on evaluating environmentally preferable flame retardants for TV enclosures by developing and using a “Green Screen” (Rossi and Heine, 2007). The criteria used by the Green Screen include: hazard endpoints with categories of high, medium, and low; criteria for determining each level of chemical concern; and consideration of degradation products and metabolites. The Screen places a substance into one of four categories:

Avoid – very high concern, Use – but search for safer substitutes, Use – but still opportunity for improvement, and Prefer – green chemical. According to Green Screen criteria in examining alternatives to c-DecaBDE, only resorcinol bis (diphenylphosphate) passed the first benchmark to land in benchmark 2: Use – but search for safer substitutes, making it the preferred chemical substitute.

For an overarching approach to the topic of alternatives assessment, the Lowell Center for Sustainable Production has developed an Alternatives Assessment Framework with the goal of, “Creating an open source framework for the relatively quick assessment of safer and more socially just alternatives to chemicals, materials, and products of concern.” (Rossi *et al.*, 2006). The Framework discusses goals, guiding principles, decision making rules, comparative and design assessment, and types of evaluation. Since the Framework is designed to be an open source tool, the Lowell Center encourages companies, NGOs, and governments to use, adapt, and expand on it.

Based upon this analysis, there are alternatives to c-OctaBDE available for which existing data do not indicate an equivalent or higher level of risk to health or the environment. This is especially true for reactive type flame retardants that will have significantly lower emissions during the service life of products. However, for all of the potential substitutes identified, the existing data on toxicological and ecotoxicological effects are fewer than for c-OctaBDE. The RPA report (RPA, 2002) pointed out that, given that none of these substances had yet undergone a risk assessment as rigorous as those carried out under the European Union Risk Assessment, it was inevitably not possible to compare the risks on a like-for-like basis. The results of the further testing and assessment that is ongoing for some of the potential substitutes should help to resolve the differences in data availability to a degree.

Table 5: Summary of Potential Substitution Options Compared to c-OctaBDE (RPA, 2002).

Substance	Potential Health Risks a)	Potential Environmental Risks a)	Cost and Other Considerations
Tetrabromobisphenol-A b)	No evidence of equal or greater risks	Data indicate may be classified as 'very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment' c)	Less expensive (~50%) but greater flame retardant loading required. ESR risk assessment ongoing and concerns expressed about substance in some member states
1,2-bis (pentabromophenoxy) ethane b)	No evidence of equal or greater risks	PBT properties appear of less concern than octa. However, fewer data and BCF values questioned	~ 30% more expensive
1,2-bis (tribromophenoxy) ethane b)	No evidence of equal or greater risks	Very limited data	Greater flame retardant loading probably required; expected to be comparable in price
Triphenyl phosphate	No evidence of equal or greater risks	High toxicity and relatively high potential for bioaccumulation but is readily biodegradable	Less expensive but polymer/flame retardant system expected to be more expensive overall. Poorer plastic recyclability
Resorcinol bis (diphenylphosphate)	No evidence of equal or greater risks	Acutely toxic or very toxic but biodegradable	Less expensive but polymer/flame retardant system expected to be more expensive overall. Poorer plastic recyclability
Brominated polystyrene	No evidence of equal or greater risks (but some concerns expressed re: impurities in commercial product)	No data but losses and exposure expected to be lower	Slightly more expensive

Notes:

- Note that in most cases, the information available on toxicological and ecotoxicological effects is less than that for c-OctaBDE.
- Can be used in ABS as well as other polymers. Other flame retardants listed are not suitable for use in ABS.
- Note that in-service losses will be lower where used as reactive flame retardant in non-ABS polymers.

Canada refers to substitution options compared to c-OctaBDE as provided by RPA (RPA, 2002) and states furthermore that alternative techniques to reduce the use of PBDEs are generally known:

- Use of materials that are less prone to fire hazard in electronics equipment (such as aluminium or "super-plastics" with very high oxygen requirements for combustion);
- use of barrier fabrics, wrapping or coatings for foams to replace chemical flame retardants;
- design-for-environment (DfE) techniques for re-use of components containing PBDEs, as an alternative to landfilling or recycling plastic materials containing PBDEs.

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Annex II

Additional information submitted by the International POPs Elimination Network on debromination and alternatives to commercial decabromodiphenyl ether

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1. Debromination

1.1 Background

The Risk Profile for c-OctaBDE (UNEP, 2007a) concluded that c-OctaBDE is a mixture of components with different properties and profiles, which may also be released to the environment due to its presence as components of other PBDE commercial products and also produced in the environment by debromination of commercial DecaBDE. The Risk Profile notes that the lower than expected bioaccumulation potential of HeptaBDE, OctaBDE, and NonaBDE may be due to debromination and subsequent formation of bioaccumulative PBDEs. In addition, the Risk Profile observes that the potential for long range transport has been observed for DecaBDE and that the lack of confirmation for Octa and NonaBDE may be related to the lower relative contribution and/or metabolism via debromination.

Photodecomposition, anaerobic degradation, and metabolism in biota are pathways of debromination that could produce other PBDEs with higher toxicity and bioaccumulation potential (UNEP, 2007a).

1.2 Photodecomposition

The photodecomposition of several BDEs has been studied in different matrices such as ethanol/water 80:20 (Eriksson et al. (2001))¹, methanol/water 80:20 under UV light in the sunlight region (Eriksson et al. (2004))²; in a sealed polyethylene tube exposed to natural sunlight for up to 120 min (Peterman et al. (2003)); in hexane under UV light in the sunlight region (Fang L et al. (2008))³ (Bezares-Cruz et al.(2004))⁴; in toluene, silica gel, sand, sediment and soil using artificial sunlight and on natural matrices of sediment, soil, and sand using natural sunlight (Soderstrom et al. (2004))⁵ or water (Sanchez-Prado et al. (2006))⁶. NonaBDEs to triBDEs were formed in these studies and some also detected polybrominated dibenzo furans. In general, degradation was faster for the higher brominated congeners than for the lower brominated congeners. Half lives on natural matrices such as sediment, soil, and sand ranged between 40 and 200 hours (Soderstrom et al. (2004). Rayne et al. (2006)⁷ suggest a short photochemical half-life for the hexa- BDE (BDE-153) in aquatic systems, with rapid reductive photodebromination to some of the most prevalent penta- and tetra-brominated diphenyl ether congeners.

Stapleton et al. (2008)⁸ investigated the degradation potential of decaBDE in house dust using both natural and BDE-209-spiked dust material. Degradation of BDE 209 was observed in both matrices but was 35% greater in the spiked dust relative to the natural dust material. Debrominated products detected in the spiked dust included all three nonaBDEs (BDE 206, BDE 207, and BDE 208) and several octaBDEs (BDE 196, BDE 197, BDE 201, BDE 202, and BDE 203/200). The results suggest the potential for reductive debromination indoors. Another recent study of BDEs also found markers of decaBDE debromination (BDE202) in house dust (Allen et al. 2008).⁹

¹ Eriksson J, Jakobsson E, Marsh G, Bergman Å, 2001. Photo decomposition of brominated diphenyl ethers in methanol/water. Abstracts. The Second International Workshop on Brominated Flame Retardants. BFR 2001 Stockholm. May 14-16. Stockholm University, Sweden. p. 203-206

² Eriksson J, Green, N, Marsh G, Bergman, A. (2004) Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. *Environmental Science & Technology* 38:3119-3125

³ Fang L, Huang J, Yu G, Wang L. (2007) Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane, *Chemosphere* 71:258-267

⁴ Bezares-Cruz J, Jafvert CT, Hua I. (2004) Solar Photodecomposition of Decabromodiphenyl Ether: Products and Quantum Yield. *Environ. Sci. Technol* 38:4149 - 4156

⁵ Soderstrom, G, Sellstrom U, De Wit CA, Tysklind M. (2004) Photolytic debromination of decabromodiphenyl ether (BDE 209). *Environmental Science & Technology* 38:127-132

⁶ Sanchez-Prado, L., Lores, M., Llompert, M., Garcia-Jares, C., Bayona, J.M. and Cela, R. (2006), 'Natural sunlight and sun simulator photolysis studies of tetra- to hexa-brominated diphenyl ethers in water using solid-phase microextraction', *J Chromatogr. A*. 1124:157-66

⁷ Rayne, S., Wan, P. and Ikonomou, M. (2006), 'Photochemistry of a major commercial polybrominated diphenyl ether flame retardant congener: 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE153)', *Environ Int.* 32:575-85

⁸ Stapleton HM, Dodder NG (2008) 'Photodegradation of decabromodiphenyl ether in house dust by natural sunlight' *Environ Toxicol Chem* 27:306-312

⁹ Allen JG, McClean MD, Stapleton HM, Webster TF, (2008) *Environ Int* In press

1.3 Anaerobic and microbial debromination

Anaerobic and microbial debromination has been studied in several different systems. The first report of reductive debromination of deca-BDE (BDE-209) was that of Gerecke et al. (2005)¹ who incubated it with sewage sludge to which certain primers (organic chemicals) had been added, over a period of 238 days. The concentration of BDE-209 was reduced by 30%, and octa-BDEs and the nona-BDEs BDE-207 and BDE-208 were formed, accounting for about 17% of the quantity lost, but a complete mass balance was not performed. Bromines were removed mainly from positions meta- and para- to the oxygen. In separate experiments, the nona-BDEs BDE-207 and BDE-206 were incubated and were degraded to mixtures of octa-BDEs.

The great variety of possible results is suggested by the highly selective reductive microbial debrominations observed in experiments reported by He et al. (2006).² Hepta- and Octa-BDE congeners were produced in cultures of *Sulfurospirillum multivorans* that was known to convert tetrachloroethylene to dichloroethylene, when decaBDE was exposed to it for two months. OctaBDE was not attacked in a similar system. Cultures of an alternative organism, *Dehalococcoides* sp., failed to attack the decaBDE but an octaBDE mixture was extensively changed, over six months yielding a mixture of hepta- through di-BDEs which included the pentaBDE, BDE-99. Tetra-BDEs were formed over longer periods. Complete quantitation was not achieved and best results were obtained with certain strains of the organism especially when grown in the presence of trichloroethylene.

In an industry-funded study, Schaefer and Flaggs (2001)³ exposed ¹⁴C-labelled BDE-47 (a tetraBDE) to anaerobic sediments for 32 weeks and found that <1% of the total radioactivity was recovered as ¹⁴CO₂ and ¹⁴CH₄, indicating that essentially no mineralization had occurred. They concluded that BDE-47 has the potential to degrade very slowly under anaerobic conditions. Schaefer and Flaggs (2001a)⁴ performed a similar study of decaBDE for the bromine industry and concluded that the presence of deca-BDE in the environment does not contribute to environmental levels of penta-BDE. A critique by US EPA (Auer (2006)⁵ noted that the intra- or extra-cellular nature of the debromination process was not identified, and that given the low water solubility of deca-BDE the incubation time of 32 weeks 'may be inadequate to represent environmentally realistic sediment residue times as well as to demonstrate debromination'.

1.4 Debromination in biota

In experiments reported by Stapleton et al. (2004)⁶, carp were fed for 62 days with food spiked with individual BDE congeners, and tissue and excreta were examined. At least 9.5±0.8% of BDE-99 in the gut was reductively debrominated to BDE-47 (one less bromine) and assimilated in carp tissues. Similarly, 17% of the heptabromo congener BDE-183 was reductively debrominated to hexabromo congeners.

Tomy et al (2004)⁷ exposed juvenile lake trout (*Salvelinus namaycush*) to three dietary concentrations of 13 BDE congeners (3-10 bromine atoms) in the laboratory for 56 days, followed by 112 days of clean food. Half-lives (*t*_{1/2}) for some BDE congeners (e.g., BDE-85 and -190) were much lower than expected based on their Kow, whereas *t*_{1/2} of other BDE congeners (e.g., BDE-66, -77, -153, and -154) were much longer than anticipated based on Kow. This was explained by reductive debromination. The detection of three BDE

¹ Gerecke, A.C., Hartmann, P.C., Heeb, N.V., Kohler, H-P. E., Giger, W., Schmid, P., Zennegg, M. and Kohler, M. (2005), 'Anaerobic Degradation of Decabromodiphenyl Ether', *Environ. Sci. Technol.* 39, 1078-1083

² He, J., Robrock, K.R. and Alvarez-Cohen, L. (2006). 'Microbial Reductive Debromination of Polybrominated Diphenyl Ethers (PBDEs)', *Environ. Sci. Technol.* 40: 4429-4434

³ Schaefer, E. C. and Flaggs, R. (2001), 'Potential for biotransformation of radiolabelled tetrabromodiphenyl oxide (TeBDPO) in anaerobic sediment. Final Report. Project 439E-105. Wildlife International, Ltd. Easton, MD

⁴ Schaefer, E. C. and Flaggs, R. (2001a), 'Potential for biotransformation of radiolabelled decabromodiphenyl oxide (DBDPO) in anaerobic sediment. Final Report. Project 439E-104. Wildlife International, Ltd. Easton, MD

⁵ Auer, C.M., US EPA, to Sandrof, N., American Chemistry Council, 28 August 2006 (www.epa.gov/oppt/vccep/pubs/ltr8282006.pdf)

⁶ Stapleton, H.M., Letcher, R.J. and Baker, J.E. (2004), 'Debrominated Diphenyl Ether Congeners BDE 99 and BDE 183 in the Intestinal Tract of the Common Carp (*Cyprinus carpio*)', *Environ. Sci. Technol.* 38: 1054-1061

⁷ Tomy, G.T., Palace, V.P., Halldorson, T., Braekvelt, E., Danell, R., Wautier, K., Evans, B., Brinkworth, L. and Fisk, A.T. (2004), 'Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile lake trout (*Salvelinus namaycush*)', *Environ. Sci. Technol.* 38:1496-504

congeners (BDE-140 plus an unknown penta-BDE, and an unknown hexa-BDE) in the fish, substances that were not present in the food or in the control fish, provided further evidence for the reductive debromination of BDEs.

Experiments involving whole animals have been less common, but when mice were treated orally and subcutaneously for 34 days with a commercial penta-BDE mixture (DE-71) (Qiu et al. (2007))¹ the recovered products were bromophenols and hydroxylated bromodiphenyl ethers. The recovered bromo-compounds were only a small proportion of the quantity of the original mixture administered to the animals.

When PBDEs, mainly deca-BDE (BDE-209), were fed to cows the congener array in the feces was the same as that in the feed, indicating that no changes took place in the rumen. (Kierkegaard et al., 2007).² Other tissues, including the milk fat were enriched in BDE-207, -196, -197 and -182, and the authors interpret this as evidence that metabolic reductive debromination of BDE-209 occurs in other body tissues. Due to the experimental procedures adopted, it was not possible quantitatively to assess the mass balance of dietary absorption. The authors cite work of Viberg et al. (2003)³ who suggested that neurobehavioural changes observed in neonatal mice treated with BDE-209 were due to its transformation in vivo to more toxic lower congeners or to hydroxylated metabolites.

Van den Steen et al. (2007)⁴ used silastic implants to expose European starlings (*Sturnus vulgaris*) to deca-BDE (BDE-209) and found octa- (BDE-196, BDE-197) and nonaBDEs (BDE-206, BDE-207, BDE-208) in muscle and liver in addition to deca-BDE, resulting in the first indications of debromination in birds.

La Guardia et al. (2007)⁵ examined fish and crayfish in rivers downstream of a waste water treatment plant. The local water and sediment contained significant levels of deca-BDE and they detected a number of PBDE congeners in the fish and crayfish, including three hepta- (BDE-179, -184, -188), and two octa-congeners (BDE-201 and -202) that were not present in the commercial deca-BDE mixture.

Sparrowhawks, buzzards, owls and kestrels in China were investigated for uptake of deca-BDE (BDE-209) from the environment (Da Chen et al. (2007)).⁶ In addition to BDE-209, the birds' tissues were also found to contain a nona-BDE (BDE-207) and other congeners that may result from debromination of deca-BDE through physical or biological reactions or by direct uptake of such species that have been produced in the environment from BDE-209.

The egg yolk and plasma of male and female glaucous gulls (*Larus hyperboreus*) from the Norwegian Arctic were found to contain a number of brominated flame retardant substances, including three nona-BDEs (BDE-206, -207 and -208) that appear to be the products of reductive debromination of deca-BDE (BDE-209) (Verreault et al. (2007)).⁷ Like the Chinese birds mentioned above, the source of the reductively debrominated compounds is unknown.

¹ Qiu, X., Mercado-Feliciano, M., Bigsby, R.M. and Hites, R.A. (2007), 'Measurement of Polybrominated Diphenyl Ethers and metabolites in Mouse Plasma after Exposure to a Commercial Pentabromodiphenyl Ether Mixture', *Environ. Health Perspectives*, 115(7) 1052-1058

² Kierkegaard, A., Asplund, L., De Wit, C., McLachlan, M.S., Thomas, G.O., Sweetman, A.J. and Jones, K.C. (2007), 'Fate of Higher Brominated PBDEs in Lactating Cows', *Environ. Sci. Technol.* 41, 417-423

³ Viberg, H., Fredricksson, A., Jakobsson, E., Orn, U. and Eriksson, P. (2003), 'Neurobehavioural derangements in adult mice receiving decabrominated diphenyl ether (PBDE 209) during a defined period of neonatal brain development' *Toxicol. Sci.*, 76: 112-120

⁴ Van den Steen, E., Covaci, A., Jaspers, V.L., Dauwe, T., Voorspoels, S., Eens, M. and Pinxten, R. (2007), 'Accumulation, tissuespecific distribution and debromination of decabromodiphenyl ether (BDE 209) in European starlings (*Sturnus vulgaris*)', *Environ. Pollut.* 148: 648-653

⁵ La Guardia, M.J., Hale, R.C. and Harvey, E. (2007), 'Evidence of Debromination of Decabromodiphenyl Ether (BDE-209) in Biota from a wastewater Receiving Stream', *Environ. Sci. Technol.* 41 (19), 6663-6670

⁶ Da Chen, Mai, B., Song, J., Sun, Q., Luo, Y., Luo, X., Zeng, E. and Hale, R.C. (2007) 'Polybrominated Diphenyl Ethers in Birds of Prey from Northern China', *Environ. Sci. Technol.* 41(6), 1828-1833

⁷ Verreault, J., Gebbink, W.A., Gauthier, L.T., Gabrielsen, G.W. and Letcher, R.J. (2007), 'Brominated Flame Retardants in Glacous Gulls from the Norwegian Arctic: More than Just an Issue of Polybrominated Diphenyl Ether', *Environ. Sci. Technol.* 41: 4925-4931

The marine food web in Bohai Bay, North China, was studied by Yi Wan et al. (2008)¹, who reported that BDE-47 was the predominant PBDE in most samples and that concentrations of this substance were biomagnified in the food web. Changes in relative concentrations with trophic level (zooplankton to gulls) led to the conclusion that BDE-99 was biotransformed into BDE-47.

The absorption, distribution, metabolism, and excretion of decaBDE were studied in rats by Morck et al. (2003)² after a single oral dose of decaBDE. Metabolites with five to seven bromine atoms were formed possessing a hydroxy and methoxy group in one of the rings (guaiacol structure). In addition, traces of nonaBDEs were formed along with monohydroxylated metabolites.

Debromination of decaBDE was studied in male Sprague – Dawley rats by Huwe et al. (2007)³ following dietary exposure using multiple low doses of decaBDE. BDE-209, three nonaBDEs, and four octaBDEs accumulated in the rats and were distributed proportionately throughout the body. Only 5% of the parent decaBDE was present in the rats after 21 days.

The disposition of decaBDE and its metabolites was studied in pregnant Wistar rats by Riu et al. (2008)⁴ after force feeding with pure decaBDE over 96 hours at a late stage of gestation. Transformation products were observed in tissues and in fetuses including three nonaBDEs and one octaBDE. The authors note that decaBDE and very likely most of its metabolites can cross the placental barrier in rats.

Thuresson et al. (2005)⁵ found that workers exposed occupationally to c-DecaBDE contain heptaBDE and octaBDE congeners that are not present in the commercial c-DecaBDE mixture or in reference groups. A follow up study found that reduced exposure decreased the decaBDE concentrations but increased the heptaBDE and octaBDE concentrations suggesting that debromination was occurring in humans (Thuresson et al. (2006)).⁶

There is a sizeable body of data on the properties of c-DecaBDE that are relevant to its debromination to form components of c-OctaBDE. C-DecaBDE is found in fish, birds, grizzly bears, and other animals at high concentrations, demonstrating that deca-BDE can be absorbed by biological systems.^{7 8 9} Deca-BDE can be absorbed by dietary intake in carp, lake trout and rats^{10 11 1 2} Given that animal uptake rates are usually in the

¹ Yi Wan, Jianying Hu, Kun Zhang and Lihui An (2008), 'Trophodynamics of Polybrominated Diphenyl Ethers in the Marine Food Web of Bohai Bay, North China', Environ. Sci. Technol., 42: 1078-1083

² Morck A, Hakk H, Orn U, Klasson WE (2003) 'Decabromodiphenyl ether in the rat: absorption, distribution, metabolism, and excretion', Drug Metab Dispos 31: 900 - 907

³ Huwe JK, Smith DJ (2007) 'Accumulation, whole-body depletion, and debromination of decabromodiphenyl ether in male Sprague – Dawley rats following dietary exposure' Environ Sci Technol 41:2372-2377

⁴ Riu A, Cravedi JP, Debrauwer L, Garcia A, Canlet C, Jouanin I, Zalko D (2008) Disposition and metabolic profiling of [(14)C]-Decabromodiphenyl ether in pregnant Wistar rats. Environ Int 34:318-329

⁵ Thuresson K, Bergman A, Jakobsson K. (2005) Occupational exposure to commercial decabromodiphenyl ether in workers manufacturing or handling flame-retarded rubber. Environ Sci Technol 39:1980 – 1986

⁶ Thuresson K, Hoglund P, Hagmar L, Sjodin A, Bergman A, Jakobsson K. (2006) Apparent half-lives of hepta- to decabrominated diphenyl ethers in human serum as determined in occupationally exposed workers. Environ Health Perspect 114:176 – 181

⁷ Johnson-Restrepo B, Kannan K, Addink R, Adams DH, Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. Environmental Science & Technology 2005, 39, (21), 8243-8250

⁸ Bixian M, Song J, Suin Q, Zeng E, Hale RC. Polybrominated Diphenyl Ethers in Birds of Prey Collected from Northern China, SETAC, Montreal, Quebec, 2006; Montreal, Quebec, 2006

⁹ Christensen JR, Macduffee M, Macdonald RW, Whitaric M, Ross PS. Persistent organic pollutants in British Columbia grizzly bears: Consequence of divergent diets. Environmental Science & Technology 2005, 39, (18), 6952-6960

¹⁰ Kierkegaard A, Balk L, Tjarnlund U, De Wit CA, Jansson B. Dietary uptake and biological effects of decabromodiphenyl ether in rainbow trout (*Oncorhynchus mykiss*). Environmental Science & Technology 1999, 33, (10), 1612-1617

¹¹ Stapleton HM, Alae M, Letcher RJ, Baker JE. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprinus carpio*) following dietary exposure. Environmental Science & Technology 2004, 38, (1), 112-119

the range of 1 – 3 % of a given dose of decaBDE³, high concentrations in terrestrial animals^{4 5} suggest that decaBDE can bioaccumulate⁶. Levels of PBDEs in the human population have been rising steadily for the past thirty years and concentrations are doubling approximately every five years.⁷ DecaBDE levels are rising along with the levels of other PBDEs in the general population.⁸ Finally, DecaBDE has been measured in human blood and breast milk^{9 10} and at high levels in electronics recycling workers.^{11]}

2. Information on alternatives (products and processes) to c-decaBDE

C-DecaBDE is used as an additive flame retardant often together with antimony trioxide in plastics (~80%) and textiles (~20%) with the predominate uses including TV enclosures made of high impact polystyrene (HIPS), coated wire, electrical parts, mattresses, draperies, commercial upholstered furniture, cars, airplanes, tents, awnings, and other fabric applications.¹² According to the industry, decaBDE is the highest use brominated flame retardant in the Americas and global volume estimates put use at more 56,400 metric tons in 2003 as opposed to negligible use of octaBDE.¹³ A number of reports address non-chemical and chemical alternatives for c-DecaBDE in these uses.^{14 15 1 2 3 4 5}

¹ Tomy GT, Palace VP, Halldorson T, Braekevelt, E, Danell R, Wautier K, Evans B, Brinkworth L, Fisk AT. Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile lake trout (*Salvelinus namaycush*). *Environmental Science & Technology* 2004, 38, (5), 1496-1504

² Morck A, Hakk H, Orn U, Wehler EK. Decabromodiphenyl ether in the rat: Absorption, distribution, metabolism, and excretion. *Drug Metabolism and Disposition* 2003, 31, (7), 900-907

³ Stapleton, H. Brominated Flame Retardants: Assessing DecaBDE Debromination in the Environment. Health and Environment Alliance, www.env-health.org, May 2006

⁴ Christensen JR, Macduffee M, Macdonald RW, Whitticar M, Ross PS. Persistent organic pollutants in British Columbia grizzly bears: Consequence of divergent diets. *Environmental Science & Technology* 2005, 39, (18), 6952-6960

⁵ Voorspoels S, Covaci A, Lepom P, Escutenaire S, Schepens P. Remarkable findings concerning PBDEs in the terrestrial top-predator red fox (*Vulpes vulpes*). *Environmental Science & Technology* 2006, 40, (9), 2937-2943

⁶ Stapleton H. Summary of Scientific Studies on Accumulation and Debromination of DecaBDE. Health and Environment Alliance, www.env-health.org, December 2006

⁷ Hites R. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. *Environ. Sci. Technol.* 38 (4): 945-56

⁸ Hites, R. op cit.; WWF UK ContamiNATION: National Biomonitoring Survey 2003 <http://www.wwf.org.uk/filelibrary/pdf/biomonitoringresults.pdf>

⁹ Schecter A, Vuk MP, Papke O, Ryan, JJ, Birnbaum L, Rosen, R. Polybrominated diphenyl ethers (PBDEs) in US mothers' milk. *Environmental Health Perspectives* 2003, 111, (14), 1723-1729

¹⁰ Schecter A, Papke O, Harris, TR, Tung, KC. Partitioning of polybrominated diphenyl ether (PBDE) congeners in human blood and milk. *Toxicological & Environmental Chemistry* 2006, 88, (2), 319-324

¹¹ Jakobsson K, Thuresson K, Rylander L, Sjodin A, Hagmar L, Bergman A. Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. *Chemosphere*. 2002 Feb;46(5):709-16

¹² Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

¹³ Minnesota Pollution Control Agency, Decabromodiphenyl ether (Deca-BDE), A report to the Minnesota legislature, January 15, 2008 <http://www.pca.state.mn.us/publications/reports/lrp-ei-2sy08.pdf>

¹⁴ Lassen C, Havelund S, Leisewitz A, Maxson P. COWI A/S, Denmark; Oko-Recherche BmbH, Germany; Concorde East/West Sprl, Belgium. Deca-BDE and alternatives in electrical and electronic equipment, Danish Ministry of the Environment, 2006 <http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf>

¹⁵ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production,

2.1 Design changes to address *c-DecaBDE*

A general substitution for uses in electrical equipment is using a metal sheet to cover plastic in contact with electrical parts.⁶ In TV design, manufacturers have been able to achieve UL standards by separating the voltage supply from ignitable plastics though this does not flame retard them from external sources of ignition.⁷ Other strategies include reducing operating voltage and removing the power supply from the product (used in printers and phones). Redesign of mattresses includes eliminating flammable foam (implemented by Herman Miller furniture), utilizing inherently fire-resistant fabrics (used in fire fighter apparel), and use of barrier layers with boric acid (used in mattresses, upholstered furniture, and draperies; see below).⁸

2.2 Chemical substitutes for *c-DecaBDE* in HIPS

Non-halogenated alternatives for this application include blends of polycarbonate and ABS (PC / ABS), polycarbonate (PC), blends of HIPS and polyphenylene oxide (HIPS / PPO), and polylactide (PLA).⁹

The PC / ABS blends use a flame retardant and polytetrafluoroethylene (PTFE) indicating that they are not halogen-free. Two common flame retardants are resorcinol bis diphenyl phosphate (RDP) and bisphenol a diphosphate (BPADP). Resorcinol bis (diphenylphosphate) is neither persistent nor bioaccumulative, however its triphenyl phosphate degradation product has moderate concern for bioaccumulation and it is harmful to aquatic organisms.^{10 11} BPADP has a high potential for persistence and includes triphenyl

University of Massachusetts – Lowell, 2005

<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

¹ Pakalin S, Cole T, Steinkellner J, Nicolas R, Tissier C, Munn S, Eisenreich S. European Chemicals Bureau, Review on production processes of decabromodiphenyl ether (DecaBDE) used in polymeric applications in electrical and electronic equipment, and assessment of the availability of potential alternatives to DecaBDE, European Commission Directorate General Joint Research Center, January 2007 http://ecb.jrc.it/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE.pdf

² Illinois Environmental Protection Agency, Report on alternatives to the flame retardant decaBDE: Evaluation of toxicity, availability, affordability, and fire safety issues. A report to the Governor and State Assembly. March 2007 <http://www.epa.state.il.us/reports/decabde-study/>

³ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005 <http://www.ecy.wa.gov/pubs/0507048.pdf>

⁴ Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007 <http://www.maine.gov/dep/rwm/publications/legislative-reports/pdf/finalrptjan07.pdf>

⁵ Stuer-Lauridsen F, Cohr KH, Andersen TT, DHI Water & Environment, Health and environmental assessment of alternatives to deca-BDE in electrical and electronic equipment, Danish Ministry of the Environment, No. 1142, 2007

<http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-351-6/pdf/978-87-7052-352-3.pdf>

⁶ Lassen C, Havelund S, Leisewitz A, Maxson P. COWI A/S, Denmark; Oko-Recherche BmbH, Germany; Concorde East/West Sprl, Belgium. Deca-BDE and alternatives in electrical and electronic equipment, Danish Ministry of the Environment, 2006

⁷ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005

<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

⁸ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005

<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

⁹ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005

<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

¹⁰ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

¹¹ Rossi M, Heine L. Clean Production Action, Green Blue, The Green Screen for Safer Chemicals –

phosphate as a degradation product.² BDADP also includes Bisphenol A as a contaminant and degradation product which displays endocrine disruption, developmental and reproductive toxicity, and other toxic effects.³ PC may be compounded similarly.

The PPO in the HIPS / PPO blends provide increased flame retardancy and the blends often utilize resorcinol bis diphenyl phosphate (see paragraph above.) These blends have a higher heat tolerance and mechanical strength than HIPS retarded with c-DecaBDE.⁴

Poly lactide needs modification for product applications due to its low melting point and brittleness. However, NEC has made a PLA resin with metal hydroxide flame retardants and kenaf fibers for improved strength making it as heat resistant, easy to process, and strong as PC.⁵ JVC, Sony, and Mitsubishi are actively developing PLA materials with aluminum hydroxide flame retardants. The Danish Alternatives report summarizes the toxicity of aluminum hydroxide as very low except when there are high exposure levels or unusual routes of exposure and estimates that it would be extremely unlikely for its use in consumer products to cause adverse effects.⁶ The German Alternatives report describes the use of aluminum trihydroxide as a flame retardant as “unproblematic.”⁷

2.3 Chemical substitutes for c-DecaBDE in polypropylene

Non-brominated flame retardants for use in polypropylene or polypropylene ether coated wire and cable include ammonium polyphosphate, magnesium hydroxide, and melamine phosphate.⁸

Ammonium polyphosphate is often used in combination with aluminum trihydroxide.

The substance metabolizes into ammonia and phosphate and is not thought to cause acute toxicity in humans.⁹ However, there are no analyses of long-term toxicity, teratogenicity, mutagenicity, or carcinogenicity. Ammonium polyphosphate breaks down rapidly and does not accumulate in the food chain.

Version1.0: Evaluating environmentally preferable flame retardants for TV enclosures, 2007
<http://cleanproduction.org/Green.Greenscreen.php>

¹ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

² Rossi M, Heine L. Clean Production Action, Green Blue, The Green Screen for Safer Chemicals –Version1.0: Evaluating environmentally preferable flame retardants for TV enclosures, 2007 <http://cleanproduction.org/Green.Greenscreen.php>

³ Rossi M, Heine L. Clean Production Action, Green Blue, The Green Screen for Safer Chemicals –Version1.0: Evaluating environmentally preferable flame retardants for TV enclosures, 2007 <http://cleanproduction.org/Green.Greenscreen.php>

⁴ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005

<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

⁵ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005

<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

⁶ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

http://www2.mst.dk/common/Udgivramme/Frame.asp?pg=http://www2.mst.dk/udgiv/Publications/1999/87-7909-416-3/html/kap08_eng.htm

⁷ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

⁸ Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007
<http://www.maine.gov/dep/rwm/publications/legislative-reports/pdf/finalrptjan07.pdf>

⁹ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

The German Alternatives report concludes that skin irritation is possible due to the formation of phosphoric acids but that the substance appears to be “unproblematic”.¹

Magnesium hydroxide is commonly ingested as an antacid and forms the active ingredient in milk of magnesia. Surprisingly, there is very little toxicological information on magnesium hydroxide. One possible problem with its use as a flame retardant is that large amounts of (~50%) are required for effective flame retardancy and this may change the properties of the material.

Melamine and its derivatives display several toxic effects. These include changed electrolyte compositions of urine, teratogenic effects in fertilized rainbow trout eggs, and reproductive effects in snails and houseflies.² In addition, melamine caused chronic injury to the male rat bladder due to stones formed during exposure which correlated strongly with carcinoma.³ In a fire, melamine cyanurate will release toxic fumes such as hydrocyanic acid and isocyanate.⁴ The Danish report notes that there is no data on emission from products and that melamine appears to have low acute and chronic toxicity. The report concludes that, “...no adverse effects are envisaged from the level of exposure expected from the use of melamine as a flame retardant. At the level of exposure precipitation in the renal tubulus and in the bladder should not be a significant risk.”⁵ In contrast, the German report describes the lack of data, presence in environmental samples and moderate organ toxicity of melamine and concludes it is a “...problematic substance.”⁶ Melamine and its derivatives are not both persistent and bioaccumulative.

2.4 Chemical substitutes for c-DecaBDE in polybutylene terephthalate (PBT) and polyamide (PA)

Alternatives to brominated flame retardants in this use for electrical parts include magnesium hydroxide, melamine cyanurate, and melamine polyphosphate in polyamide and phosphinic acid in polybutylene terephthalate.⁷ See the section above for reviews of magnesium hydroxide and melamine compounds. Phosphinic acid is not well characterized, though the Danish EPA report notes that it is considered to be very persistent.⁸

2.5 Chemical substitutes for c-DecaBDE in mattresses, upholstery, and draperies

The choice and feasibility of c-DecaBDE substitutes in textiles can be affected by the fabric which is used since the flame retardancy of various fabrics varies from those that easily burn with a vigorous flame (cotton) to those that burn slowly (wool and silk), to very slowly (modacrylic and saran), and even some that do not

¹ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

² Daugherty ML. Chemical hazard information profile draft report: Melamine, CAS No. 108-78-1, Office of Toxic Substances, US EPA, 1982.

³ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁴ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

⁵ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁶ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

⁷ Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007 <http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf>

⁸ Stuer-Lauridsen F, Cohr KH, Andersen TT, DHI Water & Environment, Health and environmental assessment of alternatives to deca-BDE in electrical and electronic equipment, Danish Ministry of the Environment, No. 1142, 2007

burn (aramid, novoloid, and melamine.)¹ Note that modacrylic synthesis utilizes highly toxic substances such as acrylonitrile and vinyl bromide.^{2 3 4 5}

Mattresses can utilize a phosphate-based flame retardant as a coating for mattress fabrics (see above) or fire barriers that place a fire-resistant material in the cushioning or between the exterior cover fabric and the first layer of cushioning.⁶ The latter method is commonly used commercially and thought to be applicable to upholstered furniture as well. Draperies can be flame retarded with phosphonate type substances or made using inherently flame-resistant fabrics.⁷

According to industry sources cited in the Pure Strategies report, "...chemical flame retardants are not necessary in 99% of cases for panel and upholstery fabrics to meet the fire codes for residential upholstered furniture."

2.6 Assessing *c-DecaBDE* alternatives

Given the range of alternative flame retardants and techniques available, a wise course of action would be to examine the toxicity of the substance, its breakdown products, manufacturing processes, and the use of synthetic materials, and give preference to those that pose least risk. As noted in the Danish EPA report, "Criteria for developing functional flame retardants should include non-hazardous synthetic pathway, minimum human and environmental toxicity, minimum release during product use, minimum formation of hazardous substances during incineration or burning, recyclable, degradable, and decompose into a non-hazardous substance."⁸

In general, chemical alternatives that exhibit properties such as persistence and bioaccumulation seem inappropriate as replacements for a POP with these same properties. Two chemical substitutes are persistent: bis (tribromophenoxy) bisphenol a diphosphate (BPADP) and phosphinic acid. Resorcinol bis (diphenylphosphate) is neither persistent nor bioaccumulative, however its triphenyl phosphate degradation product has moderate concern for bioaccumulation and it is harmful to aquatic organisms.^{9 10 11} Melamine is not persistent or bioaccumulative but displays several toxic effects which the German report describes as

¹ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005

<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

² <http://www.britannica.com/eb/article-9053135/modacrylic>

³ National Toxicology Program, Report on carcinogens background document for vinyl bromide. <http://ntp.niehs.nih.gov/ntp/newhomeroc/roc10/VB.pdf>

⁴ <http://www.atsdr.cdc.gov/tfacts125.html>

⁵ World Intellectual Property Organization, WO/2005/111289, Fire blocker fiber composition, high loft web structures, and articles made therefrom, undated
<http://www.wipo.int/pctdb/en/wo.jsp?IA=WO2005111289&DISPLAY=DESC>

⁶ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005
<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

⁷ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005
<http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf>

⁸ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁹ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

¹⁰ Rossi M, Heine L. Clean Production Action, Green Blue, The Green Screen for Safer Chemicals –Version1.0: Evaluating environmentally preferable flame retardants for TV enclosures, 2007 <http://cleanproduction.org/Green.GreenScreen.php>

¹¹ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

“problematic”.¹ The metal hydroxides are approved by both the Danish EPA and German reports through they note that more information is needed.^{2 3]}

¹ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

² Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

³ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

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- <http://www.wipo.int/pctdb/en/wo.jsp?IA=WO2005111289&DISPLAY=DESC>
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