# Multiple Framework Contract with Re-opening of competition for Scientific Services for ECHA

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Service Request SR 14:

Support to an Annex XV Dossier on Bis-(pentabromophenyl) ether (DecaBDE)

**Final Report** 

prepared for

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#### List of acronyms

ABS Acrylonitrile Butadiene Styrene

AMAP Arctic Monitoring Assessment Programme

ATH Aluminium trihydroxide
ATO Antimony trioxide

BAT Best Available Techniques

BC Basel Convention

BDE Brominated Diphenyl Ether

BEST Subcommittee in flame-retardant chemicals; Committee on Toxicology;

Board on Environmental Studies and Toxicology

BFR Brominated flame retardant
BREF BAT reference document

BSEF Bromine Science and Environmental Forum

bw Body weight

CAS No Chemical Abstract Service registry number

CBI Confidential business information c-DecaBDE Commercial grade of DecaBDE

CEPE European Association of Coatings and Paints

CLP Regulation (EC) No. 1272/2008 of the European Parliament and of the

Council of 16 December 2008 on classification, labelling and packaging substances and mixtures amending and repealing Directives 67/548/EEC

and 1999/45/EC, and amending Regulation (EC) No. 1907/2006

CLS Commission on Life Sciences

CMHR Combustion modified high resistance (foam)

COMMPS1 COmbined Monitoring-based and Modelling based Priority Setting

scheme

CPR Construction Products Regulation No. 305/2011 of the European

Parliament and of the Council of 9 March 2011 laying down harmonised conditions for the marketing of construction products and repealing

Council Directive 89/106/EEC

DecaBDE Bis-(pentabromophenyl) ether

DEFRA Department for Environment, Food and Rural Affairs

DELS Division on earth and life studies

dw Dry weight

EBFRIP European Brominated Flame Retardant Industry Panel

EBP Ethane, 1,2-Bis (pentabromophenyl)

EC No European Inventory of Existing Commercial chemical Substances (EINECS)

number

ECB European Chemicals Bureau
ECHA European Chemicals Agency
ECJ European Court of Justice

EEE Electrical and electronic equipment
EFRA European flame retardant association

EoW End of waste Ep Epoxy resins

EPDM Ethylene propylene diene monomer EPER European Pollutant Emission Register

EPS Expanded polystyrene

ESR Existing Substances Regulation

EVA Ethylene Vinyl Acetate
EVC Ethylene Vinyl Chloride

FR Flame Retardant

HBCD Hexabromocyclododecane
HeptaBDE Heptabromodiphenyl ether
HexaBDE Hexabromodiphenyl ether
HFR Halogenated Flame Retardant
HFFR Halogen-free Flame Retardant
HIPS High impact polystyrene

HSE UK Health and Safety Executive IED Industrial Emissions Directive

IPPC Integrated Pollution Prevention and Control

JRC European Joint Research Centre

LOI Limiting oxygen index

LRT Long-range transport potential

LRTAP Long-range transport atmospheric pollution

lw Lipid weight

MDH Magnesium dihydroxide

MSCA Member State Competent Authority

MSW Municipal solid waste

NACE European classification of economic activities

nd Not detected

NonaBDE Nonabromodiphenyl ether
OctaBDE Octabromodiphenyl ether

OECD Organisation for Economic Co-operation and Development

PA Polyamide

PBDDs Polybrominated dibenzo-p-dioxins
PBDE Polybrominated diphenyl ethers
PBDFs Polybrominated dibenzofurans
PBT Persistent, bioaccumulative and toxic

PBTE Polybutylene terephthalate

PC Polycarbonate
PE Polyethylene

PentaBDE Pentabromodiphenyl ether

PES Polyesters

PET Polyethylene terephthalate

PI Polyimides

POPs Persistent Organic Pollutants

PP Polypropylene
PPE Polypropylene ether
PPO Polyphenylene oxide

PRTR Pollutant Release and Transfer Register

PS Polystyrene
PU / PUR Polyurethane
PVC Polyvinyl chloride

REACH Regulation (EC) No. 1907/2006 of the European Parliament and of the

Council of 18 December 2006 concerning the Registration, Evaluation,

Authorisation and Restriction of Chemicals

RoHS Directive 2011/65/EU of the European Parliament and of the Council of 8

June 2011 on the restriction of the use of certain hazardous substances in

electrical and electronic equipment Text with EEA relevance

RPA Risk & Policy Analysts Ltd
SBR Styrene Butadiene Rubber
SC Stockholm Convention
SLF Shredder Light Fraction

SVHC Substance of Very High Concern

TBBPA Tetrabromobisphenol-A
TBNPA Tribromo-neopentyl alcohol
TCDD Tetrachlorodibenzo-p-dioxin
TCPP Tris(2-chloroisopropyl)phosphate
TDCPP Tris(1,3-dichloro-2-propyl) phosphate

TPO Thermoplastic polyolefins
TPU Thermoplastic polyurethanes

UNECE United Nations Economic Commission for Europe

UPE Unsaturated polyesters
UPR Unsaturated polyester resin

US EPA US Environmental Protection Agency

VECAP Voluntary Emissions Control Action Programme

Vinyon is a synthetic fibre made from polyvinyl chloride

vPvB very Persistent and very Bioaccumulative

WEEE Wastes from electrical and electronic equipment

WFD Directive 2008/98/EC on waste (Waste Framework Directive)

WHO World health organisation

w/w Weight per weight XPS Extruded polystyrene

#### 1 Background to this report

#### 1.1 Background to this analysis

On 19 August 2013, ECHA requested services to support the preparation of an Annex XV Restrictions Dossier on the uses of bis-(pentabromophenyl) ether (hereafter referred to as DecaBDE) (EC No. 214-604-9, CAS No. 1163-19-5).

DecaBDE is an organohalogen substance that industrially has found a wide range of applications due to its intrinsic properties as a flame retardant (FR). DecaBDE belongs to the polybrominated diphenyl ethers family that includes other FRs, such as pentabromodiphenyl ether (PentaBDE), and octabromodiphenyl ether (OctaBDE). DecaBDE can transform over time through debromination into other less brominated PBDE congeners, thus implications of photochemical and thermal degradation of DecaBDE should be addressed in order to provide control measures for the less brominated congeners which already considered persistent organic pollutants (POPs).

Certain restrictions on the use of DecaBDE are already in place. Directive 2002/95/EC (RoHS) and its recast Directive 2012/19/EU require that new electrical and electronic equipment (EEE) placed on the market shall not contain PBDEs, including DecaBDE, in concentrations higher than 0.1% w/w in homogeneous materials (i.e. materials of uniform composition or combination of materials that cannot be mechanically separated). Additionally, the Water Framework Directive also considers PBDEs as priority substances, with PentaBDE being a priority hazardous substance.

Within a REACH context, DecaBDE is considered a "substance of very high concern" (SVHC) and was included in the Candidate List for Authorisation on 19 December 2012. Recently, DecaBDE was one of the six substances included in the 5<sup>th</sup> draft recommendation for inclusion of substances in the Authorisation list, published by ECHA in June 2013.

Meanwhile, Norway submitted a proposal to include DecaBDE in Annexes A, B and/or C to the Stockholm Convention (SC) requiring the consideration of its global consumption, persistence, potential for long-range transport and adverse effects. The SC already lists PentaBDE and OctaBDE under its Annex A due to their high persistence, long-range transport properties and demonstrated toxicity in a range of non-human species as well as because they may cause significant adverse effects on human health or the environment.

As the inclusion of DecaDBE in the SC Annex could lead to a restriction or prohibition of the use of the substance in certain applications, ECHA has decided to remove the substance from the public consultation and the draft recommendation list. Subsequently, the European Commission has requested the preparation of an Annex XV Restrictions Dossier for the substance.

ECHA intends to submit this Annex XV Restrictions Dossier by 1 August 2014 and RPA's task has been to analyse and provide supporting information that can be used to develop relevant parts of the dossier.

#### 1.2 Project objectives and structure of this report

ECHA has requested Risk & Policy Analysts Ltd (RPA) to collect and provide information on:

- Identified uses of DecaBDE and estimated related tonnages
- Estimated emissions per use
- Alternatives: availability and technical feasibility per use
- Alternatives: substitution costs per use and a market overview
- Alternatives: assessment of risks for the most important alternatives

#### The report is organised as follows:

- **Section 2**: This Section provides information about the substance, the restriction proposal, and the regulatory status of DecaBDE
- **Section 3**: This Section describes the products and materials in which DecaBDE has been used and gives information on manufacture, imports and consumption of the substance
- **Section 4**: This Section describes releases and environmental fate information for DecaBDE as well as available monitoring data
- **Section 5**: This Section provides an overview of potential alternatives and then examines in more detail the technical applicability, economic feasibility and hazard profile of a shortlist of key alternative FRs
- Section 6: This Section presents the bibliography
- Sections 7-11: These are Annexes 1-5 which provide background information on the consultation findings, relevant use descriptors, literature on alternative FRs, the approach followed for the creation of a shortlist of key alternatives and some background information on the comparison between DecaBDE and EBP (the main alternative FR)
- Section 12: This is the Confidential Annex, which provides sensitive information on tonnages, emissions, consultation and detailed calculations of the substitution cost. This publicly available version of the report does not include this Section/Annex.

#### 2 Bis-(pentabromophenyl) ether – (DecaBDE)

#### 2.1 Definition of DecaBDE

DecaBDE is an organohalogen substance that industrially has found a wide range of applications due to its intrinsic properties as a FR. DecaBDE belongs to the polybrominated diphenyl ethers family (PBDE) that includes other FRs, whose use has been banned in the EU, such as pentabromodiphenyl ether (PentaBDE) and octabromodiphenyl ether (OctaBDE). In total there are 209 different PBDEs with different degrees of bromination (bromine atoms substituting hydrogen on the aromatic rings), called congeners. DecaBDE is defined as BDE-209, as it is the most brominated one, with ten bromine atoms.

It has been found that DecaBDE can transform over time through debromination into other less brominated PBDE congeners (Christiansson, et al., 2009), thus implications of photochemical and thermal degradation of DecaBDE should be addressed in order to provide control measures for the less brominated congeners, which are already considered persistent organic pollutants (POPs)<sup>1</sup>.

#### 2.2 Proposal of restriction

In December 2012, ECHA published a Decision to include bis(pentabromophenyl) ether (decabromodiphenyl ether, DecaBDE, EC No. 214-604-9, CAS No. 1163-19-5) in the Candidate List of Substances of Very High Concern (SVHC)<sup>2</sup>.

In June 2013, DecaBDE was one of the six substances included in the 5<sup>th</sup> draft recommendation for inclusion in the Authorisation list (Stockholm Convention, 2012). In July 2013, ECHA decided to remove the substance from the public consultation and the draft recommendation list<sup>3</sup>, following a request from the European Commission to prepare a restriction proposal, and in accordance with the evaluation of the substance under the Stockholm Convention, following a proposal by Norway (Stockholm Convention, 2013).

ECHA intends to submit this Annex XV Restrictions Dossier by 1 August 2014 and, if the dossier demonstrates that action on a community-wide basis is necessary beyond any measures already in place, ECHA shall propose restrictions in order to initiate the restriction process.

For this study, RPA provides services under Framework Contract No ECHA/2011/01, and has been tasked to provide ECHA with the necessary information for the quantitative assessment of DecaBDE emissions from its uses, a market overview and sufficient information about the availability, technical feasibility and the risks of alternatives for the preparation of the Annex XV restriction dossier. Due to difficulties in calculating costs for non-chemical alternative the focus of RPA's study was on identifying and assessing the chemical alternatives. Where information about non-chemical alternatives was available or received through consultation, it has been included in the report.

#### 2.3 Regulatory status of the substance

European legislative controls exist for the DecaBDE directly or indirectly from a decade ago. The relevant controls are provided below and are linked to marketing, use and disposal of DecaBDE.

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Debromination of brominated flame retardants UNEP/POPS/POPRC.7/16 and UNEP/POPS/POPRC.7/INF/18

<sup>&</sup>lt;sup>2</sup> ECHA Decision ED/169/2012 (<u>link</u>).

Commenting on Decabromodiphenyl ether (DecaBDE) is discontinued (ECHA) (link).

Consideration of other international initiatives of relevance and downstream policies regarding FRs in general are included.

#### 2.3.1 REACH Regulation

Under Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Official Journal of the European Union, 2007), DecaBDE has passed the pre-registration and registration phases<sup>4</sup>.

DecaBDE has already been the subject of an evaluation under the ESR Risk Assessment procedure, which was concluded without recommendation for restrictions, due to the lack of significant risks identified for the use of this substance. The Risk Assessment was finalised and published on the EU Official Journal in May 2008 (Official Journal of the European Union, 2008). The results of the DecaBDE Risk Assessment were transferred into REACH.

#### 2.3.2 Existing regulatory controls

Restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) Directive

Directive 2002/95/EC (Official Journal of the European Union, 2003) on the restriction of the use of certain hazardous substances in electrical and electronic equipment (EEE) known as RoHS, which seeks to protect human health and the environment from certain hazardous substances by the environmentally friendly recovery and disposal of WEEE.

RoHS includes all electrical appliances, including components, excluding medical devices and monitoring and control equipment. According to the Directive, no PBDEs were allowed in EEE entering the EU market. Applications of DecaBDE were to be evaluated as soon as possible, in order to see if they would need to be amended. Commission Decision 2005/717/EC had exempted DecaBDE from the restriction of RoHS but, in 2008, the European Court of Justice (ECJ) annulled that decision (ECJ, 2008).

The original RoHS has been recast into Directive 2011/65/EU, taking the technical development of EEE without PBDEs into account. The recast Directive expands the scope of the original to also include medical devices and control and monitoring equipment. All PBDEs, including DecaBDE, are included in the restricted substances list and are not allowed in quantities higher than 0.1% w/w (weight by homogeneous material) in the EEE mentioned, although some categories of EEE are exempted, as shown in Table 2-1 below. The RoHS also states that EEE compliant with the CE certification is considered compliant with the requirements of the Directive.

The restriction under the recast RoHS prevents DecaBDE from being used in the majority of its previous uses.

Registration data **ECHA** on the website http://apps.echa.europa.eu/registered/data/dossiers/DISS-9eafd491-d447-3617-e044-

00144f67d031/DISS-9eafd491-d447-3617-e044-00144f67d031 DISS-9eafd491-d447-3617-e044-00144f67d031.html

are

available

at:

Table 2-1: Scope of the RoHS Directive	
EEE under the scope of RoHS	Exempted EEE
Large and small household appliances	EEE used for military and defence purposes
IT and telecommunication equipment	Equipment that will be sent to space
Consumer equipment	Large-scale stationary industrial tools (i.e. large-scale
	machinery, equipment and components functioning together)
Lighting equipment	Large-scale fixed installations (combination of several types of apparatus in a fixed location)
Electrical and electronic tools	Transport vehicles (excluding two-wheeled electric vehicles)
Toys, leisure and sport equipment	Non-road mobile machinery exclusively for professional uses
Medical devices	Active implantable medical devices (e.g. pacemakers)
Monitoring and control instruments, including industrial monitoring and control instruments	Photovoltaic panels, that are to be installed by professionals
Automatic dispensers	B2B equipment designed and used solely for R&D
Other EEE not covered by the categories above	Specifically designed components of equipment excluded from the scope of the directive, without which the equipment cannot function and which have to be replaced by the same component

#### Risk Assessment under the Existing Substances Regulation (ESR) 793/93

Regulation (EEC) No 793/93 (Official Journal of the European Union, 1993) on the evaluation and control of the risks of existing substances aimed to collect and disseminate information on the substances that were being circulated in the EU. 'Priority substances', that required immediate attention because of their potential risks to human health and the environment, were subject to a risk evaluation by Member States Competent Authorities (MSCA), assisted by information provided by manufacturers and importers.

DecaBDE was identified as a priority substance in the framework of Regulation (EEC) No 793/93, with Commission Regulation (EC) No. 1179/94. The Risk Evaluation was performed by France (human health) and United Kingdom (environment) and resulted in the Risk Assessment Report of 2002 and its two subsequent amendments in 2004 and 2007. These concluded that the substance is mainly used as a FR in the manufacture of polymers, mainly for use in electrical equipment, and in drapery and upholstery textiles. Other minor uses reported are as a FR additive in styrenic rubbers, polycarbonates, polyamides and terephthalates and in hot melt adhesives.

Conclusions regarding workers exposure showed that there was a need for further information and/or testing and to consumers that there is, at present, no need for further information and/or testing or for risk reduction measures beyond those which are being applied already and finally, to humans exposed via the environment there is a need for further information and/or testing. Based on humans health (physicochemical properties), the conclusion is that at present there is no need for further information and/or testing or for risk reduction measures beyond those which are being applied. Regarding the environment, the conclusion for aquatic and terrestrial ecosystem is that there is a need for further information and/or testing, and regarding to atmosphere there is no need to get further information or for risk reduction measures beyond the ones applied, the same to micro-organisms in sewage treatment plants.

#### Waste Electrical and Electronic Equipment Directive

Directive 2002/96/EC on waste electrical and electronic equipment (WEEE) (Official Journal of the European Union, 2012) aimed to prevent and to promote reuse, recycling or other recovery methods for WEEE, while improving the environmental sound management of the processes along the EEE supply chain. Its scope is waste from EEE, with the exception of equipment for defence, safety and security (Official Journal of the European Union, 2003). This Directive, has been now recast, with Directive 2012/19/EU (Official Journal of the European Union, 2012), taking into account the technical progress in EEE and the waste hierarchy. The directive also promotes separate collection of WEEE and sets collection and recovery targets, based on declared quantities of EEE by importers and manufacturers.

Annex VII of the recast WEEE Directive describes the selective treatment for materials and components of waste electrical and electronic equipment and include plastic containing brominated flame retardants (BFRs). It specifies that separately collected plastics that contain BFRs (therefore, including DecaBDE) should be removed and treated separately, in compliance with the Waste Framework Directive 2008/98/EC.

For the purposes of environmental protection, Member States may set up minimum quality standards for the treatment of the WEEE that has been collected, and this includes:

- Separate collection and pre-treatment for ensuring specific treatment and recycling of WEEE
- Consumers have to actively contribute to the success of such collection and should be encouraged to return WEEE
- The collection, storage, transport, treatment and recycling of WEEE as well as its preparation for
  re-use shall be conducted with and the approach be geared to protecting the environment and
  human health and preserving raw materials, and shall aim at recycling valuable resources
  contained in EEE with a view to ensuring a better supply of commodities within the European
  Union
- Where appropriate, priority should be given to preparing for re-use of WEEE and its components, sub-assemblies and consumables. Where this is not appropriate, all WEEE collected separately should be sent for recovery, in the course of which a high level of recovery and recycling should be achieved.
- To facilitate the management, and in particular the treatment and recovery or recycling of WEEE that producers provide information on component and material identification.

#### **Waste Framework Directive**

Directive 2008/98/EC on waste (Waste Framework Directive – WFD) (Official Journal of the European Union, 2008) repealed Directive 2006/12/EC on waste, Directive 91/689/EEC on hazardous waste and the Directive 75/439/EEC on waste oils. It provides a general framework of waste management requirements and sets basic waste management definitions. The new waste hierarchy prioritises the prevention of waste and preparation for reuse over recovery (i.e. recycling and energy recovery). Furthermore, material recovery is considered preferable to energy recovery, while disposal is the last choice.

Another important component of the WFD is the introduction of the concept of "End-of-Waste" (EoW), which refers to waste streams that can cease to be considered as waste, after a recovery process has taken place. Basic principles for EU-wide criteria, as laid down in the Waste Framework Directive (WFD) are:

- Existence of a market or demand
- Common use for specific purposes
- Compliance with established technical specifications and legislation requirements
- Its use will not lead to overall adverse effects to human health and the environment.

The European Joint Research Centre (JRC) is tasked with evaluating waste streams and proposing EU-wide EoW criteria for these. Such criteria have already been published for iron, copper and aluminium scrap and glass cullet<sup>5</sup>. Of relevance to DecaBDE is a draft technical proposal for plastic waste (JRC, 2013). The proposed criteria include the hazard classification of the waste plastic according to CLP, as well as the presence of SVHC or POP above the acceptable concentration limits. It must be noted, however, that a recovery operation must have taken place before a material achieves EoW status. For the purposes of reaching EoW status, a recovery operation may be as simple as the checking of waste to verify that it fulfils the EoW criteria (DG Env, 2012).

Annexes to the WFD define the disposal operations, recovery operations and the properties of waste which render it hazardous and examples of waste prevention measures, e.g. the promotion of research and development into the area of achieving cleaner and less wasteful products and technologies and the dissemination and use of the results of such research and development.

Another important document, Decision 2000/532/EC<sup>6</sup>, establishes a list of wastes, which is a classification system for wastes, including a distinction between hazardous and non-hazardous wastes. It is closely linked to the list of hazard classification criteria which are contained in Annex III to the WFD.

The classification of waste as hazardous should be based, inter alia, on the Community legislation on chemicals, in particular concerning the classification of preparations as hazardous, including concentration limit values used for that purpose. Hazardous waste should be regulated under strict specifications in order to prevent or limit, as far as possible, the potential negative effects on the environment and on human health due to inappropriate management. Furthermore, it is necessary to maintain the system by which waste and hazardous waste have been classified in accordance with the list of the types of waste as last established by Commission Decision 2000/532/EC in order to encourage a harmonised classification of waste and ensure the harmonised determination of hazardous waste within the Community.

There should be no confusion between the various aspects of the waste definition, and appropriate procedures should be applied, where necessary, to by-products that are not waste, on the one hand, or to waste that ceases to be waste, on the other hand.

The decision that a substance is not waste can be taken only based on a coordinated approach, to be regularly updated, and where this is consistent with the protection of the environment and human health. If the use of a by-product is allowed under an environmental licence or general environmental rules, this can be used by Member States as a tool to decide that no overall adverse environmental or human health impacts are expected to occur.

When certain waste ceases to be waste, laying down EoW criteria that provide a high level of environmental protection and an environmental and economic benefit; possible categories of waste for which "EoW" specifications and criteria should be developed are, among others, construction

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Available at: <a href="http://susproc.jrc.ec.europa.eu/activities/waste/index.html">http://susproc.jrc.ec.europa.eu/activities/waste/index.html</a>

Commission Decision of 3 May 2000, replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.

and demolition waste, some ashes and slags, scrap metals, aggregates, tyres, textiles, compost, waste paper and glass.

#### Landfill Directive (1999/31/EC) & Council Decision 2003/33/EC

Directive 1999/31/EC on the landfill of waste aims to reduce the impact of landfilling of waste to the environment, through the introduction of strict technical requirements and procedures for waste and landfills (Official Journal of the European Union, 1999).

The Directive defines different classes of landfills, which should only accept certain types of waste that fulfil specific criteria. Before landfilling, every waste stream must be treated. The three classes of landfill are:

- Landfills for hazardous waste
- Landfills for non-hazardous waste
- Landfills for inert waste.

The Council Decision 2003/33/EC specifies criteria, which waste must fulfil in order to be accepted in a certain landfill class (Official Journal of the European Union, 2003). These criteria include the identification of the composition, the source and origin of the waste and could include testing to determine the degree of leaching of certain inorganic and organic parameters (e.g. heavy metals, chlorine, fluorine, organic content, PCBs).

Neither the Directive nor the Council Decision mention DecaBDE or PBDEs explicitly. Nevertheless, the documents are briefly mentioned in order to indicate the approach regarding the characterisation of waste (which could include DecaBDE) and the protection of soil and water.

It should be noted that depositing sludge on soil, which has been mentioned as a significant source of DecaBDE contamination (COHIBA, 2012), falls outside the scope of the landfill directive. The criteria described in the Council Decision include other halogen atoms as chlorine and fluorine concentrations in the leachate of the waste, but do not include bromine.

#### **EU Water Framework Directive and amendments**

This Directive entered into force in 22 December 2000, and it has subsequently been amended by Decision No. 2455/2001/EC and Directives 2008/32/EC, 2008/105/EC and 2009/31/EC (Official Journal of the European Union, 2000).

Its ultimate aim is the elimination of priority hazardous substances and to contribute to achieving concentrations in the marine environment near background values for naturally occurring substances. This Directive establishes a framework for control of certain "priority substances" that present a significant risk to or via the aquatic environment. A list of 33 substances (or groups thereof) was adopted towards the end of 2001, through Decision No. 2455/2001/EC named as the Fist List of Priority Substances, to become the Annex S of the Water Framework Directive. Amongst the priority substances, there are certain priority hazardous substances for which the Commission will submit proposals for a cessation or phase-out of discharges, emissions and losses.

The first list was replaced by Annex II of the Directive 2008/105/EC on Environmental Quality Standards (Official Journal of the European Union, 2008), also known as Priority Substances Directive, which sets the Environmental Quality Standards (EQS) for the substances in surface waters (river, lake, transitional and coastal) and confirms their designation as priority or priority hazardous substances, the latter being a subset of particular concern.

The first list already included PBDEs among which only PentaBDE had been identified as a priority hazardous substance in 2001, following the COMMPS1 (COmbined Monitoring-based and Modelling based Priority Setting scheme) procedure. The substance OctaBDE has recently been prioritised in the context of the second European Commission proposal for a new list of priority substances, for the reason that it is a PBT (Persistent, Bioaccumulative and Toxic) and a vPvB (very Persistent and very Bioaccumulative) substance. Following this latter prioritisation and the fact that PentaBDE EQS needed to be revised, it was decided to produce a unique fact sheet reporting a common EQS for all BDE congeners linked to c-PentaBDE and c-OctaBDE, that is to say Tetra- to NonaBDE congeners.

The second list already mentioned polybrominated diphenyls as priority substances but it did not specify DecaBDE, although it said that these groups of substances normally include a considerable number of individual compounds. DecaBDE was not prioritised along the prioritisation process. However, given the faculty of brominated diphenyl ether compounds – including DecaBDE – to degrade into lower brominated ones (UNEP, 2010), a revised proposal for a list of priority substances in the context of the Water Framework Directive was developed (COMMPS procedure (Klein, et al., 1999)). For DecaBDE as a priority substance the aim is for a progressive reduction in discharges, emissions and losses to be achieved through a combination of emission limit values and environmental quality standards.

#### The Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC) and Industrial Emissions Directive (2010/75/EC)

The purpose of Directive 96/61/EC (IPPC) (Official Journal of the European Union, 1996) was to achieve integrated prevention and control of pollution arising from industrial activities. It lays down measures designed to prevent or, where that is not practicable, to reduce emissions to air, water and land from the above mentioned activities, including measures concerning waste, in order to achieve a high level of protection of the environment taken as a whole.

Emission limit values, parameters or equivalent measures prescribed by the MSCA should be based on the best available techniques (BAT) without prescribing the use of one specific technique or technology and taking into consideration the technical characteristics of the installation concerned, its geographical location and local environmental conditions. BAT are described in the BAT reference documents (known as BREF) which apply to the different industry sectors that fall under the provisions of the IPPC Directive.

The BREF on the textile industry mentions backcoating and DecaBDE, in an Annex describing the various chemical agents that can be used. It does not discuss in length its relevance to environmental risks, however. Furthermore, the BREF has not been updated since 2003, so it has not taken into account any more recent information that has been produced.

The current draft for wastewater treatment plants mentions that PBDEs were contained in the sludge and monitoring requirements, but this particular entry appears removed, therefore it should not be taken into account, as it will probably not be included in the amended document.

The provisions of the IPPC Directive have now been included in the Industrial Emissions Directive 2010/75/EU (IED) (Official Journal of the European Union, 2010) which is effective as of January 2014. This Directive has integrated the IPPC directive with six other directives, including Directive 2000/76/EC on waste incineration.

The IED includes emission limit values for waste incineration plants (and therefore the requirement for monitoring), but PBDEs are not included in them. Instead of that, it sets limit values for dioxins and furans. These substances are also included in the list of "polluting substances", along with

organohalogens, which also include PBDEs. The limit values for these substances should be respected before a permit is issued to a facility.

#### European Pollutant Release and Transfer Register (E-PRTR)

The European Pollutant Release and Transfer Register (E-PRTR) according to Regulation (EC) No 166/2006 (Official Journal of the European Union, 2006) is the Europe-wide register that provides easily accessible key environmental data from industrial facilities in European Union Member States and in Iceland, Liechtenstein, Norway, Serbia and Switzerland. It replaced and improved upon the previous European Pollutant Emission Register (EPER).

The register contributes to *transparency and public participation in environmental decision-making*. It implements for the European Community the UNECE (United Nations Economic Commission for Europe) PRTR Protocol to the Aarhus Convention on "Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters".

Brominated diphenyl ethers are included in the E-PRTR and information about releases per industrial activity and number of facilities notifying can be scrutinised by year and geographical area.

PBDEs are included in the chemicals whose emissions need to be reported if the relevant emission values are exceeded. For these substances, there is only a water threshold value of 1 kg/y per each installation falling under the provisions of the IPPC Directive.

#### **Urban Waste Water Treatment Directive 91/271/EEC**

Directive 91/271/EEC (Official Journal of the European Union, 1991) concerns the collection, treatment and discharge of urban wastewater and the treatment and discharge of waste water coming from certain industrial sectors. Its aim is to protect the environment from any adverse effects due to discharge of such waters. It should be noted that neither the polymers nor the textile finishing sectors are specifically covered by the Directive.

This Directive touches upon the potential risks from DecaBDE to the aquatic environment only indirectly, as it targets the organic load of wastewater without specific reference to any substance or group of substances. It is evident that adherence to the provisions of the Directive must provide some protection to surface waters from releases of DecaBDE; however, this measure has a rather weak and undefined effect on the potential risks from the substance in question.

#### Transboundary movement of waste

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (Basel Convention – BC) is the piece of international legislation governing the transboundary movement of waste and it was passed in 1989 (UNEP, 1989). In order to achieve its objective of protecting the environment and human health from adverse effects of waste, it requires that all signatory countries should submit a prior notification before they ship hazardous or certain other wastes across international borders. Every year each party has to submit a report containing the annual amounts of hazardous waste that it generated, imported or exported. The BC also prohibits the export of hazardous waste to non-OECD members, but this is not yet globally in force (EEA, 2012).

The Waste Shipment EU Regulation 1013/2006 implements the provisions of the BC in the EU (Official Journal of the European Union, 2006). The Regulation follows the provisions of the BC regarding prior notification, but it also adapts them to the European principles of waste management. It places a ban on the export of hazardous waste to non-OECD countries for recovery,

while, at the same time, restrictive measures on it. i.e. in one of the nearest ap	Waste disposal shall t	ake place according to t	

### 3 Identity of the uses of DecaBDE and estimated related tonnages

#### 3.1 Production process

#### 3.1.1 Synthesis of DecaBDE

Polybrominated diphenyl ethers (PBDEs) are produced by direct bromination of diphenyl ether using a Friedel-Crafts catalyst. The production of DecaBDE is carried out by using bromine as both reactant and reaction medium. Diphenyl ether is added to the bromine in the presence of a catalyst and the rate of addition of diphenyl ether effectively controls the rate of reaction. The reaction is a batch process and the temperature of the reaction is around the boiling point of the bromine solvent ( $\cong 59^{\circ}$ C) (ECB, 2002).

#### 3.1.2 Composition of commercial DecaBDE (c-DecaBDE)

Commercial DecaBDE (c-DecaBDE<sup>7</sup>) products do not contain only the fully brominated congener BDE-209, they may also contain other lower brominated congeners (mainly NonaBDE and OctaBDE congeners). Older c-DecaBDE products contained a higher proportion of lower brominated PBDEs than more recent formulations. For instance, FR-300-BA which was produced in the 1970s and is no longer commercially available contained 77.4% DecaBDE, 21.8% NonaBDE and 0.8% OctaBDE (Environment Canada, 2010).

According to the World Health Organization (WHO, 1994) manufactured formulations of DecaBDE typically contain 97 - 98% DecaBDE, and 0.3 - 3.0 w/w other PBDEs (mainly NonaBDE). Based on these concentrations and of the fact that the other congeners are not intentionally added to the mixture, commercial DecaBDE formulations could qualify as a mono-constituent substance, based on the ECHA guideline on substance identification and naming (ECHA, 2012).

La Guardia et al. (2006) analysed compositions of the currently manufactured DecaBDE products, Saytex 102E and Bromkal 82-ODE, see **Table 3-1**. They found Saytex 102E and Bromkal 82-ODE contained 96.8% and 91.6% BDE-209, respectively. Both formulations contained NonaBDEs, with BDE-206 in the highest quantity, followed by BDE-207, then BDE-208. In addition, Bromkal 82-ODE contained 0.56% OctaBDEs, with BDE-196, BDE-203 and BDE-197 identified. OctaBDEs were not identified in the Saytex 102E product. This would suggest that higher purity of the current Saytex 102E product may indicate improvements in manufacturing practices, fuelled by growing concerns over products containing trace levels of lower brominated PBDEs.

Table 3-1: Concentrations (%, w/w) of PBDEs in selected commercial DecaBDE products					
PBDE congener	Saytex 102E	Bromkal 82-ODE			
BDE-154	nd <sup>2</sup>	nd			
BDE-144	nd	nd			
HexaBDE <sup>1</sup>	nd	nd			
BDE-153	nd	nd			
BDE-139	nd	nd			

<sup>7</sup> 

Whenever the congener number is referred (BDE-209), it should be assumed that it refers to the substance, while in other cases it refers to the mixture.

Table 3-1: Concentrations (%, w/w) of PBDEs in selected commercial DecaBDE products					
PBDE congener	Saytex 102E	Bromkal 82-ODE			
BDE-140	nd	nd			
BDE-138	nd	nd			
BDE-184	nd	nd			
HeptaBDE	nd	nd			
BDE-175/183	nd	nd			
BDE-191	nd	nd			
BDE-180	nd	nd			
BDE-171	nd	nd			
BDE-201	nd	nd			
BDE-197	nd	0.03			
BDE-203	nd	0.07			
BDE-196	nd	0.46			
BDE-194	nd	nd			
OctaBDE	nd	nd			
BDE-208	0.06	0.07			
BDE-207	0.24	4.1			
BDE-206	2.19	5.13			
BDE-209	96.8	91.6			

<sup>&</sup>lt;sup>1</sup>categorised only based on degree of bromination

Source: La Guardia et al. (2006)

Other products that were found during the online research include DE-83R $^8$ , DE-83, Bromkal 70-5, FR1210 $^9$ , Flamecut 110R $^{10}$  and Milebrom 102 $^{11}$ .

Chen et al. (2007) also reported that the OctaBDE and NonaBDE content of two commercial DecaBDE products from China was in the range of 8.2 to 10.4%. This would appear to suggest a higher level of impurities in these products compared with the products typically supplied in the EU.

#### 3.2 Manufacture, Imports, Exports and Consumption

#### 3.2.1 Production of DecaBDE

In the early 1990s there were thought to be eight global producers of PBDEs (although the industry indicated that there were nine), with one located in the Netherlands, one in France, two in the United States, three in Japan and one in the United Kingdom (WHO, 1994). The same total number of manufacturers was reported by Keml (1994), but production was also reported to occur in Israel. Past production data indicate that about 75% of all the world production in PBDEs was DecaBDE. In 1994, the global production volume for DecaBDE was ca. 30,000 tonnes (ECB, 2002).

Available online at: <a href="http://www.specialchem4coatings.com/tds/de-83r/chemtura/26237/index.aspx#">http://www.specialchem4coatings.com/tds/de-83r/chemtura/26237/index.aspx#</a>

Available online at: <a href="http://www.tosoh.com/our-products/organic-chemicals/flame-retardants">http://www.tosoh.com/our-products/organic-chemicals/flame-retardants</a>

<sup>&</sup>lt;sup>2</sup>not detected

Available online at: <a href="http://icl-ip.com/?products=fr-1210">http://icl-ip.com/?products=fr-1210</a>

Available online at: <a href="http://www.mpi-chemie.com/category/brominated-flame-retardants/product/cas-1163-19-5-milebrome-102.html">http://www.mpi-chemie.com/category/brominated-flame-retardants/product/cas-1163-19-5-milebrome-102.html</a>

DecaBDE has not been manufactured in the EU since 1999 (RPA, 2003). Information from the REACH Registration process has confirmed this assertion (ECHA, 2013).

Nevertheless, DecaBDE is a registered substance and the registration tonnage band is 10,000 – 100,000 tonnes per year. According to ECHA's Dissemination Portal<sup>12</sup>, the companies that have registered this product are shown in **Table 3-2**.

Table 3-2: Companies that have registered DecaBDE				
Company	Location			
Albemarle Europe SPRL	Parc Scientifique (Einstein) Rue du Bosquet 9, 1348, LOUVAIN-LA-NEUVE, Belgium			
Chemical Inspection & Regulation Service Limited <sup>13</sup>	Laurence Street, Co. Louth, Drogheda, Ireland			
Chemtura Europe Limited (US03)	Kennet House, 4 Langley Quay, SL3 6EH, Langley, Slough, United Kingdom			
Everkem	Piazza Carbonari, 12, 20125, Milano, Italy			
ICL-IP Europe B.V. (OR1)	Fosfaatweg 48, 1013 BM, Amsterdam, The Netherlands			
Source: ECHA (2013)				

The registrants include the three major global producers of DecaBDE, namely Albemarle Corporation, Chemtura Corporation (Great Lakes Solutions) and ICL Industrial Products, Everkem and an Only Representative of a non-EU manufacturer.

In December 2009, three major manufacturers of DecaBDE sent letters to the US EPA informing it that they would be phasing-out the production or import of DecaBDE in the United States, as part of the EPA-Industry DecaBDE Phase-Out Initiative, resulting from recent discussions between the authorities and the major manufacturers and importers. The commitment includes the discontinuation of the use of DecaBDE in electrical and electronic equipment (EEE) (except as used in transportation equipment) and in all other uses except transportation and military uses by the end of 2012. Transportation (e.g. automobiles, airplanes, and certain warehousing and shipping equipment) and military uses were believed to require an additional year to complete the phase out. This was primarily because of the complexity of these uses (cars and planes have a very large number of parts that rely on FR chemistry) and long lead times for qualifying new materials. The complete liquidation of any residual inventory of DecaBDE after six months of the phase-out was also in the commitment. The three companies who agreed to take part in this Phase-Out Initiative were Albemarle (producer), Chemtura (producer) and ICL Industrial Products (importer producing in Israel) (US EPA, 2012b). Consultation with the industry has not been able to confirm if the phase-out has been successfully implemented.

Chemtura Corporation (July 2010), Albemarle Corporation (October 2010) and ICL Industrial Products (December 2010) have also made a voluntary commitment referring to DecaBDE in Canada, specifying that:

 Phase-out of DecaBDE exports and sales for electrical and electronic equipment by the end of 2010

Bis(pentabromophenyl) ether. Available online at:
<a href="http://apps.echa.europa.eu/registered/data/dossiers/DISS-9eafd491-d447-3617-e044-00144f67d031/DISS-9eafd491-d447-3617-e044-00144f67d031">http://apps.echa.europa.eu/registered/data/dossiers/DISS-9eafd491-d447-3617-e044-00144f67d031/DISS-9eafd491-d447-3617-e044-00144f67d031</a>. DISS-9eafd491-d447-3617-e044-00144f67d031.html

<sup>&</sup>lt;sup>13</sup> This company acts as an Only Representative for a non-EU manufacturer.

- Phase-out of DecaBDE exports and sales for all other uses, except transportation and military, by the end of 2012
- Phase-out of DecaBDE exports and sales for transportation and military uses by the end of 2013.

This is aligned with the Commitment introduced in the USA.

It has been stated in the consultation process that production takes place in China, which is a very large market for DecaBDE, but its extent is not known. It was not possible to collect information from Chinese companies on the quantities they export to the EU. Some Japanese manufacturers, members of the Japanese Flame Retardant Association, who had been contacted earlier, responded that they either did not produce DecaBDE or they did not export it to the EU.

#### 3.2.2 Imports and exports

#### Imports and exports of DecaBDE as a substance

Given that manufacture of DecaBDE does not take place within the EU, the tonnages of DecaBDE used in the EU are imported from outside the continent. REACH Registration data are believed to be of most relevance, although Eurostat data are also available. Eurostat data for EU-Extra Imports by Tariff regime, product: *brominated derivatives of aromatic ethers, 29 09 30 38*<sup>14</sup>, related to EU-27 members are shown in **Table 3-3.** Eurostat data for EU-27 Exports are shown in **Table 3-4.** 

The Eurostat data appear to be considerably different to the available Registration data and are lacking information from several EU countries. These are replicated here for completeness and for supporting that there are downward trends in the imports and consumption of the substance.

Consultation has identified some small-scale importers of DecaBDE, of which only one has been importing in a systematic way from Asia. The imported quantities have declined, from between 10 - 1,000 t/y in 2007 to between 10 - 100 t/y since 2010. Other respondents reported very low quantities and one-off or intermittent orders (e.g. 1 tonne just once or 10 kg/y only for laboratory use).

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Brominated derivatives of aromatic ethers (excl. pentabromodiphenyl ether, 1,2,4,5-tetrabromo-3,6-bis"pentabromophenoxy"benzene and 1,2-bis"2,4,6-tribromophenoxy"ethane for the manufacture of acrylonitrile-butadiene-styrene [ABS]).

Table 3-3: Eurostat data on EU27 imports of DecaBDE (Tonnes) from the rest of the world years 2000-2012 (tonnes)								
Year	Belgium	Germany	United Kingdom	Ireland	Italy	Netherlands	Other	All EU27 Members States
2000	6,935	415.5	1968.5	1583.6	262	37.2	15.3	11,290
2001	6,810	183.3	1589.8	1317.1	148.8	0.4	55.9	10,173
2002	6,820	124	1531.3	1150.6	330.4	10.7	21.4	10,300
2003	8,093	199.5	1586.6	1450.1	834.4	54.6	50.8	12,338
2004*	6,354	205.1	1799.6	1244.7	839.8	88.8	92.6	10,624
2005	6,567	378.9	1338.9	1255.8	1261.5	43.8	147.3	10,994
2006	5,122	317.9	1693.1	195	1409.4	520.5	529.4	9,787
2007	5,743	280.6	1513.8	2.5	2851.6	661.2	430.9	11,484
2008	5,145	271.6	983.1	21.7	2470.2	787.1	209.3	9,888
2009	4,710	283.8	328.5	15.4	1719.1	455.7	190.7	7,703
2010	5,517	192.9	236.1	1.9	1417.7	570.9	186.6	8,083
2011	3,356	196.3	202.6	3.5	993.2	470.4	215.5	5,498
2012	2,352	183.7	86	5.4	732.1	634.2	139.1	4,133

Source: Eurostat (2013)

<sup>\*</sup> Eight countries of central and eastern Europe — the Czech Republic, Estonia, Latvia, Lithuania, Hungary, Poland, Slovenia and Slovakia — joined the EU. Cyprus and Malta also became members.

<sup>&</sup>quot;Other" include: Bulgaria, Czech Republic, Denmark, Spain, Finland, France, Greece, Hungary, Poland, Romania, Sweden, Slovenia, Slovak Republic

Table 3-4: Eurostat data on EU27 exports of DecaBDE (Tonnes) to the rest of the world years 2000-2012							
Year	India	United States	Switzerland	Russian Federation	Turkey	Other	EU27_EXTRA
2000	9.9	13	110.4	107.6	1.4	0.1	327
2001		1.3	120.9	103.2	5.78	2.7	306
2002		1.3	155.3	168.7	4.52	19.7	474
2003		8.5	122.4	202.6	5.57	16.1	432
2004*		65.7	166.2	311.1	22.04	19.2	843
2005		21.6	51.1	272	9.41	3	479
2006	1.7	0.3	35.6	310	9.55	27.6	531
2007	2.6	0.3	10.4	327.9	11.5	15.6	586
2008	35.7	1.9	16.6	259	7.42	77.4	490
2009	22.4	0.4	3.4	199	9.95	7.6	410
2010	3.7	0.4	17.4	236	6.9	34.3	442
2011	2.5		27		2.63	25.7	105
2012	1.9	18.8	14	327	8.5	0.7	482

Source: Eurostat (2013)

<sup>\*</sup> Eight countries of central and eastern Europe — the Czech Republic, Estonia, Latvia, Lithuania, Hungary, Poland, Slovenia and Slovakia. Cyprus and Malta also became members.

<sup>&</sup>quot;Other" includes: China, Japan, Brazil, Korea, Morocco, Norway, Tunisia

# Imports and exports of DecaBDE in articles

According to RPA (2003) the estimates of the European Brominated Flame Retardant Industry Panel (EBFRIP) on the quantities of DecaBDE that were imported into the EU from other markets in 2003 in the form of finished products (articles) are shown in **Table 3-5.** 

Table 3-5: Estimated Extra-EU imports of DecaBDE in products (2003)						
Origin Quantity of DecaBDE (t/y) Products involved						
Asia	500	Non-TV consumer electronics				
Asia	400	TV sets				
Unspecified	400	Flame retardant polystyrene				
Total 1,300						
Source: EBFRIP, as mentioned in RPA (2003)						

KemI (1994) estimated the quantities of DecaBDE imported into Sweden in 1993. It was thought that 17 tonnes of DecaBDE were imported as substance, with a further 20 tonnes imported in plastic compounds for use in the production of printer housings, plastic foils, cable and electrical components. It was also estimated that a further 400 t/y of DecaBDE could be imported into the country in pre-formed plastic goods, such as televisions and computer casings.

# Consumption of DecaBDE as a substance

Several sources can be used for a basic calculation of the tonnage of DecaBDE consumed in the EU. Based on the Eurostat data presented above, the simple difference between imports and exports could give a good indication of the tonnage of the substance consumed in the EU, as shown in **Table 3-6** and **Figure 3-1**. However, it cannot be guaranteed that the products generated with the substance remain within the EU for use in industrial, professional or consumer settings.

Table 3-6: Estimate of DecaBDE consumption in the EU based on the difference of imports and exports (Eurostat data)						
Year	Imports	Exports	Assumed consumption			
2000	11,290	327	10,963			
2001	10,173	307	9,867			
2002	10,030	474	9,556			
2003	12,338	432	11,906			
2004	10,624	843	9,781			
2005	10,994	479	10,515			
2006	9,787	531	9,256			
2007	11,484	586	10,898			
2008	9,888	490	9,398			
2009	7,703	410	7,293			
2010	8,083	442	7,641			
2011	5,498	105	5,393			
2012	4,133	482	3,651			
Source: Eurostat (2013)						

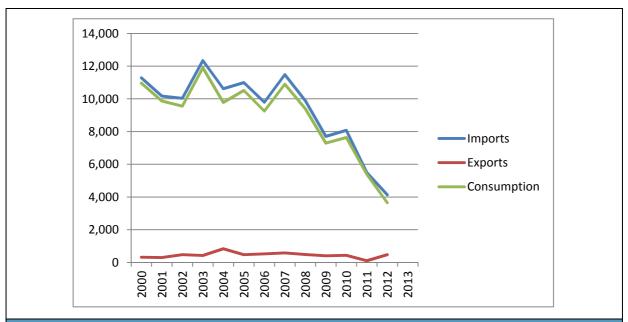


Figure 3-1: Estimate of DecaBDE consumption (tonnes) in the EU based on the difference of imports and exports

Source: Eurostat (2013)

Historical information on the consumption of DecaBDE can be found in RPA's work on the Risk Reduction Strategy for the substance. This report includes information from several sources as well as information from consultation that was undertaken at the time (RPA, 2003). Consultation with EBFRIP (a sector group of CEFIC representing BFRs, now part of EFRA) had suggested that, in 2003, the overall market for DecaBDE was increasing and was estimated at about 8,300 tonnes per year. Of this, 30% was estimated to be used in the textile sector (2,500 t/y) (RPA, 2003). Notably, according to information collected by HSE for the preparation of the Annex XV dossier in 2012, the share of plastics in the use of DecaBDE has decreased from 81.7% in 2002 (ECB, 2002) to roughly two thirds (~66%) in 2010 (VECAP, 2010) and was lower than 50% in 2012 (VECAP, 2013). For textiles, the transport and construction sectors are proving to be significant consumers of the substance as fire safety standards are becoming stricter. On the other hand, the plastic and flame retardant plastic production is closely following global and EU economic developments (UK HSE, 2012). Consultation with the textile industry has indicated that the use of DecaBDE in textile applications has declined considerably since 2012, possibly as a result of the substance being identified as a SVHC.

Another source of information is VECAP, the Voluntary Emissions Control Action Programme, which encompasses users of DecaBDE and "has evolved from its original concept of a tool to control emissions during handling and use of brominated flame retardants (BFRs) into a system for more efficient management of chemicals"<sup>15</sup>. DecaBDE consumption information is available from a series of annual reports by VECAP which show that the tonnages have varied over the years (period 2007-2012), starting from over 5,000 t/y in 2007, increasing to over 7,500 tonnes in 2011 and then declining drastically in 2012 to below 5,000 tonnes (VECAP, 2013). There are a number of potential shortcomings and caveats to the completeness of the VECAP data. For example, some of the companies using it as secondary users belong to VECAP but others do not, so some of the numbers may be underestimated, as VECAP cannot comment on the techniques used by the non-members (UK HSE, 2012).

<sup>&</sup>lt;sup>15</sup> Available online at: <a href="http://www.vecap.info/about-vecap/">http://www.vecap.info/about-vecap/</a> (accessed on 28 November 2013).

The VECAP reports provide information since 2007. In recent years, the use of ranges instead of exact figures is preferred by the industry for confidentiality reasons.

# Summary of available statistics

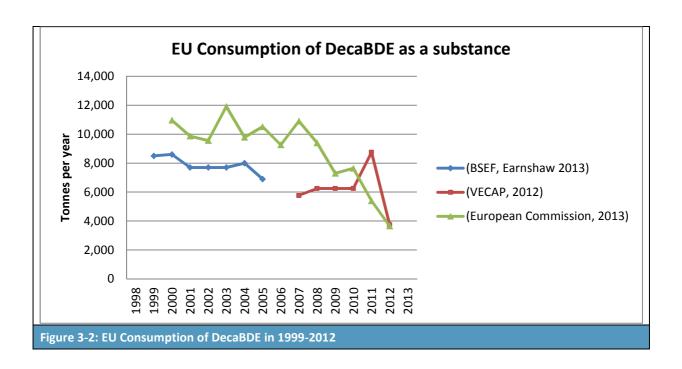
Information about consumption of DecaBDE (as a substance) in the period 1998-2012 in the EU is shown in **Table 3-7** and **Figure 3-2**. The most continuous set of data is provided by Eurostat (Eurostat, 2013). BSEF reported tonnage information from its members until 2005, while VECAP has been providing information since 2007. In recent years, the use of ranges instead of exact figures is preferred by the industry in the VECAP reports for confidentiality reasons. There are clearly discrepancies among sources but the overall picture is reasonably clear in that the consumption of DecaBDE has been declining. This links to regulatory pressures over a number of years with most prominent the provisions of the RoHS Directive which prohibits the use of DecaBDE in a wide range of EEE.

Table 3-7	Table 3-7: Comparison of Estimates of imports of DecaBDE to the EU in 1999-2012						
Year	BSEF, Earnshaw et al. (2013)	VECAP (2013)*	Eurostat (2013)				
1999	8,500						
2000	8,600		10,963				
2001	7,700		9,867				
2002	7,700		9,556				
2003	7,700		11,906				
2004‡	8,000	Start	9,731				
2005	6,900		10,515				
2006			9,256				
2007		5,767	10,898				
2008		5,000 – 7,500 (7,030) † †	9,398				
2009		5,000 – 7,500 (6,648) ‡ ‡	7,293				
2010		5,000 – 7,500	7,641				
2011		7,500 – 10, 000	5,393				
2012		2,500 – 5,000	3,651				

<sup>\*</sup> The figures do not include DecaBDE imported in the preparations or articles (VECAP, 2013)

<sup>†</sup> Eight countries of central and eastern Europe — the Czech Republic, Estonia, Latvia, Lithuania, Hungary, Poland, Slovenia and Slovakia — joined the EU. Cyprus and Malta also became members

<sup>† †</sup> Figures in parentheses were taken from VECAP (2009) and VECAP (2010) and are included for comparison purposes



# 3.2.3 Information on quantities from consultation with Member State Competent Authorities

Some MSCA have submitted information about the known quantities of DecaBDE imported into their country. As can be seen in **Table 3-10** below, these quantities were insignificant compared to the total imports. It should also be noted that, if Eurostat data are indicative, the major importing countries (**Table 3-3**) either did not submit a questionnaire or did not submit imported quantities, with the exception of Germany who submitted a figure of consumption of 1,837 tonnes for 2004. Those Member States that are not mentioned in the table either did not provide information about quantities or commented that there were no imports or consumption of DecaBDE in their territory.

Table 3-8: Quantities of DecaBDE as reported by MSCA (in tonnes)								
Year	DE	DK	FI	FR*	NO	SE		
2004	1,837	0				3.3		
2005				34.5				
2006				19				
2007		0		18		<1		
2008			Confidential	8	Confidential			
2009			information	10.5	information			
2010		0				<1		
2011								
2012								
2013		0				<0.1		

<sup>\*:</sup> The monitoring programme in France ended in 2010, but DecaBDE continued being used after that time Source: Consultation

Earnshaw et al. estimated that a total of 185,000-250,000 tonnes of DecaBDE were consumed in Europe between 1970 and 2010. Consumption peaked in the late 1990s at approximately 9,000 tonnes/year and had declined by 30% in 2010 (Earnshaw, et al., 2013).

# 3.2.4 The global flame retardant market and future trends

# Information on DecaBDE consumption outside the EU

Variations in the consumption of DecaBDE outside the EU may not follow EU patterns. For example, DecaBDE use in China increased significantly in the first half of the 2000's, as shown in **Table 3-9**.

Table 3-9: Historical data on DecaBDE consumption in China (tonnes)							
Source		Year					
Source	2000	2001	2004	2005			
Xia et al. (2005), Zou et al. (2007)		13,500		30,000			
Xiang et al. (2007)	10,000		25,000				
Chen et al. (2007)	10,000			30,000			

With regard to North America, the production/import volume of DecaBDE in the USA is reported to have been in the range of 25,000 – 50,000 tonnes in the period 2002-2006 (Stockholm Convention, 2013). As mentioned above, however, a DecaBDE Phase-Out Initiative is in place, agreed between the US EPA and the DecaBDE manufacturers and importers in North America. Accordingly, production or import of DecaBDE is expected to have ceased in the USA and Canada by the end of 2013.

According to information that was submitted to the POPRC following the 9<sup>th</sup> meeting of the Committee, Japan estimates production in 2013 of 600 tonnes and import of 1,000 tonnes, mainly to be used for vehicle seats (60%), construction materials (19%) and textiles (15%)<sup>16</sup>.

# The global brominated flame retardant market

In a 2010 market research report by Freedonia on the world FR industry, the global demand for FR additives is expected to rise by over 6% per year to 2.2 million tonnes in 2014<sup>17</sup>. This is partly due to more stringent safety requirements and the use of more flammable materials. The Asia/Pacific region will continue to be the largest and fastest-growing market for FRs through 2014, accounting for nearly half of the world demand.

The total market for FRs in the US, Europe and Asia in 2007 amounted to about 1.8 million tonnes and was valued at US\$4.2 billion (in 2011 \$4.8 billion) or ca. €3.5 billion (in 2011 still ca. €3.5 billion). **Table 3-10** shows the breakdown of the FR market by volume.

Available online at: http://www.freedoniagroup.com/industry-study/2709/world-flame-retardants.htm

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Information from Japan, available at:
<a href="http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC9Followup/decaBD">http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC9Followup/decaBD</a>
<a href="mailto:ESubmission/tabid/3570/ctl/Download/mid/11314/Default.aspx?id=15&ObjID=17562">http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC9Followup/decaBD</a>
<a href="mailto:ESubmission/tabid/3570/ctl/Download/mid/11314/Default.aspx?id=15&ObjID=17562">http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC9Followup/decaBD</a>
<a href="mailto:ESubmission/tabid/3570/ctl/Download/mid/11314/Default.aspx?id=15&ObjID=17562">http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC9Followup/decaBD</a>
<a href="mailto:ESubmission/tabid/3570/ctl/Download/mid/11314/Default.aspx?id=15&ObjID=17562">http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC

Table 3-10: Global market of flame retardants by value. Data for 2007 and 2011						
Flame retardant	2007	2011				
Brominated	34%	20%				
Antimony trioxide	16%	8%				
Chlorinated	7%	11%				
Organophosphorous	20%	15%				
Aluminium hydroxide 13% 10%						
Other	10%	6%				
Source: http://www.flameretardants-online.com/web/en/home/index.htm						

Halogen (brominated and chlorinated) FRs and antimony trioxide accounted for 57% of the market value in 2007 (as opposed to 38% by volume) because of the extensive use of BFRs in Asia, see **Table 3-11**.

<b>Table 3-11:</b>	Global market of flame retardants. Sales of Flame Retardants by Region.	Figures are in US \$
million, with	n a total of US \$ 4.2 billion, data for 2007	

Region	Brominated	Antimony oxides	Chlorinated	Organo- phosphorous	Aluminium hydroxide	Other			
United States	260	102	100	306	248	110			
Europe	250	110	103	328	232	228			
Asia	918	485	88	204	79	86			
Source: http://	/www.flamereta	rdants-online co	m/weh/en/hom	e/index htm					

**Table 3-12** provides the consumption of FRs by region by volume. The value of the market is projected to grow at 6.9% per year to US\$7.1 billion in 2017. Different FRs are prominent in different world regions. China and India are focusing on increased fire safety, particularly in the area of electronics. It should be noted though that a significant portion of electronic parts or products are manufactured in China and India and are exported to Europe and the US, and so demands and regulations there will affect FR use worldwide. Asia/Pacific is expected to account for 50% of the world demand by 2014 as measured by value (Clariant International, undated) (Markets and Markets, undated).

Table 3-12: Consumption of flame retardants by volume (in 1,000 tonnes) for 2007

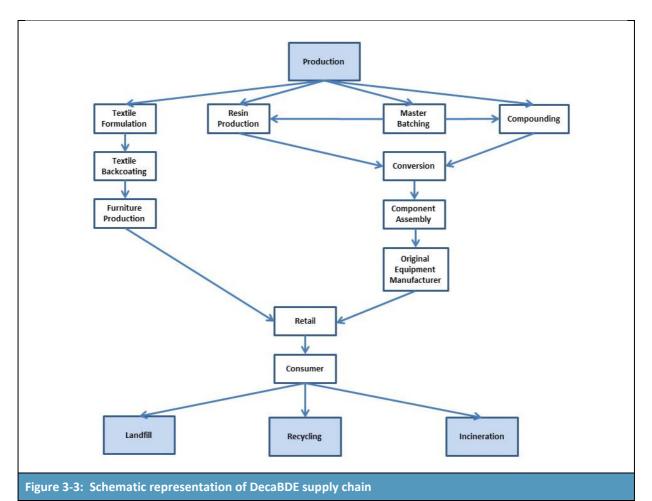
Region	Brominated	Antimony oxides	Chlorinated	Organo- phosphorous	Aluminium hydroxide	Other
United States	64	33	33	72	345	75
Europe	45	20	40	83	280	61
Asia	302	88	58	54	110	58

Consumption of Flame Retardants by Region, based on volume. Figures are 1,000 tons, with a total of 1.8 million tonnes, data for 2007

Source: http://www.flameretardants-online.com/web/en/home/index.htm

# 3.3 Analysis and mapping of DecaBDE use

The DecaBDE supply chain (**Figure 3-3**) comprises several distinct links, which – together with the large number of actors and their diverse characteristics – makes it difficult to track accurately the quantities of DecaDBE at each stage.



The supply chain can be split as follows:

- 1. Production (discontinued in the EU in 1999, after which demand has been met by imports)
- 2. Formulation for textiles and plastics (including compounding, masterbatch production and resin production) and potentially for adhesives, sealants and coatings
- 3. Backcoating for textiles
- 4. Article manufacture with textile or plastic components or by application of adhesives, sealants or coatings
- 5. Service life
- 6. End-of-life, waste disposal or recycling (including reuse, where applicable)

Users that purchase FRs through distributors (and not from importers or producers) are considered 'second-line' users by the industry and, as they are further removed, are harder to monitor. It must also be noted that, in the textile sector, FR formulations can be manufactured by compounders, who then sell the product to finishers or by self-compounders, who mix the formulation themselves and then apply it on the textile (UK HSE, 2012).

The finished article is sold for industrial, professional or consumer use. After the end of its service life, if it is not reused, it enters the relevant waste stream. The main treatment methods in the EU are material recovery (recycling), energy recovery (incineration) and landfilling. The large number of links in the DecaBDE supply chain may result in poor communication along it and make it difficult for downstream (end) users to determine the substances contained in their products.

# 3.3.1 DecaBDE production and formulation

#### **Production**

As mentioned earlier, DecaBDE is produced through the direct bromination of diphenyl ether over a Friedel-Crafts catalyst in a batch process (ECB, 2002) but does not take place in the EU.

#### **Plastics formulation**

As an additive FR, DecaBDE does not react with the material or substrate but, rather, is mixed with it. Therefore, a formulation stage precedes the actual manufacturing of the finished article. For plastics, this stage usually takes the form of a resin or masterbatch production or compounding. These products are then used further downstream. The resins or plastic pellets can be used by manufacturers of finished articles or for plastic components in other articles.

The compounding process for thermoplastics usually involves mixing the polymer with the additives in an extrusion screw. The mixture solidifies and is reduced in size to form pellets, which are dried and packaged. These plastic pellets can then be turned into plastic articles by a variety of techniques, but most commonly by extrusion and injection moulding <sup>18</sup>. Extrusion produces a 'continuous' product (e.g. pipes or tubes, wire insulation, window frames and plastic coating). Injection moulding mainly produces smaller parts in moulds. The compounding process usually takes place in temperatures below 200°C but the forming of semi-finished or finished articles from that plastic often requires higher temperatures (RIKZ, 2000). The processing temperature depends on the melting point of the plastic.

Thermosets cannot be easily extruded because they tend to harden when heated and cannot be remelted, like thermoplastics. They are produced by mixing two ingredients that produce the plastic when they react. Usually one of the two ingredients contains the additives for the finished plastic.

One of the reasons that DecaBDE has gained popularity among FRs is that it can be used with a variety of materials. The plastics listed in the following table have been associated with DecaBDE.

Table 3-13: Plastics associated with DecaBDE						
Plastic	Туре	Typical applications	Comments			
Polypropylene (PP)	Polyolefin	Injection moulded parts, stadium seating, shipping pallets, roofing membranes, cladding panels				
Polyethylene (PE)	Polyolefin	PE/wood composites, power cables, conduits, electrical connectors and boxes, wire and cable insulation, heat shrinkable material	PE foam can be used as thermal or acoustic insulation			
Ethylene Vinyl Acetate (EVA)	Polyolefin/Elastomer	Wire and cable insulation, extrusion, coatings				
High Impact Polystyrene (HIPS)	Polystyrenic	Plastic parts, panels, keyboards, casings, TV	Their use in EEE is restricted			
Acrylonitrile / Butadiene Styrene (ABS)	Polystyrenic	General appliance moulding, car bumpers				

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http://www.nist.gov/el/fire\_research/upload/2-Reilly.pdf.

Table 3-13: Plastics associated with DecaBDE						
Plastic	Туре	Typical applications	Comments			
Polyphenylene Oxide / Polystyrene blends (PPO/PS)	Polystyrenic					
Polyethylene Terephthalate (PET)	Polyester	Textile fibres, plastic parts, switches, sockets, electrical appliances				
Polybutylene Terephthalate (PBTE)	Polyester	Circuit breakers, sockets and electrical connectors, textiles, switches				
Polyamides (nylon)	Engineering thermoplastic	In injection moulding for transport apps: (e.g., wheel covers and handles, chair and seat-belt mechanisms, under hood applications).  High T engineering application, textile fibres, coils, electrical components				
Polycarbonates (PC)	Engineering thermoplastic	Mirror housings, lights for cars, bumpers, window housings for trains and aircraft, casings, panels, keyboards	Including blends PC/ABS			
Polyimides (PI)	Engineering thermoplastic	Bearings in aircraft, seals, gaskets				
Melamine	Thermoset	Textile finishing				
Unsaturated Polyester Resins (UPR)	Thermoset	Articles for construction (modular building parts, roofing materials, porch canopies, decorative mouldings) Fibre reinforced plastics, automobile parts				
Epoxy resins	Thermoset	Adhesives, adhesive tapes, electronics, construction, aerospace	Epoxy adhesives were identified by MSCA as a past use of DecaBDE			
Polyurethanes (PU)	Thermoset	EEE, coating material				
Ethylene Propylene Diene Monomer (EPDM)	Elastomer	Car radiator hoses, roofing membranes, cable and wire insulation				
Styrene Butadiene Rubber (SBR)	Elastomer	Carpet reinforcements, interior redecoration.				
Thermoplastic Polyurethanes (TPU)	Elastomer	Automotive, wire and cable applications, gaskets				
Waterborne emulsions and coatings		Adhesive applications (e.g. wall coverings, furniture, flooring), protective coatings, saturation of fibrous materials (paper, textiles), special protective uniforms	e.g. acrylic, PVC, Ethylene Vinyl Chloride emulsions			
Sources: UK HSE (2012),	PlasticsEurope (2013),	ICL Industrial Products (2012), Consulta	ation			

The importance of DecaBDE is not the same for all of the plastics mentioned above and additionally cannot be considered fixed over time. For example, in the past, HIPS was among the most important materials for DecaBDE use, because it was used for the production of screen (TV) casings. This use

has been discontinued now in the EU, however, and HIPS has lost its importance for DecaBDE use. DecaBDE loading in these polymers typically ranges from 10 - 15%, although loadings of 20% have also been reported (UK HSE, 2012). **Table 3-14** contains an overview of the end-uses of polymer materials, in which DecaBDE may be used.

Table 3-14: End-	Table 3-14: End-uses for polymer materials that can contain DecaBDE								
	End-use applications								
Polymer group	Electronics	Wire and cable	Public buildings	Construction materials	Automotive	Aviation	Storage and distribution products	Textiles	Waterborne emulsions and coatings
Polyolefins	✓	✓	✓	✓	✓	✓	✓	✓	✓
Styrenics	✓		✓	✓	✓	✓	✓		
Engineering Thermoplastics (PA, PC, Polyesters)	<b>√</b>	<b>√</b>	<b>~</b>	<b>√</b>	<b>√</b>	<b>√</b>		<b>√</b>	<b>~</b>
Thermosets	✓		✓	✓	✓	✓	✓	✓	✓
Elastomers	✓	✓	✓	✓	✓	✓	✓	✓	✓
Waterborne emulsions and coatings*	✓	<b>√</b>	<b>✓</b>	<b>√</b>	✓			<b>√</b>	<b>✓</b>

\* Includes PVC, ethylene vinyl chloride and urethane emulsions

Source: US EPA (2012)

#### **Polyolefins**

DecaBDE is commonly used in three polyolefins, namely polypropylene (PP), polyethylene (PE), polyphenylene ether/oxide (PPE or PPO) and ethylene vinyl acetate copolymer (EVA). Their applications include seat cushions, arm rests, etc. (Mark, 2009) and also wires and cables, electrical connectors, battery casings, foamed sheets and pipes (Keml, 2005). Use in PE/wood composites for construction applications has also been mentioned and is also included as an identified use in the REACH registration dossier of DecaBDE (ECHA, 2013). Expanded polyethylene can be used for thermal and acoustic insulation applications and DecaBDE is considered a suitable FR for that use (ICL Industrial Products, 2012). During consultation, several manufacturers of alternative substances mentioned that their alternative could be used in polyolefin applications instead of DecaBDE. Such applications may include PP or PE plastics for EEE, automotive or aviation applications, construction materials and wires and cables. The use of DecaBDE for the production of FR additive masterbatch was also confirmed after consultation.

#### **Styrenics**

DecaBDE can be found in two styrenic polymers, High Impact Polystyrene (HIPS), Acrylonitrile Butadiene Styrene (ABS) co-polymers and also in polymer blends such as polyphenylene oxide / polystyrene (PPO/PS) blends. These plastics are used mainly as casing materials for electrical and electronic equipment, but also in automotive components and some household applications, because of their high impact resistance (US EPA, 2012). As mentioned above, DecaBDE's use in electrical and electronic equipment is restricted by the RoHS Directive. Styrene – acrylonitrile (SAN) resin is also considered a suitable thermoplastic substrate in a commercial brochure of a DecaBDE

producer (Albemarle, 2013). Use of DecaBDE in polystyrene foam was not identified during consultation.

#### **Engineering thermoplastics**

These include the polyester (PES), polyamide (PA), polycarbonate (PC) and polyimide (PI) families of polymers.

PES and PA are used: in automotive parts; in connectors and switches for EEE; and to make the fibres for carpets and textiles. PBTE, a PES polymer, is used in headlights, wipers, gear housing components, ESP control modules and airbag connectors (PlasticsEurope, 2013). PET, another PES polymer, is used in heat-shrinkable tubing, which contracts in diameter when heated to seal around cables and similar items. The Danish EPA has made mention of the use of DecaBDE in such materials (at a content of 10% w/w) but it added that the traded quantities in Denmark were very small (<5 kg/y) (Danish EPA, 2007).

PA are versatile and widely used in transport, where they appear in steering wheel covers and the mechanisms that control chair adjustments and seat-belts. The flame resistance of the material can be improved with a variety of FRs such as organic and inorganic phosphates and including DecaBDE (UK HSE, 2012).

PC is commonly used in roofing panels, window housing components, many applications in the transport sector, CDs, DVDs, electrical equipment and motorcycle helmets. DecaBDE-containing PC is mostly relevant to transport applications (US EPA, 2012), however.

PI are highly resistant polymers, and as such they find application in aircraft components, such as gaskets, seals and bearings, although their attractiveness is limited somewhat by their high costs and processing difficulties, which include a need for high temperatures (IDES, 2013). Other applications include insulating film on electrical wire and high-temperature adhesives in the semiconductor industry (PlasticsEurope, 2013). Use of DecaBDE in such plastics is mentioned by the Annex XV dossier (UK HSE, 2012), but it could not be determined exactly which applications the annex referred to.

Polyvinylchloride (PVC) and fluoropolymer resins are inherently flame resistant because of their halogen content, but the plasticisers added to PVC are not, so additional FRs have to be added to PVC for use in some wiring applications. Fluorinated ethylene propylene (FEP) is more flame resistant than PVC, but the hydrofluoric acid released when it is exposed to heat is more toxic than the hydrochloric acid released by PVC (BldgDESIGN 2020, 2004).

## **Thermosets**

This category includes plastics that undergo an irreversible cross-linking reaction during curing (hardening) and thus cannot be reprocessed as, for example, polyolefins or styrenics can. Unsaturated polyester resin (UPR), epoxy resin (EP), polyurethane (PU) and melamine-based resins are all thermosets.

UPRs are used in construction applications, such as roofing materials, moulded parts and modular building parts. Although the majority of UPR composite materials (containing reinforcing fibres) are used in construction applications, a significant proportion are used for transport industry components (in cars, buses and flat panels), electrical end uses (in wind mills and other appliances) and construction components for (mainly pleasure) boats (European UP/VE Resin Association, 2013).

EP are used mainly as the encapsulation material of electric components, but also in adhesives and coatings applications for construction and aerospace applications. They have excellent adhesive properties and very good heat and chemical resistance. They are usually flame retardant with halogenated compounds such as TBBPA, but DecaBDE may be used as well (UK HSE, 2012) (Keml, 2005). The use of DecaBDE in epoxy adhesive mixtures has been mentioned MSCA during consultation. However, this use appears to have stopped.

Three European associations, together representing a significant share of PU manufacturers and users, have commented that DecaBDE is not used by their members in PU foam for mattresses, upholstered furniture, transport applications (such as seat cushions) or thermal insulation. DecaBDE in PU has been mentioned during consultation, but it was not relevant to the above uses. Melamine-based resins are produced through the combination of melamine ( $C_3H_6N_6$ ) and formaldehyde (HCHO). They are mainly used as textile finishing materials to increase the wear resistance of cellulosic fabrics (US EPA, 2012).

#### **Elastomers**

DecaBDE can be used in ethylene propylene diene monomer (EPDM) rubber, thermoplastic polyurethane (TPU) and EVA. These materials are elastomers (EVA is also a polyolefin). Viewed together, they are most commonly used in cable and wiring applications (sheathing). EPDM rubber is mainly used in automotive hoses and seals, roofing membranes for buildings and liners (UK HSE, 2012).

TPU is versatile and can be used in automotive applications and medical equipment, as well as wire and cable applications. It can also be used in flexible coatings for textiles and adhesives for film and fabric laminates. Use of TPU as a fabric coating material in the textile industry is mentioned. The corresponding fabrics are used industrially, as seals in fuel tanks<sup>19</sup>, and for consumer products (IDES, 2013; Randall & Lee, 2003).

#### Waterborne emulsions and coatings

DecaBDE can be used in acrylic, PVC and urethane emulsions. Acrylic emulsions are used in paints and coatings, as well as nonwoven fabric and paper saturations. PVC and ethylene vinyl chloride (EVC) emulsions are mainly used: for coating, impregnating and saturating textiles (see also, Section 3.3.2 – Backcoating) and other fibrous materials (such as paper and nonwoven fabric); in wall coverings and in flooring. Finally, polyurethane emulsions are used in mixtures for paints and finishing coats for textiles and wood (UK HSE, 2012). A consultee from the textile industry mentioned that DecaBDE is used in a PU-based coating for textiles, specifically a transfer coating.

The German MSCA commented during consultation that the total amount of DecaBDE consumed in the country was 1,837 tonnes in 2004 (MONARPOP Technical Report, 2009). Some identified uses were: the production of polymers; FRs for ABS, epoxy and nitrile resin, PES, PS and polyolefins.

# 3.3.2 Formulation for textile use

# Textile finishing processes

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DecaBDE is a very popular FR for increasing the fire retardancy of textile fibres, especially those in upholsteries for furniture and seating.

http://www.entremonde.com/products/speciality\_fabrics/tpu\_coated\_fabric.php

There are different techniques to improve textile flame retardancy; FRs may be incorporated into fibres, applied to the surface of textiles or applied to the back of textiles in the form of a polymeric coating. Chemical post-treatments for flame retardancy include topical treatments and so-called functional finishes that become part of the final fibre structure. Fibres that are not inherently fire resistant can be made so using chemical substances under one of two mechanisms (Lowell Center for Sustainable Production, 2005):

- **Chemical post treatment**: the fibre is treated with a FR chemical. Chemical post treatments include FR finishes and FR coatings:
  - FR finishes are usually applied by the "pad-dry method", in which fabric is passed through the (usually aqueous) chemical formulation, then through rollers to squeeze out the excess and finally dried in an oven to give a non-durable finish. To get a semi-durable or durable finish, fabric is passed through another oven, set at a higher temperature, which drives a curing stage that allows a degree of interaction between the finish and the fibre. Finishes are generally applied to fabrics made of natural fibres, although there are some commercially available finishes intended for synthetic fibres (Gnosys, et al., 2010)
  - FR coatings can be applied to the surface of the fabric (including on the back) to confer fire retardancy to the overall fabric. Typical polymer textile coatings include: natural and synthetic rubbers; PVC plastisols and emulsions; poly(vinyl alcohols); formaldehyde-based resins; acrylic copolymers; polyurethanes; silicones and fluorocarbons. These coatings modify a range of properties including water resistance, flexibility, moisture permeability and fire retardancy. Some, such as those comprising chlorine- and fluorine-containing polymers (including PVC), inherently provide some fire retardancy, although the more commonly used polymers are quite flammable and consequently fire retardant additives are necessary for both the polymer matrix and the underlying textile (Gnosys, et al., 2010)
- Inclusion of an additive in the fibre melt spinning process: FRs are added into the molten plastic during the spinning process and become physically part of the fibre matrix. An example of this would be organophosphorous FR added to viscose fibres. Natural fibres are more easily treated in this way because they absorb the FR more readily.

# Backcoating

Backcoating is a form of textile treatment that involves the application of a FR coating on the back surface of a textile. DecaBDE-based coatings are not applied on the front surface of fabrics. DecaBDE is commonly used with antimony trioxide (ATO), which acts as a synergist, and this leads to a white colour after application. Therefore, where appearance is important as in, for example, furniture upholstery, it is preferable to apply the coating to the back.

Antimony-halogen FRs are the most successful FRs for textile backcoating, based on cost and efficacy (Fretwork, 2011). Unlike the fibre-reactive, durable phosphorus- and nitrogen-containing FRs used for cellulosic fibres, they can only be applied topically in a resin binder, usually as a backcoating.

DecaBDE is first mixed with ATO to form an aqueous dispersion. Then this dispersion is mixed with a polymer emulsion, containing for example natural or synthetic rubber, EVA, styrene-butadiene copolymer or PVC (UK HSE, 2012). An effective mass ratio for the backcoating mixture is one part ATO to three parts incorporated bromine (each DecaBDE contains 10 incorporated bromine atoms), which translate to roughly one part ATO to two parts DecaBDE to three parts resin (or 20–30% w/w FR in the mixture) (KemI, 2005). Typically, the FR mixture consists of about 67–75% DecaBDE and

25–33% ATO. The amount of DecaBDE added to the mixture varies depending on the desired properties of the fabric.

Such backcoatings are effective on a wide range of fabrics, including nylon, polypropylene, acrylics, and other blends, such as nylon–polyester. They have important applications in domestic, industrial and automotive upholstered furniture, as well as draperies for hotels and other public buildings. The versatility of DecaBDE backcoating is among the main reasons it is considered a good choice for the textile industry (Fretwork, 2011).

During the backcoating process, the FR formulation is applied to the back of the fabric with a running roller and then passed through an oven at 130–140 °C to dry the new coat. The loading will usually be 7.5–20% depending on the weight of the fabric (ECB, 2002). ECB has suggested the following loadings as typical (the figures refer to g of dry coating/m² of fabric; DecaBDE makes up around 30–40% of the dry coating weight):

- Velour pile fabrics: 70–80 g/m<sup>2</sup>
- Cotton: 30–40 g/m<sup>2</sup>
- Flat woven (other types): 30–80 g/m<sup>2</sup> (likely to be 40–50 g/m<sup>2</sup>).

In 2003, RPA reported that there were 3-4 major and 3-4 smaller compounders and self-compounders in the UK, and approximately 25 in the EU. It was estimated there were up to 40 finishers dealing with FR coatings, many of them SMEs (RPA, 2003). Textile finishers, who perform backcoating of textiles, are also considered 'second-line' users in the supply chain because they purchase the FR blend from the formulators (VECAP, 2013).

Consultation with companies performing backcoating and textile manufacturers confirmed that DecaBDE has been used for backcoating of textiles. One textile finisher has mentioned a former use of DecaBDE in the region of 100 t/y for the production of backcoated fabric.

#### Transfer coating

Transfer coating is another way to apply a polymer-based coating to a fabric. It is an indirect method of application, meaning that the coating is first applied to a transfer paper and from there to the textile. The paper is removed and the textile, with the coating now on it, passes through a curing phase, usually facilitated by an oven. The polymer coating material can be PU, PVC or polyacrylate and contains several additives, including FRs (Kovacevic, et al., 2010).

Use of DecaBDE in such processes has been verified through consultation. DecaBDE was used in mattress covers and in composite multi-layered textiles for use in protective (extreme heat resistant) uniforms. These uses have now been discontinued.

#### **Fibres**

The textile industry supply chain is quite complicated and composed of a large number of subsectors, starting from production of raw materials (for man-made fibres), progressing to production of semi-processed fibres, such as yarns and woven fabrics with their finishes and ending with final products (carpets, home textiles, clothing and industrial textiles).

Fibres can be categorised as either natural or man-made, depending on their origin. Natural fibres are those produced from plants or animals, the most common examples being cotton and wool. In contrast, man-made fibres are usually some type of synthetic polymer. The most important man-made fibres are polyester, polyamide (nylon), polypropylene, viscose and acetate. Blends of all these fibres are also widely used.

The market share of man-made fibres has been increasing consistently, as can be seen in **Table 3-15**. In 2012, man-made fibres accounted for around 68% of the total world production of fibres. In Europe, this trend was even more prominent, with synthetic fibres responsible for 82%.

Table 3-15: Market share of natural and man-made fibres							
Dundrick	World production						
Product	1992	2002	2012				
Raw cotton	46%	35%	31%				
Wool	5%	2%	1%				
Man-made fibres 49% 63% 68%							
Source: CIRFS (2013)	Source: CIRFS (2013)						

In general, cellulosic fibres, such as cotton and viscose (regenerated cellulose fibre), present more serious fire hazards than thermoplastic synthetic ones, such as nylon, polyester and polyolefins (e.g., PP), despite the higher flammability of the latter. This is because thermoplastics tend to melt when heated. Such melting however is not universally beneficial as the molten plastic is itself hazardous (Lacasse & Baumann, 2004).

Blends of cellulosic and thermoplastic fibres are often used to increase the flame resistance of flammable fibres such as polyesters. However, these blends may present a greater threat because the cellulosic fibres provide a matrix that can hold the molten plastic and prevent it flowing away from the flame.

#### Wool

Wool is mainly produced by sheep (of which there were more than 1 billion heads, in 200 different breeds, in 2009) but other animals such as goats can also produce wool as cashmere or angora. Wool is a natural fibre with a wide range of applications. Its natural crimpiness makes it easy to spin. Wool fibres are usually more bulky than other fibres and therefore can provide better insulation from cold<sup>20</sup>. In addition, wool has an inherent flame resistance that is better than most synthetic fibres owing in part to its intrinsic water content. The Limiting Oxygen Index (LOI) is the amount (content in air) of oxygen required for a textile to maintain combustion. For wool, the LOI is 25.2%, which is higher than the ambient concentration of oxygen 21% and comparable to artificially flame retardant materials. This means that it is less flammable and can be self-extinguishing<sup>21</sup>. Wool is predominantly used for clothing, but it can also be used for the production of insulation for buildings. Literature suggests that DecaBDE may have been used in wool (Lowell Center for Sustainable Production, 2005; National Research Council, 2000) but this has not been confirmed as a current use for the substance. Other FRs relevant to wool, when used in airplane seating, contain hexafluorotitanate, hexafluorozirconate or tetrabromophthalic acid (Weil & Levchik, 2008).

#### Cotton

Cotton is the most commonly used natural fibre and among the major fibres collectively. FR cotton can be achieved with DecaBDE (in synergy with ATO), but in practice phosphorous-based FRs are more commonly employed (Keml, 2004).

Information available at: <a href="http://www.naturalfibres2009.org/en/fibres/wool.html">http://www.naturalfibres2009.org/en/fibres/wool.html</a>

Information available at: http://www.chocolatefishmerino.co.uk/technical/research.html

#### Polyester

The most common polyester fibre is Polyethylene Terephthalate (PET), which is also the world's most important man-made fibre. Other polyesters, such as PBTE, are produced, albeit in smaller quantities. Clothing applications account for a large share of PES production, but there are industrial (tyre cord fabrics) and commercial (furniture fillings) uses as well (CIRFS, 2013). The latter use especially could be of relevance to DecaBDE. However, according to a study for DEFRA, viscose and polyester fibres can be treated with phosphorus-based fire retardants during finishing (Gnosys, et al., 2010). A modified polymer of PET that includes phosphorus in the chain, can also be used and was considered a good substitute to DecaBDE by KemI (KemI, 2004).

# Acrylic

Acrylic (and modacrylic) fibres are soft, flexible and widely used in knitted clothing end-uses such as sweaters and socks. Home furnishing and blankets are other important applications owing to the high heat retention. Modacrylic fibres may contain halogens from other monomers, raising their degree of flame resistance (CIRFS, 2013). It is not known if DecaBDE is used as a FR in these fibres. However, it has been mentioned that backcoating with DecaBDE—ATO mixtures has good results on almost all textiles (Fretwork, 2011).

#### Viscose

Viscose fibres (or rayon, as they are called in the US) are produced from treated cellulose from wood pulp. Their properties (easy to dye, biodegradable, heat resistant) make them better suited to clothing applications. They also find application in linings and in the industrial sector, where they reinforce high speed tyres. Their use in home furnishing is limited (CIRFS, 2013).

# Polyamide

The main use of polyamides (or nylons) is in the clothing industry, to make for example stockings, hosiery and outwear, but they can also be used for technical applications in cars, such as in airbags or in tyres. Other important sectors for them are carpets and ropes. A Swiss company has been identified that produces nylon carpets for aircraft and bus use<sup>22</sup>.

The main technique for increasing flame resistance of a polyamide textile is through back coating because additives are not easily retained in polyamide fibres. It is expected, therefore, that DecaBDE may be used in such materials, but probably not for consumer clothes such as stockings.

# Polypropylene

Polypropylene is the most important polyolefin fibre (the only other one being polyethylene). It is generally thicker than other man-made fibres and can give more cover. In recent years, its consumption has grown and this can be attributed to its increasing use as carpet fibre and some unwoven uses, such as geotextiles. Other end-uses for PP fibres are in ropes, tapes and flexible intermediate bulk containers (FIBC) or 'big bags' (CIRFS, 2013). RPA (2003) has shown that DecaBDE is widely used for flame retarding polypropylene drapery and upholstery fabrics.

For PP fibres, it seems that halogen-antimony or halogen-tin systems are the most effective at low loadings, allowing for better processing of the fibres. Other types of FRs can be used in principle, but would require high loadings (>20% w/w) (Gnosys, et al., 2010).

Available online at: <a href="http://www.textilemedia.com/latest-news/mobiletex/lantal-launches-100-polyamide-carpet-for-aircraft/">http://www.textilemedia.com/latest-news/mobiletex/lantal-launches-100-polyamide-carpet-for-aircraft/</a>.

**Table 3-16** provides a brief overview of the end-uses of the different textile fibres that may be treated with DecaBDE.

Table 3-16: End uses of textile fibres										
	Domest	ic Sector		Contract Sector						
Material	Upholstery	Filters for cookers	Blinds	Blackout	Upholstery (theatres, hospitals etc.)	Automotive textiles	Geotextiles, wall coverings	Other		
Cotton	✓		✓	✓						
Polyester	✓	✓	✓	✓	✓	✓		✓		
Acrylic	✓									
Viscose	✓									
Polyamide	✓									
Polypropylene	✓									
Blends of the above	✓									
Polyester cotton	✓		✓	✓	✓			✓		
Glass*		✓	✓				✓			
Wool								✓		

<sup>\*:</sup> Glass is not relevant to the purposes of this study but is included here for completeness Source: RPA (2003), Consultation process

In the 2003 RPA study, EBFRIP commented that the use of DecaBDE in synthetic carpets was insignificant. Such carpets, usually made from nylon and PP, were mainly treated with a backcoating of aluminium trihydroxide (Al(OH) $_3$  or ATH). DecaBDE could be used to provide flame retardancy (encapsulated within these fibres), but at that time its share of the market appeared to be small (RPA, 2003).

# 3.3.3 Article manufacturing

According to the European Flame Retardant Organisation (EFRA), there are four major market sectors, where FRs are used (EFRA, 2013):

- Electronics, and more specifically, printed circuit boards, enclosures, cables and connectors
- Furniture and textile, mainly in upholstered furniture, mattresses
- Construction, in cables and electronic installations, for thermal insulation and also as structural elements
- **Transportation**, both in the public and the private sector.

This is confirmed by the latest VECAP report for 2012, and also from the consultation with EFRA, where it is stated that DecaBDE is used as a FR in textiles, in the transport sector and in construction and building (VECAP, 2013b). In the EU, the use of DecaBDE in Electrical and Electronic Equipment (EEE) is currently restricted under the provisions of the RoHS Directive (Official Journal of the European Union, 2011). Uses of DecaBDE in EEE falling under the scope of the RoHS Directive (in for example large or small domestic appliances and lighting equipment) are not mentioned in the report, so it is assumed that such uses have been discontinued.

DecaBDE is incorporated in the plastic at a loading of roughly 12% in a ratio of three parts DecaBDE to one part ATO. Information from consultation suggests that the proposed content of DecaBDE in plastic materials depends on the polymer. In general, the FR mixture amounts ranged between 15–25% of the plastic compound.

Between 10 and 20% of the quantity of DecaBDE used in the US before 2005 was for textile applications, while minor uses in paper, mineral wool and connectors are mentioned (Lowell Center for Sustainable Production, 2005). No information could be found on the uses in paper and mineral wool in the EU, while connectors have been identified as a current use for transport and construction applications.

As will be shown in the following sections, DecaBDE can be used in a range of articles. Some of these articles will find application in more than one of the major sectors mentioned above.

**Table 3-17** presents the relevance of the end-uses of DecaBDE, as they will be described in the sections below, to the major sectors of use.

Table 3-17: Applications of potential DecaBDE-based articles in major end-use sector							
		End-use Sector					
Application	Textiles & Furniture	Building & Construction	Transport				
Foam / furniture filling	✓		✓				
Upholstery	<b>√</b>		✓				
Plastic parts/components	,	✓	✓				
Cables & wires		✓	✓				
Adhesive & Sealant	<b>√</b>	✓	✓				
EEE			✓				

# 3.3.4 Uses as mentioned in the registration dossier

Five companies have submitted dossiers for the registration of DecaBDE under the REACH Regulation. Information about the uses relevant to this registration has been published in the ECHA dissemination portal (ECHA, 2013). According to the provisions of REACH, use of DecaBDE is only allowed for registered uses. Downstream uses which are not covered by this registration should be brought into scope or cease. The following **Table 3-18** includes distinct uses as described by the registrants, sorted alphabetically.

The table also contains an assumption of the most relevant life cycle stage(s) of the identified uses, based on the description of the uses given by registrants. The short length and consequent vagueness of the descriptions do not allow for an exact allocation to a life cycle stage. Annex 8 presents the identified uses as they were submitted in the registration dossier, with the relevant use descriptors and life cycle stages.

Tab	Table 3-18: Identified uses in the REACH registration dossier								
	Has described as	Identified through	Life cycle stage						
#	Use description	consultation	М	F	С	U	w		
1	Adhesive and sealant	✓		•		•			
2	Coatings and inks formulation	?		•					
3	Coating used in textile backcoating	✓		•	•				
4	Coating and inks application (consumer, industrial and professional use)	j			•	•			
5	Coating used in textile	<b>√</b>		•	•				

Tab	Table 3-18: Identified uses in the REACH registration dossier							
#	Use description	Identified through	Life	cycle s	stage			
6	Coatings – Industrial application of coatings	✓		0				
7	Converting	✓		•				
8	Filled dispersion used in transportation	✓		•	•			
9	Filled dispersion used in construction	?		•	•			
10	Foam production for construction	?	•	•	•			
11	Formulation of flame retardant preparation	✓	•					
12	Formulation coating preparation	✓	•					
13	Formulation polyester and S102E* – liquid filled dispersion	✓	•					
14	Industrial composites manufacturing	✓	•	•				
15	Manufacturing of formulated resins (gel coats, etc.)	✓	•	•				
16	Manufacturing of vinyl ester resins	?	•					
17	Professional application of coatings	?		•	•			
18	Professional composites manufacturing	?		•	•			
19	Recycling	✓				•		
20	Thermoplastic production (masterbatch and compound)	✓	•					
21	Thermoplastic used in automotive	✓	•	0	0			
22	Thermoplastic used in construction	✓	•	•	0			
23	Transformation**	?		•				
24	Wire and cable used in automotive	✓	•	•	•			
25	Wood and plastic composite	?	•	•	•			

<sup>√:</sup> Has been identified through consultation

Life cycle stages: m: manufacture (not relevant); f: formulation and compounding; c: conversion; u: use of article; w: waste

Source: ECHA (2013), consultation

DecaBDE importing companies in the EU and non-EU manufacturers seem to comply with the restriction on the use of the substance in EEE outlined in the RoHS Directive. The only uses relevant to EEE are in wires and cables used in automotive components, which are excluded from the scope of the Directive.

# 3.3.5 Textiles and furniture

# Fire resistance of textiles

Synthetic fibres used in textiles and furniture, in general burn faster than natural fibres, such as wool and cotton. Taking into account that the atmospheric concentration of oxygen is roughly 21%, materials with an LOI at or below that value will burn readily. The higher the value of LOI is, the harder it would be for the material to burn. The application of this parameter to the flammability of plastics is supported by international standardisation bodies (ASTM D2863) (IDES, 2013).

As explained earlier, wool is inherently flame resistant. **Table 3-19** shows the flame resistance of several natural and synthetic fibres. It has been mentioned that tightly woven heavy wool fabrics

<sup>?:</sup> It was not possible to identify or clearly reject this application during this study

<sup>\*</sup> S102E probably refers to a commercial DecaBDE mixture. The use most likely describes the preparation of the formulation that will be applied as backcoating on textiles

<sup>\*\*</sup> The term "transformation" most likely refers to the production of (semi-finished or finished) plastic articles

(with area density  $\geq$  600 g/m<sup>2</sup>) can meet the requirements of the UK FFFSR without treatment, but loosely woven and lighter weight wools require some treatment with, for example, zirconium hexafluoride or titanium hexafluoride based products (Gnosys, et al., 2010; Weil & Levchik, 2008).

Table 3-19: Flame resistance of natural and synthetic fibres								
Fibre	Limiting Oxygen Index (LOI)	Ignition T (°C)	Comments					
PVC	35-40	575	Flame resistant					
Wool	24-25	590	Difficult to ignite					
Polyester	20-23	485	Combustible					
Acrylic	18-20	390	Combustible					
Polypropylene	17-18	350	Burns easily					
Cotton 18-21 390 Burns easily								
Source: http://www.textilesfr.co.uk/FibresFlammability.html								

Fire safety requirements for furniture vary across Europe, with UK and Irish standards being the most stringent. While various member states have regulations in place that require the furniture be tested for flammability, the UK regulations require that the components (fillings, upholstery, loose fillings and cover) should pass similar tests as well (Gnosys, et al., 2010). This means that manufacturers have to comply with different standards for their products depending on the market they want to place them in. Additionally, the materials they will use must be able to pass the required fire safety tests.

# Uses of textiles

The furnishing textiles can be used as upholstery in the domestic sector for furniture that could include sofas, cushions, carpets and armchairs, and possibly curtains and mattresses as well. In the contract sector, they can be used as upholstery in office furniture (such as chairs), in drapes or curtains, seats and other articles for public buildings, and also in seats and carpets used in transport vehicles (UK HSE, 2012).

Furniture may include FRs in the following components (EFRA, 2012):

- Covering materials, which can be made from a variety of fibres, such as wool, cotton, viscose, polyacrylic, polyester, PP or polyamide but also natural or imitation (PVC or polyurethane) leather
- Filling materials, mainly from polyurethane foam, flexible polyurethane or latex
- Interlining, which may be from non-woven materials, non-flammable material (such as glass fibres) or aramid fibres (such as Kevlar fibres)
- Plastic parts of furniture (such as desk-chair handles).

In the USA, DecaBDE is not used in consumer clothing or in residential carpets (US EPA, 2012). Use in consumer clothing has not been identified in the EU. However, the presence of DecaBDE in protective clothing has been reported by the Norwegian Environmental Agency, during the public consultation for the identification of DecaBDE as a Substance of Very High Concern (SVHC). Use was not on the fabric itself, but rather on the adhesive part of the reflective tapes<sup>23</sup>. Nightwear fire resistance is also regulated in the UK and the Netherlands, but DecaBDE is not used in this application (Gnosys, et al., 2010).

<sup>&</sup>lt;sup>23</sup> 19 November 2012, Comments on an Annex XV Dossier for Identification of a substance as SVHC and responses to these comments – found online <a href="here.">here.</a>

The use of DecaBDE in tents seems to be important, but it was not possible to verify this use through the consultation process already performed. Military tents are usually coated with a PVC layer for water-proofing and it is possible that the canvas is also backcoated. PVC canvas is inherently fire retardant, and so, for the production of tarpaulins, it is usually preferred over materials that must be made fire retardant somehow. Other products, such as awnings, do not include fire retardants. In addition, it is possible for DecaBDE to be used for manufacture of disaster relief tents in Italy. These tents need to be both waterproof but also FR because people might cook inside them. A recent study in the USA has found DecaBDE present in tents for general use. The study comments that FRs from the tents are transferred to skin during contact. The highest concentration of FR was 3.8%, but the relevant FR is not mentioned in the abstract (Keller, 2014). It is not known if these tents are also used in the EU.

In a study by the Danish Environmental Agency, use of DecaBDE in (camping) tents has been identified. The tents were produced in China using DecaBDE in quantities of about 2g per tent and imported into Denmark, from where the majority were exported to other EU countries. Based on the projected import of 160,000 tents in 2007, about 320 kg of DecaBDE was expected to be imported through this route (Danish EPA, 2007).

# Foam fillings

Polyurethane foam and flexible polyurethane are the most common materials for foam fillings for sofa cushions, armchairs and mattresses. There are two main types of foam, polyether (which is the most commonly used) and polyester (which is more expensive, but has higher tensile strength). Higher density foams are in general more flame resistant, and thus require less FR, but they are also more expensive (EFRA, 2012).

Flame resistance is usually increased with nitrogen-based or halogenated additive FRs. Nitrogen-based FRs are mainly melamine, which can be used either on its own (although in practice it is a synergist) or in combination with chlorinated phosphate esters, such as TCPP, TDCP or TL-10-ST. Reactive brominated FRs, such as tribromoneopentyl alcohol (TBNPA) may also be used in combination with TCPP, but this carries higher cost. Finally, Combustion Modified High Resilience (CMHR) foam can achieve very high quality in terms of fire resistance, but it is considerably more expensive than the rest (EFRA, 2012).

The use of DecaBDE in flexible polyurethane foams has been mentioned in the past (BSEF, 2006). In the USA, its use was identified in the fabric covering the mattress foam (Lowell Center for Sustainable Production, 2005). More recent information indicates that DecaBDE is not used for increasing fire resistance in PU foams in mattresses (EFRA, 2012). Recent consultation with the flexible PU foam industry has shown DecaBDE is not used when FR properties are required in fillings. Wherever FR standards are strict, such as in the UK and Ireland, TCPP is predominantly used. In continental Europe, regulations only demand FRs in exceptional circumstances, and in such instances DecaBDE is not considered for use. The latest information applies to at least 75% of the market, which is the share covered by the members of the contacted association.

Other materials that were identified for foam fillings were polystyrene and unwoven polyester fibres, such as PET (PlasticsEurope, 2013). DecaBDE is not used in expanded or extruded polystyrene but could be present in PET. In the Annex XV dossier, it has been mentioned that DecaBDE may be used in synthetic rubber (latex) foam for mattresses, according to consultation with undisclosed stakeholders (UK HSE, 2012).

Use of DecaBDE in foam materials was not identified during consultation. Two associations of PU foam manufacturers and moulders commented that DecaBDE is not used by their members. These

associations accounted for roughly 75% of the PU foam for furniture and 85% of the foam for transport applications.

#### **Upholsteries and draperies**

A wide range of fibres, both natural and man-made, can be used for upholstered furniture, curtains and carpets.

In 2003, EBFRIP commented that use of DecaBDE in domestic carpets was not a significant use (RPA, 2003) and the HSE reported that during their consultation for the Annex XV dossier it was reported that DecaBDE is not used in commercial and residential carpets, even though some aircraft manufacturers identify carpets as a possible application (UK HSE, 2012).

Currently, there is no harmonised fire safety standard for furniture in the EU, with different countries employing their own regulations. The UK has the strictest regulatory framework in the form of the Furniture and Furnishings Fire Safety Regulations (FFFRS), which require testing of upholstery separately from other components. The textile must be tested for fire resistance over untreated foam or filling, which means that it has to compensate for a more flammable substrate as well (UK HSE, 2012).

The covering fabric (upholstery) in furniture and mattresses can be a critical factor for the propagation or the suppression of flames. A 1995 study has shown that the upholstery is the controlling element in small fires on upholstered furniture (Sundstrom, 1995). Since 1995, the materials used in upholstery have changed and now include a wide range of natural and synthetic fibres, as well as blends. Backcoating of these textiles is a very common practice and DecaBDE–ATO is probably the most widely used FR mixture because it is very insoluble, is chemically inert and can be used on a wide range of fibres (Fretwork, 2011) (Keml, 2005).

Criteria for choosing a FR for a textile may include (EFRA, 2012):

- Achieving sufficient flame retardancy, according to the regulations in force
- Having minimum impact on the aesthetic properties of the fabric, such as colour and texture
- Durability, especially if the fabric will be washed frequently.

Drapes and curtains intended to be used in public places, such as schools, hospitals and theatres, are also required to meet established flame retardancy requirements and must be able to withstand repeated washing.

Use of DecaBDE in textiles intended for upholsteries, contract applications and curtains has been verified through consultation, mainly by UK responses. Major manufacturers and finishers of textiles have informed RPA that their final products are intended for use in contract furniture (for public buildings), curtains and domestic furniture. In the EU, a German association of textile manufacturers has commented that backcoating with DecaBDE is not a common practice in Germany. Indeed, German formulators have either stopped using DecaBDE in their mixtures or are in the process of stopping, with only a few still producing DecaBDE mixtures for a small number of customers. The demand has fallen significantly after DecaBDE was included in the Candidate List.

It should be noted that, according to consultation, upholsterers in the UK order FR fabric to comply with the more stringent fire safety regulations. However, they are not always aware how compliance with the regulations is achieved and do not keep records on quantities bought or imported. That said, textile manufacturers and finishers have commented that increasingly clients are asking for products that do not contain SVHCs, including DecaBDE. According to a stakeholder from the furniture industry, around nine million upholstered items (with an estimated value of £1.58)

billion) are sold in the UK market per year, with a lifetime of roughly 9 years, but, owing to the designation of DecaBDE as a SVHC, most if not all textile finishers have switched to alternatives.

A manufacturer of textiles for contract applications has commented that they are using DecaBDE (in the range of <100 t/y) but are currently in the process of evaluating potential alternatives.

In backcoated textiles, the FR coating is carried in relatively low loadings. However, in other applications, the FR mixture can act as a carrier to the textile, as, for example, in window blinds (RPA, 2003).

It has also been mentioned that until recently (2013), DecaBDE was used in the manufacture of covers for mattresses to be used in medical beds. The quantities of DecaBDE used for this were in the range of < 100 t/y.

#### Interliners

Interliner fabrics are commonly used as a fire barrier, delaying the spread of fire to the more flammable fillings. They are usually made from fabrics that have been treated with a FR and find use in seats for public venues, such as cinemas and theatres.

In general, different types of textiles are used as fire barriers in mattresses and upholstered furniture. Mattresses usually contain non-woven fibre batting, while furniture (upholstered and institutional) more commonly contains coated or laminated textiles for the same purpose.

Passive fire barriers are usually made from inorganic or inherently flame resistant organic fibres, the latter having high heat capacity and undergoing an endothermic phase change when heated. Examples of materials used in fire barriers are FR viscose or polyester, cotton treated with boric acid, glass fibre and inherently FR fibres (such as fibreglass, aramids and melamines). The last of these are rather expensive and restricted to mass transport seating and public buildings, where the less expensive thermoplastic polymers are not good candidates because they tend to melt or crack when heated. Upholstered furniture can use interliners made from FR viscose, when this is combined with inherently FR fibres (Nazare & Davis, 2012).

In conclusion, cotton fabric or polyester fibres may be used, but they would have to be rendered fire retardant first. DecaBDE could facilitate this but the compound is not mentioned explicitly in this context and it is possible that it does not find applications at all in interliners.

#### Protective clothing

One rather specialised use of DecaBDE in textiles was identified through the consultation process. This was in textiles mainly used for the production of heat resistant uniforms for workers exposed to extremely high temperatures. The uniforms need to allow workers to safely approach equipment in smelters, foundries and similar facilities with temperatures that might at times reach up to 2000°C. The same textiles are used to make protective suits to be worn while fighting fires on board ships. Such textiles protect the wearer not only from extremely high temperatures but also from contact hazards, such as drops of molten metal. Specifically, they encourage the molten metal to bounce or roll away on contact. DecaBDE was chosen as the FR because of its long-term stability at high temperature in general but also specifically with respect to dramatic fluctuations in surface temperature in excess of 100°C.

An alternative substance is now being used instead of DecaBDE, since 2012. However, in any case, before this the relevant quantities were very small, in the order of < 10 tonnes per year.

As mentioned above, DecaBDE has been detected in the adhesive layers of reflective tapes for fire-fighters uniforms in Norway. The tapes were textile-based and DecaBDE content was measured at 1–5%. The use was intentional, but the importers of the tapes were not aware of the presence of DecaBDE in the tapes. The investigating Norwegian authorities concluded that tapes originated in Asia. There were nine importers in Norway in 2012, but they have stopped relevant imports since then. The Norwegian Authorities have reported that more than 30 t/y of reflective tapes were imported into Norway, containing 0.3–1.5 t of DecaBDE.

Attempts at communicating a number of Asian manufacturers of reflective tapes showed that they were not using or have never used DecaBDE.

# 3.3.6 Buildings and construction

Materials, in which DecaBDE may be present, can be used in a wide range of building elements. In 2006, the BSEF published a list of potential uses of DecaBDE in the building sector. Building and construction applications of DecaBDE include (BSEF, 2006):

- Pipes
- Lamp holders
- Stadium seats (mentioned in a Danish EPA report but without further clarification (Danish EPA, 2007))
- Switches and connectors
- Facing laminates for insulation panels
- Films for use under the roof and to protect building areas
- Electrical ducts and fittings
- Components in analytical equipment in industrial and medical laboratories
- Air ducts for ventilation systems
- Pillars for telephone and communication cables.

The list above could be applied nowadays with a few exceptions. (The use in analytical equipment in industrial and medical laboratories could not be verified.) Uses related to buildings and construction could be classified as follows:

- Structural elements (roofing, wall and floor coverings)
- Insulation (thermal)
- Cables and wiring.

Stakeholders relevant to building and construction products have not responded to RPA's call for information. It has been mentioned that DecaBDE could be used in extruded sheets and generally in bigger structures for construction applications.

# Production of wood-plastic composites

The production of wood–plastic composites represents a viable construction application for DecaBDE. Indeed, it is mentioned as an identified use in the DecaBDE registration dossier. Wood–plastic composites contain about 70% cellulose, with the rest being plastic material such as PP, PE or PVC. These composites are used commonly for outdoor uses, such as benches, but certain indoor uses, such as in door frames and furniture, have been mentioned as well<sup>24</sup>. A non-EU manufacturer of DecaBDE mentions in one of their brochures that the DecaBDE-containing product is suitable for

Available online at http://www.ktron.com

use in wood-plastic composites used in decking (outside flooring, for patios, verandas and similar structures) (ICL Industrial Products, 2012).

There are three major types of wood–plastic composites; layered composites used in the production of sheets and sections, particle composites and fibre composites, such as fibreboard. These composites may contain plastics or other materials, such as glues, and are used in a variety of structural applications<sup>25</sup>.

#### Roofing

Important properties for a synthetic roof include (EFRA, 2012b):

- Thermal stability (stability at a wide range of temperatures)
- UV stability (resistance to sunlight)
- Good ageing properties (a lifetime of 15-20 years)
- No leaching and no sensitivity to moisture.

Bitumen, PVC, thermoplastic polyolefins (TPO) and ethylene-propylene-diene monomer (EPDM) rubber represent typical materials for roofing. In the past, recycled polyolefins (PE or PP) were used as well.

DecaBDE can be used in these plastics with ATO as a synergist, especially in TPO, and in blends of PVC and nitrile rubber. It appears that DecaBDE is used, in particular, for the construction of opaque roofs (EFRA, 2012b). The suitability of DecaBDE for use in roof sheeting applications is claimed by ICL in one of its commercial brochures, where it mentions that DecaBDE is suitable for use in PP copolymers and PE (ICL Industrial Products, 2012). The use of DecaBDE in roofing applications has been implied by some of the consultees, but no strong evidence arose during consultation.

# Flooring and wall coverings

There are a wide range of materials that can be used for floors and wall coverings (wallpapers), with plasticised PVC being the most common. Other polymers used are polyolefins, polyamides (nylons), polyester and acrylic and cellulosic blends. Epoxy resin floor finishes are used when a durable material is required, as in, for example, public buildings, schools and fuel stations. Wallpapers are usually made out of PVC and vinyl, as well as woven textiles, although woven textiles represent a smaller share. Some performance criteria for flooring materials are (EFRA, 2012b):

- Abrasion resistance
- Aesthetics

UV and colour stability.

DecaBDE is apparently not used in wall coverings (EFRA, 2012b). Certain waterborne emulsions with adhesive properties used for wall or floor coverings may include DecaBDE (US EPA, 2012), but this has not been verified through consultation or research.

One consultee reported that DecaBDE is suitable for use in PE and PP intended for cladding panels.

Available online at <a href="http://www.trada.co.uk/techinfo/library/view/3B8B8E98-9D09-43BD-9177-32B952B5C3CC/Timber+composites/index.html">http://www.trada.co.uk/techinfo/library/view/3B8B8E98-9D09-43BD-9177-32B952B5C3CC/Timber+composites/index.html</a>.

#### Insulation

The most common material for thermal insulation of houses in Europe is polystyrene (PS) foam, available in two forms: expanded PS (EPS) and extruded PS (XPS). PS is popular because of its low risk to human health and the environment and because it does not require personal protective equipment when used. XPS is mainly used when moisture resistance is needed, while EPS is mainly used in building facades and flat roofs (EFRA, 2012b).

Polyurethane foam is gaining market share and is suitable for very low energy buildings, owing to its low thermal conductivity. It can be used in walls, roofs and floors as well. It is marketed as boards, sandwich panels and foam produced on site, and it tends to be more expensive than other insulating materials, such as mineral wool and EPS. Cross-linked elastomeric compositions based on plasticised PVC—nitrile rubber blends or PE can be used for insulation of heating pipes and A/C systems (EFRA, 2012b).

DecaBDE is not used as a FR for PS or PU foam. This has been confirmed through consultation with industry members, who stated that PU foam does not contain DecaBDE as a FR and that they are unaware of any similar imported products which do contain DecaBDE.

DecaBDE is however used in PVC—nitrile rubber blends, which are commonly used in piping insulation. The source (EFRA, 2012b) does not explicitly mention it in the insulation chapter, but it seems likely that the resulting material is used for heating-pipe insulation.

Another material that can be used for thermal or acoustic insulation applications is PE foam, and it is reported that it could contain DecaBDE as a FR (ICL Industrial Products, 2012).

#### Cabling, wiring and piping

Electrical installations are a major cause of building fires, and consequently cables (and wires) have specific fire safety requirements that apply regardless of whether they are be used in construction, transport or industrial applications. Wires and cables in buildings have to possess (EFRA, 2012b):

- Excellent mechanical properties, flexibility (in some instances reduced slightly by incorporated FRs) and tension resistance,
- Good conductivity
- Resistance to abrasion
- Low smoke emissions
- Excellent thermal stability.

Types of wire are frequently categorised according to application, as can be seen in the following list (Greiner Environmental, 2002):

- Building wire, which is used to distribute electricity to buildings
- Telephone wire, for telecommunications purposes
- Cords, appliance wire and similar wires (in which the use of DecaBDE is probably restricted under RoHS)
- Power cable for the transmission of electricity
- Coaxial and antennae cable, used in broadcasting or computer networking applications
- Electronic and data wire, made of copper and fibre optic cable
- Magnet wire, for use in electrical motors, generators, transformers, automobiles and small electrical appliances (in which DecaBDE may be restricted in for some uses).

Some common resins used in wire, cable and piping applications are polyethylene (cross-linked and thermoplastic) and PVC, but other plastics such as polyamides, polypropylene or polyurethane may also be used (ICL Industrial Products, 2012).

Brominated FRs can increase the flame retardancy of polyolefins or neoprene rubber used for wires and cables. A loading of 12% DecaBDE and 6% ATO can be sufficient for a UL-94 V0 rating, the highest degree of flame retardancy according to the UL-94 standard. DecaBDE is considered a very good FR for these applications and materials (Greiner Environmental, 2002). In PVC, a synergistic agent, most commonly ATO, can be used in combination with a halogenated compound. A typical concentration of DecaBDE in electrical insulation of 10-30% was reported by the Swedish MSCA, according to information found in the Swedish Products Register in years 2007-2012.

Another potential use was examined by the Danish EPA in a 2007 use-mapping exercise. Heat-shrinkable materials that can be used on wires were reported to contain DecaBDE, although the quantities sold in Denmark were very small and the total estimated quantity of DecaBDE was in the range of a few kilograms. The content of DecaBDE in the material was stated to be 10% w/w (Danish EPA, 2007).

Consultation with the cable and wiring industry was inconclusive. However, it has been mentioned that some of the alternatives could be used to replace DecaBDE in such applications. During a survey that ended in 2010, a MSCA identified a manufacturer of fireproof cables as a user of DecaBDE.

# 3.3.7 Sealants, adhesives and coatings

Flame retardancy for sealants can be achieved either through a reactive system, based on bromine or chlorine, or through an additive FR system based on a combination of a halogen with phosphorus (EFRA, 2012b).

Adhesives are usually based on acrylic emulsions, neoprene rubber or reactive polyurethane. Their fire resistance is usually increased with the use of halogenated substances using ATO as a synergist or with a combination of a phosphorus compound and inorganic mineral filler, such as ATH or magnesium hydroxide (MDH). Hot-melt adhesives are usually manufactured from mixtures of three components: a thermoplastic resin to provide cohesion, a petroleum resin to provide the tackiness and paraffin or a wax to adjust the viscosity. EVA is a commonly used thermoplastic resin in such products. DecaBDE is the FR of choice in adhesives for polyurethane foams and fabrics, even though it is solid and can settle outside the mixture, clogging the equipment (Atwell, 1991). In a 2007 report for the Danish EPA, it was mentioned that use of DecaBDE in 'hot-melt glues' had stopped (Danish EPA, 2007).

Some companies offer FR adhesive films or sheets for flexible electronics applications, but it seems PBDEs are not used<sup>26</sup>. A manufacturer of adhesives and sealants claims that reactive phosphorus FRs are used in their products because either there are concerns over the toxicity of more established ones or the more established ones cannot be used in such a wide range of applications<sup>27</sup>. Information coming from a brochure from a DecaBDE manufacturer implies DecaBDE is not suitable for hot-melt applications (Albemarle, 2013).

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Dupont adhesive range, available at:

http://www2.dupont.com/Pyralux/en US/assets/downloads/pdf/FRadhesive H-73235.pdf.

<sup>&</sup>lt;sup>27</sup> Struktol epoxy resins, available at: <a href="http://www.struktol.net/markets-products/epoxy-resins-and-flame-retardants/flame-retardants.html">http://www.struktol.net/markets-products/epoxy-resins-and-flame-retardants/flame-retardants.html</a>.

Consultation with MSCA has identified that, until 2010, an epoxy adhesive containing DecaBDE was imported, but this has since stopped and no similar product has been reported in this context in the relevant chemical products registry. The concentration of DecaBDE in these adhesives was <30%.

Another important use of adhesives is in composites: (usually construction) materials composed of layers of different materials, such as wood and metal. The individual components may be inherently fire resistant, but the adhesives are unlikely to be<sup>28</sup>.

There are a large number of different adhesive tapes for aircraft applications. These applications can include (Berry Plastics, 2011):

- Cargo pit tapes, for cargo hold floor seam sealing, insulation and other uses. They could contain DecaBDE or other brominated substances, but the relevant manufacturer declares they are 'DecaBDE free'
- Carpet and double-coated tapes, for fixing carpets on the floor and for temporary fixing of aircraft parts. Some may be FR, using a FR-rubber
- Moisture barrier tapes, with acrylic or polyurethane adhesive. They are in general FR, but whether DecaBDE is involved is unknown
- Surface protection and masking tapes. These seem to be for temporary use
- Aluminium foil tapes, for masking and sealing in aircraft. Flame retardancy is not mentioned
- Duct tapes
- Electrical and safety tapes.

Coatings can be based on intumescent systems, which prevent the flame reaching structural materials such as steel beams. Such coating systems are based on polyurethane, acrylic or epoxy resins and fire retardant with phosphorus FRs combined with nitrogen-based materials. Suitability of DecaBDE in coatings (mainly backcoating and paints) is confirmed in a commercial brochure from a DecaBDE manufacturer (Albemarle, 2013). Furthermore, the European association for coatings and paints (CEPE) has stated during consultation that the intumescent and protective coatings subsectors are the ones relevant to DecaBDE, but the consultation did not provide any further details about this (CEPE, 2013). A consultee implied a company may be using DecaBDE for the manufacturing of FR coatings. The annual quantities of DecaBDE supply for 2013 were <100 t/y.

In general, it seems that DecaBDE has been used in these applications, and there are indications that such use continues. It must be noted, however, that, according to the Annex XV dossier, the use of DecaBDE in adhesives is unconfirmed (UK HSE, 2012). As can be seen from **Table 3-18**, 'adhesives and sealants', 'paints and inks' and coatings are all identified uses in the submitted registration dossier, and this could mean that the REACH consortium has identified this specific use after consultation with downstream users or based on information from client.

During the consultation process, it was asserted that DecaBDE is not used in sealants. Consultation with the relevant industry association did not produce any reaction from its members, and thus it was concluded that the sealant industry would not affected by the proposed DecaBDE restriction.

# Adhesive tapes

Adhesive tapes have a variety of applications that in general overlap with the applications of DecaBDE, in for example construction and transport. They are commonly used for thermal insulation, so the adhesive layer must display similar heat transfer properties as the rest of the product (Kim, 2007). The Norwegian MSCA found DecaBDE in the adhesive layer of reflective tapes in fire-fighters uniforms, but further communication with the industry provider has shown that this

Available at: http://www.adhesivesmag.com/articles/fire-retardant-adhesives.

use has stopped. Nine or ten importers of tapes containing DecaBDE were identified during consultation, all of whom were importing from Asia. Apparently, this application has ceased.

Consultation with European manufacturers of adhesive tapes has not provided evidence that DecaBDE is currently used in the EU in such products. Companies of the European association for adhesive tape manufacturers have declared that they do not use or import DecaBDE in their products or that they are in the process of phasing out DecaBDE from their products.

Communication has also been attempted with non-EU manufacturers of such tapes, mainly based in Asia. A response from a company in Asia indicated that, as of August 2013, they were using DecaBDE in their products but they have switched to an alternative since then.

# 3.3.8 Transport

DecaBDE has been widely used in components for a range of vehicles.

The transport vehicle manufacturing industry is a complex one, in that vehicles are constructed from a large number of individual components that are not necessarily manufactured in-house. Furthermore, suppliers of components such as seating, air-conditioning units and electronic equipment have their own suppliers of parts.

The supply chain of vehicle part suppliers has undergone significant changes. It appears that the number of suppliers associated with vehicle manufacturers has declined considerably, while at the same time, relocation to lower-cost locations has been observed. This trend was recorded in the late 1990s and early 2000s (Helps, 2001), but it is not known if it has persisted in more recent years.

#### **Road transport**

The Annex XV dossier for DecaBDE (UK HSE, 2012) has identified a list of components that may contain DecaBDE:

- PE wiring sleeves in electrical harnesses
- High performance polyester materials and textiles in interior surface materials
- EPDM rubber and PP coatings in fuel systems
- Polymer components and housings (ABS/PP)
- Low density polyurethane foams
- Aramid tapes
- Polyethylene naphthalate flexible circuits
- Shrink tubes
- · Head linings.

Polyurethane foams for seat cushions and head- or arm-rests do not require DecaBDE for sufficient flame retardancy, according to consultation with the industry.

According to the BSEF, in 2006 DecaBDE was being used in the following articles in cars and mass transportation (BSEF, 2006):

- In fabrics (backcoated) in the rear deck, upholstery, headliner, sun visor, head rest or trim panels
- In reinforced plastics in the instrument panel and interior trims
- Under the hood or dashboard in terminals and fuse blocks and in higher amperage wires and cable jacketing
- In EEE, namely in battery cases and trays, engine controls, electrical connectors and components of radio disk, GPS and computer systems.

The same general categories (plastic components, circuit boards, textiles, upholstery and small EEE components) are also mentioned in the context of brominated FRs in a Swiss Agency for the Environment study (SAEFL, 2003). An industry brochure mentions that DecaBDE could be used in backcoating textiles for seating, in cross-linked PE foam for acoustic insulation and door and partition internal panels made of PP or PC (ICL Industrial Products, 2012). In 1999, it was estimated that small EEE components accounted for around 10% of all plastics used in cars (by weight). As part of a study, the Danish Environmental Protection Agency contacted importers of cars to Denmark regarding DecaBDE use in components for their cars. One importer of Asian cars responded that DecaBDE was used in wire lugs, in amounts in the region of 1-5 g/car (Danish EPA, 2007). If cabin parts contain DecaBDE, the amounts would be higher. The situation was quite unclear, however, as the importers could not state with certainty whether DecaBDE was present in their cars or not.

DecaBDE is also included in the Global Automotive Declarable Substance List (GADSL) in a generic entry about PBDEs. Consequently, the supplier must notify the vehicle manufacturer when it is present in automotive parts in concentrations above 0.1% w/w. DecaBDE is the only PBDE to which this rule applies. The use of other PBDEs is simply prohibited (GADSL, 2013).

EU car manufacturers have not provided any information regarding the presence of DecaBDE in cars. Additionally, a European association of car suppliers was not able to collect any information pertaining to DecaBDE in automotive parts from its members.

Some MSCAs have provided relevant data, however. One MSCA has submitted information provided by an Asian car manufacturer. According to this information, the following parts, intended for the assembly of cars in the country, have been analysed for presence of PBDEs:

automobile seats, inner door panels, upper quard plates – pillars, upper panel – pillar, lower fender of right and left pillar, inner guard plates - door, lower guard panel pillars, car carpets, car visor, vehicle roofs, down dashboard, front and rear bumper body, ventilation grill, outside rearview mirror, belts, wire harness vehicle roof, harn of antenna, harn of defrost, harn of tail door, engine harn".

The detected concentrations were low, in the range of < 1 to < 10 mg/kg of car. Based on the quantities provided, the total quantity of PBDEs was very low compared with the overall tonnage. Furthermore, the number of cars involved was also very low. As a result, this avenue of investigation was not taken further.

The German CA shared a document from a car manufacturer based in Germany, according to which no DecaBDE was detected in foam in four models.

A manufacturer of textiles for use in transport and contract (public building) applications has reported that they have been using DecaBDE for automotive applications. They had several materials that contained DecaBDE; the FR content and the associated tonnages cannot be disclosed. Based on the information submitted, almost all automotive clients have switched to an alternative (EBP, see below).

Another company that supplies the automotive industry with plastic parts, commented when contacted that they intend to switch from DecaBDE. They have evaluated another material without DecaBDE and were in the process of final approval by the client.

#### Mass transport (aviation, trains, marine)

#### **Aviation**

DecaBDE's importance for the aerospace industry is high, because it helps the manufacturer to assure the safety during flight and to allow for longer escape time in case of a fire while on the ground. Additionally, DecaBDE contributes in achieving compliance with the US Federal Aviation Administration standards for compartment interiors, cargo and baggage compartment, thermal and acoustic insulation and wire flammability (Boeing, 2011). DecaBDE is considered important for meeting the stringent safety requirements for aviation. According to the Federal Aviation Administration (FAA) of the US, a wide-body transport category aircraft could contain between 3,000 and 7,000 kg of combustible components in the cabin (Lyon, 2008).

A (probably non-exhaustive) list of components that may contain DecaBDE contains adhesives and tapes, composites, ducting and moulded parts, emergency equipment, electrical and electronic equipment (not further specified), fabrics and films, insulation, interiors and sealants (UK HSE, 2012).

A study by Allen(2013) detected DecaBDE, along with a number of other FRs including Penta- and OctaBDE, in all samples of dust collected from airplanes operating in the US and on the hands of flight crew members. DecaBDE was the most common FR detected, with concentrations in the dust at least an order of magnitude higher than the rest. XRF analysis showed that the potential dust source with the highest bromine concentration was the carpet. It is interesting to note that the authors did not find significant differences between the two major aircraft manufacturers, namely Boeing and Airbus. However, the quantities detected in this study seem to be higher than in other, similar studies, and in particular from a Swedish study a few years earlier, potentially because of different sampling methods (Allen, 2013).

The aviation sector has recognised the past and current use of DecaBDE in parts and systems used in airplanes, mainly because of the strict safety regulations, both in the US (FAA) and in the EU (EASA). DecaBDE has been preferred because it is quite versatile and can be used with a number of other substances or in different calibrations required for a part to comply with all necessary standards (not just fire safety).

The industry is taking steps towards substituting DecaBDE, but it has given several reasons why this is difficult. The most significant is the complexity and global extent of the supply chains. Components may consist of many different parts, and production may be spread around the globe, encompassing countries where DecaBDE is still commonly used. This would mean it is difficult to control each one of the upstream parties, which are the ones that would have to implement the changes to their products. Owing to the strict regulations and certification procedures, changing a material or component can be time-consuming, and it was commented that some parts may be produced even more than 18 months in advance of the production of the relevant aeroplane.

It was also commented that, although the aviation sector is a high value one, the quantities of materials used (especially chemicals) are very low (sometimes in the region of a few gallons/y).

Although the presence of DecaBDE has been identified in some aviation parts, and manufacturers have begun the process of replacement, there remain DecaBDE containing parts for which replacement is not yet an option. The industry has expressed its commitment to complete phase out of DecaBDE but there is no clear date for when this will be achieved.

An aircraft and related hardware and parts manufacturer has commented that they expect complete phase out of DecaBDE from their products by the beginning of 2017. Communication with the suppliers is considered critical to identify all parts containing DecaBDE.

It has been reported that use of DecaBDE in the rail industry may occur in seat fabrics for passengers and drivers, intercar barriers and hoses (in an ethylene acrylic elastomer) and in some electrical components, which are exempted from the scope of the RoHS directive (UK HSE, 2012).

A textile manufacturer has reported supplying a product containing DecaBDE to the maritime industry, but added that there are plans for switching from DecaBDE to an alternative FR for this product.

# 3.3.9 Electrical and electronic equipment

#### The RoHS Directive

The RoHS Directive restricts the use of DecaBDE (along with other PBDE) in some Electrical and Electronic Equipment (EEE) and components of EEE. DecaBDE is not allowed in quantities higher than 0.1% w/w in the EEE mentioned in the following table.

Tabl	2 ما	-20.	Scor	10 O	F +1	aa F	PAHS	Dire	ctive
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#### **EEE** within the scope of RoHS

Large and small household appliances

IT and telecommunication equipment

Consumer equipment

Lighting equipment

Electrical and electronic tools

Toys, leisure equipment and sport equipment

Medical devices

Monitoring and control instruments, including industrial instruments

Automatic dispensers

Other EEE not covered by the categories above

#### **Exempted EEE**

EEE used for military and defence purposes

Equipment that will be sent to space

Large-scale stationary industrial tools (i.e. large-scale machinery, equipment and components functioning together)

Large-scale fixed installations (combination of several types of apparatus in a fixed location)

Transport vehicles (excluding two-wheeled electric vehicles)

Non-road mobile machinery exclusively for professional uses

Active implantable medical devices (such as pacemakers)

Photovoltaic panels, that are to be installed by professionals

B2B equipment designed and used solely for R&D

Specifically designed components of equipment excluded from the scope of the directive, without which, the equipment cannot function and which have to be replaced by the same component

The RoHS Directive prevents DecaBDE from being used in the majority of EEE previously containing the substance, including TV and computer enclosures made out of HIPS. Indeed, according to the industry, use of DecaBDE in HIPS has in effect stopped, although appliances that contain DecaBDE in their casings are still in circulation.

It has been mentioned above that, DecaBDE is used in insulation materials (mainly PP or PE) for wires and cables that can be used in construction or transport applications. DecaBDE seems to be used in plastic parts of connectors, switches and other small electronic components, which are mainly constructed out of polyesters (PBTE or PET) or polyamide. According to a Danish EPA study, in EEE, DecaBDE accounted for about 10% of FRs used in PBTE and PET and 6% of those used in PA. DecaBDE is cheaper than other FRs, but not considered the best FR in technical terms for these plastics (taking into consideration compatibility and mechanical properties) (Danish EPA, 2006).

Regarding the potential restriction of DecaBDE, a representative of the European EEE industry commented that they were not concerned by it, but suggested that a "repair-as-produced" restriction would be needed.

#### Historical use in EEE

DecaBDE was used extensively in the EEE sector before restriction, helping the products achieve the required flame retardancy. In EEE, as elsewhere, it was used in combination with ATO. The most common application of DecaBDE in EEE was to increase the flame retardancy of High Impact Polystyrene (HIPS), so that it would comply with the fire safety standard UL94 V-0. HIPS is mainly used in TV casings, but also for printers and scanners. (ECB, 2007) However, such use has stopped in the EU since the RoHS Directive imposed a restriction on the use of DecaBDE in electrical and electronic consumer goods. Indeed, the most recent VECAP report does not mention the use of DecaBDE in EEE at all (VECAP, 2013b), and this has been confirmed through consultation with EFRA.

Other applications of DecaBDE in plastics used for EEE have been mentioned and, as discussed above, may still be relevant for exempted applications (ECB, 2007):

- Polyolefins (PE and PP) in computers, connectors, electrical boxes and wire cables
- Acetate polymers (EVA) or ethylene copolymers (EPDM rubber) and thermoplastic elastomers for wire and cable
- Polyester resins for electronics
- Styrenic rubbers (ABS), polycarbonates, polyamides and polyesters (PET, PBTE and thermoplastic).

A 2002 study, however, identified that the dominant use of DecaBDE was in HIPS, while it found rare application in nylons and thermoplastic polyesters (such as PET and PBTE). ABS, PC–ABS blends, PPO–PS blends and epoxy resins were not, reportedly, using DecaBDE for flame retardancy. Clearly, this list is not complete and probably not wholly representative of the current situation (Lowell Center for Sustainable Production, 2005).

Use in epoxy resins for printed wiring boards (PWB) used to be another important application for BFRs, including DecaBDE (US EPA, 2014).

# Current use in EEE

It has been mentioned above that DecaBDE can be used in boxes and covers for electrical and electronic components in cars and for defence applications, which are exempted uses under RoHS.

# 3.3.10 Storage and distribution products

The US EPA mentions shipping pallets made of plastic and incorporating FRs, including DecaBDE. The reason was compliance with US national (National Fire Protection Association – NFPA 13) and international (International Fire Code – IFC) fire resistance standards. Plastic pallets (usually made out of polyolefins) without FRs are considered to have higher fire risks compared with wooden pallets, because, even though they ignite at a higher temperature than wood, they produce more heat when burning (US EPA, 2012).

# 3.3.11 Military equipment

It has been reported that DecaBDE is being used in military applications and more specifically army tents (BSEF, 2006). In addition, since EEE pertaining to military purposes is outside the scope of the

RoHS directive, DecaBDE may be used in military vehicles or other equipment. Unfortunately, it has not been possible to either confirm or deny this information because of the proprietary nature of the materials in question.

Military clothing has very demanding specifications. It must provide comfort in environmental extremes (i.e. good insulation), protection against the elements (by being, for example, waterproof) and visual and near-infrared camouflage. Several fabrics have been examined and among them are commercial products under trademark, but also FR-treated fibres such as Lyocell rayon, cotton and blends (Winterhalter, 2005).

It appears that most military clothing manufacturers are either using, or switching to the use of, inherently flame resistant fabrics. In a 2005 review, however, it was mentioned that a number of inherently flame resistant fabrics were not taken into consideration when determining suitable fabrics for soldiers, owing to their high cost or lack of compatibility with the dyes that are normally used for US-army articles (Winterhalter, 2005). An important requirement also seems to be "no-drip" performance under fire, as drips might cause injury to the wearer.

According to information in online trading sites<sup>29</sup>, it seems that most tents (and tarpaulins) available for military purposes or at military standards receive a PVC coating (probably for waterproofing but possibly also for flame retardancy). Consumer camping tents from China have been identified as containing DecaBDE, but it is unknown whether military tents also contain the substance (Danish EPA, 2007).

# **3.3.12Other uses**

Two other uses have been identified and are mentioned in the confidential annex.

The REACH registration dossiers mention inks as a possible downstream use of DecaBDE. Unfortunately, no information was received from the industry through consultation with the ink and coatings association. However, online research has indicated that DecaBDE might be in use in FR formulations that are used in screen printing inks (ISCA, 2014). However, the specific product series also contains halogen-free products, so it is not certain that DecaBDE is used in inks. Another company has issued a statement, according to which they do not use DecaBDE in their inks (Siegwerk, undated).

#### 3.3.13Historical DecaBDE content of articles

The following table summarises information readily available in the literature on the concentration of DecaBDE in a variety of articles.

Available online at: <a href="http://www.alibaba.com/showroom/flame-retardant-tent-tarpaulin.html">http://www.alibaba.com/showroom/flame-retardant-tent-tarpaulin.html</a>

Table 3-21: Concentration of DecaBDE in different article types						
Article type	DecaBDE concentration	Source				
	0.625 g/kg *	SAEFL (2003)				
Cars	1-5 g/car	Danish EPA (2007)				
	<1 to < 10 mg/kg car	Consultation				
Rail vehicles**	85 g/kg	SAEFL (2003)				
Plastics	10-15% w/w	UK HSE (2012)				
FR2 laminates	36 g/m <sup>2</sup>	SAEFL (2003)				
PE insulating foam	20 g/kg	SAEFL (2003)				
PE plastic sheeting	100 g/kg	SAEFL (2003)				
PP plastic sheeting	100 g/kg	SAEFL (2003)				
PVC plastic sheeting	50 g/kg	SAEFL (2003)				
Heat shrinkable products	10% w/w	Danish EPA (2007)				
Tents	2 g/tent	Danish EPA (2007)				
Velour pile fabrics: $70 - 80 \text{ g/m}^2$ Cotton: $30 - 40 \text{ g/m}^2$ Flat wovens (other types): $30 - 80 \text{ g/m}^2$ ( $40 - 50 \text{ g/m}^2$ )	$21 - 32 \text{ g/m}^2$ $9 - 16 \text{ g/m}^2$ $9 - 32 \text{ g/m}^2$	ECB (2002)				
Various textiles	1.55-6.42% ***	Earls (2007)				
Adhesive layer of reflective tapes	1 – 5% (w/w)	Consultation				

<sup>\*</sup> the concentration is quoted with respect to the total weight of plastics in cars exclusive of EE plastic components (switches, transformers, lighting appliances)

<sup>\*\*</sup> plastics account for 5 % of the total weight, of which 75 % are UP resins. The concentration above is applicable to UP resins only

<sup>\*\*\*</sup> extraction from textile fabrics was achieved by ASE and concentration determined by GC-MS. The concentrations given are expressed per unit mass of the entire textile in DecaBDE % (m/m) in textile fabric

# 3.4 Summary of relevant uses of DecaBDE

The following table contains a summary of the confirmed and possible uses of DecaBDE at the EU level, based on the current information.

Table 3-22: Co	nfirmed and possi	ible uses of Dec	aBDE	
Use	Sector	Confirmed	Possible	Comment
Upholstery	Textiles	✓		Potentially on the outside covering of
	&Furniture			mattresses.
				Upholstery for seating in public buildings and
	Transport			vehicles
				Usually applied as backcoating
Foams and	Textiles &		✓	Potential use in synthetic latex foam for
fillings	Furniture			mattresses mentioned
Army tents	Military		$\checkmark$	Not confirmed but possible, assuming
	equipment			inherently FR fibres are not used.
				Use in disaster relief tents possible
Draperies	Building &	✓		In public buildings (e.g. hospitals, prisons,
	Construction			theatres)
				Confirmed from an American study and from
				consultation.
				Backcoating is usually applied on synthetics
				because they cannot retain DecaBDE as an
				additive
Carpets	Transport		✓	Use in aircraft carpets mentioned as possible
				in the Annex XV dossier. Use in consumer
				carpets probably not present
Roofing	Building &	<b>√</b>		Opaque roofs (from Unsaturated PES) are
	Construction			mentioned by EFRA.
				Polyolefin-based roof.
				Cross-linked elastomeric compositions based
1 1 1	D :1 1: 0		<b>√</b>	on plasticised PVC / nitrile rubber or PE
Insulation	Building &		•	Not explicitly mentioned, but DecaBDE is
	Construction			used in PVC/nitrile blends (see roofing).
				Such blends can be used for heating pipes or
				A/C systems
				PU-Europe denies the use of DecaBDE in PU- based thermal insulation
Cables wires	Duilding 9	<b>✓</b>		
Cables, wires and piping	Building & Construction	,		Not in EEE, unless exempted. Piping might use DecaBDE.
and piping	Construction			Fibling might use Decabble.
	Transport			A company using DecaBDE for cables was
	Transport			reported
Sealants &	Building &	<b>√</b>		Adhesive tapes, as Norway identified.
adhesives	construction			Adhesive tapes, as not way identified.  Adhesives imported until 2010 also
2011251425				contained DecaBDE
	Transport			Also included as identified use in the
				registration dossier.
				Industry denied this use
Coatings	Building &	<b>√</b>		In textiles as backcoating.
	construction			In buildings possibly in protective coatings.
	Textiles &			
	Furniture			

Table 3-22: Confirmed and possible uses of DecaBDE					
Use	Sector	Confirmed	Possible	Comment	
Automotive	Transport	<b>√</b>		Wire and cables, small components (e.g. switches, connectors), other thermoplastics, textiles and upholstery.	
Aircraft	Transport	<b>√</b>		Adhesives & tapes, ducting, moulding parts, composites, fabrics, films, insulation, interiors and sealants.	
Trains	Transport		<b>√</b>	In seat fabrics, intercar barriers and hoses, some electrical components	
Pallets	Storage & Distribution		<b>√</b>	Mentioned as possible in (US EPA, 2012), but it was not possible to confirm the application at EU level.	
Inks and paints			<b>√</b>	Consultation did not provide any conclusive data. Research has shown some possible use, but it is not confirmed.	

Confirmed: Indicates that the use has been confirmed during consultation with industry partners

Possible: Indicates that the use has been found in literature but subsequent research and consultation could
not verify its relevance to the EU market

# 3.5 Waste

# 3.5.1 Waste categorisation

Based on the current version of the European List of Waste (ELW)<sup>30</sup> and the information that has been collected so far on the potential end-uses of DecaBDE, we have collected a list of potential waste codes in **Table 3-23**. Interestingly, waste furniture does not have a separate entry. It is assumed that furniture is covered by the component materials, i.e. textiles, wood, plastic, metal, etc.

ELW code	Description
16 01 06	End-of-life vehicles not containing liquids or other hazardous components
16 01 19	Plastic from end-of-life vehicles
16 01 22	Components of end-of-life vehicles not otherwise specified
17 02 03	Plastic from construction and demolition waste
17 02 04*	Plastic from construction and demolition waste containing or being contaminated with
	dangerous substances
17 04 10*	Cables containing oil, coal tar and other dangerous substances
17 04 11	Cables other than those mentioned in 17 04 10
17 06 03*	Insulation materials (not containing asbestos) consisting of or containing dangerous substances
17 06 04	Insulation materials other than those mentioned in 17 06 01 and 17 06 03
20 01 11	Separately collected textiles from municipal waste
20 01 27*	Separately collected paint, inks, adhesives and resins from municipal waste containing dangerous
	substances
20 01 28	Separately collected paint, inks, adhesives and resins from municipal waste
20 01 39	Separately collected plastics
Note: We	have not included general categories (i.e. those ending with 99) because they could cover a very

Note: We have not included general categories (i.e. those ending with 99) because they could cover a very wide range of waste. WEEE also was not included since it falls outside the scope of the possible restriction. Entries marked with an asterisk (\*) are considered hazardous waste

Commission Decision of 3 May 2000, replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste, and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.

# 3.5.2 Waste management

DecaBDE is expected to be present in plastics and textiles in several waste streams. These streams may comprise specific articles, such as End of Life Vehicles (ELV) and WEEE, or mixed waste, such as household waste.

Member States are currently implementing several legislative measures to reinforce waste management (for plastics, as well as for other wastes), the hierarchy of which is analysed below:

- 1. Prevention: measures taken before a substance, material or product has become waste in order to reduce waste quantities
- Preparing for reuse: any recovery operation through which products or components that do not constitute a waste are used again for the same purpose for which they were initially created
- 3. Recycling: any recovery operation through which waste materials are re-processed into products, materials or substances for their original or other purposes
- 4. Other recovery, energy recovery: any operation, the principal result of which is waste that serves a useful purpose

According to the European Commission Green Paper on plastic waste, of the total 24.9 million t/y of plastic waste, 16 million t/y are covered by the existing legislation and could potentially be recycled. This covers WEEE, construction and demolition waste, end-of-life vehicles, packaging, battery waste and municipal solid waste. The Green Paper acknowledges that plastic in furniture and in equipment other than EEE is not currently covered by the waste legislation. The fate of such waste is largely unknown, but it is expected that the largest portion is incinerated or landfilled.

In Norway, waste containing > 0.25% DecaBDE is considered hazardous and must be handled by facilities accredited for handling hazardous waste.

## 3.5.3 Waste plastics

In 2011, 25.1 million tonnes of post-consumer plastic waste was collected. This represents an increase of 2.4% in comparison with 2010. In the same period, the recovery rate rose by almost 4.8%, whereas mechanical recycling increased by 5.7% and energy recovery by 4.2%. Meanwhile, there was a 1% decrease in disposal quantities.

The total share of different applications remains at approximately the same level as in 2010, with packaging still making the biggest contribution, as can be seen in **Figure 3-4**.

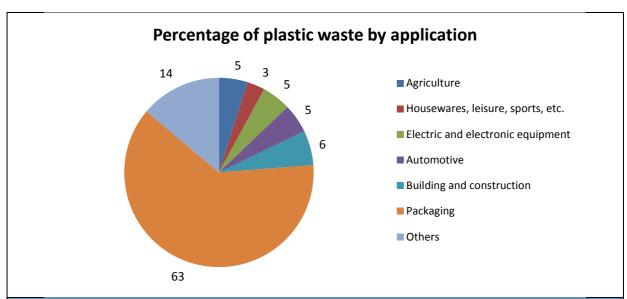


Figure 3-4: Generation of post-consumer plastic waste by application Source: Plastic Recyclers Europe (2012)

The following **Table 3-24** and **Figure 3-5** contain information about the different rates of the various waste treatment methods in the EU for plastic waste, for different applications.

Table 3-24: Data on disposal	collection for recycling and recovery rates on ne	rcentage (%) (Vear 2011)

Application	Disposal	Mechanical recycling	Energy recovery	Feedstock recycling		
Agriculture	48	25	27	-		
Electric and						
electronic	46	14	40	-		
equipment						
Automotive	64	12	22	2		
Building and	43	21	26			
construction	43	21	36	_		
Packaging	34	33	32	1		
Source: Plastic Recyclers Europe (2012)						

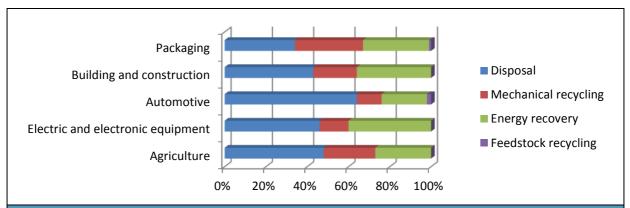


Figure 3-5: Breakdown of treatment of plastic waste - disposal, collection for recycling and recovery rates (Year 2011)

**Source: Plastic Recyclers Europe (2012)** 

The following **Table 3-25** presents the recycling rates of plastic in the EU-27 member states (plus Norway and Switzerland) in 2010, according to a German study. Germany and Sweden have stated, however, that waste containing PBDEs is not recycled in their territory, but it is mostly incinerated in authorised facilities (Stockholm Convention, 2012). It is expected that other countries will be following the same practices.

Table 3-25: Recycling rate of plastic waste in Europe (2010)						
Country	Recycling Rate (%)		Country	Recycling Rate (%)		
Sweden*	35.4		United Kingdom	22.6		
Norway	33.1		Slovenia	21.4		
Germany*	31.5		Poland	19.7		
Czech Republic	31.5		Lithuania	19.5		
Estonia	29.6		Romania	19.2		
Belgium	29.1		Portugal	19.2		
Ireland	27.0		Hungary	18.9		
Austria	26.6		Luxemburg	18.0		
Netherlands	26.2		Finland	17.7		
Denmark	24.3		France	17.5		
Italy	23.7		Greece	15.9		
Switzerland*	23.7		Bulgaria	13.3		
Slovakia	23.5		Cyprus	11.1		
Latvia	23.3		Malta	9.9		
Spain	22.7					
* Germany and Sweden do not	recycle WEFF containing	g Do	ecaBDF			

<sup>\*:</sup> Germany and Sweden do not recycle WEEE containing DecaBDE.

Source: Lindner (2012)

The Danish MSCA has commented during consultation that the plastic fraction from WEEE in Denmark is recycled, while plastic from household waste is incinerated. Plastic-based construction waste is recycled. More than 99% of the recycled fraction is exported to other EU states, 0.5% is landfilled locally and 0.1% is incinerated locally.

## Energy recovery

**Table 3-26** presents information about the share of plastic waste that was incinerated in 2010.

Table 3-26: Incineration rate of plastic waste in Europe (2010)						
Country	Incineration Rate (%)		Country	Incineration Rate (%)		
Switzerland	76.0		Spain	17.3		
Luxemburg	74.5		Czech Republic	13.5		
Denmark	71.5		Estonia	9.2		
Austria	71.0		Ireland	8.7		
Netherlands	65.9		United Kingdom	8.4		
Belgium	65.7		Poland	7.3		
Germany	65.2		Slovenia	7.1		
Sweden	60.9		Romania	5.3		
Norway	58.3		Bulgaria	3.2		
France	40.3		Greece	2.2		
Finland	27.0		Latvia	1.1		
Italy	26.9		Cyprus	0		
Slovakia	26.3		Lithuania	0		
Hungary	20.3		Malta	0		
Portugal	17.7					
Source: Lindner (2012)						

In Germany, articles containing DecaBDE most likely end up in the high calorific value fraction during pre-treatment (incineration or MBT) and are incinerated. According to the German MSCA response to consultation, car seats may contain DecaBDE in the polyurethane foam, some of which is removed from ELV to facilitate reuse of spare parts. The majority however is processed in shredder facilities together with the "depolluted" waste vehicle. PBDEs from ELV end up in the shredder light fraction (SLF), which may lead to emissions of PBDEs. High calorific value SLF is incinerated or used for energy recovery, and it is expected that any PBDEs within are destroyed. The low calorific value SLF is used for landfill construction or back-filling of mines, which means that PBDEs may still be present. Plastics from waste electrical and electronic equipment are used for energy recovery. Landfilling without pre-treatment is not allowed.

#### Landfilling

**Table 3-27** contains information on the rate of landfilling of plastic waste in the EU Member States in 2010. It can be seen that, with the exception of the Nordic and a few central European countries, landfilling of plastic waste is a very common practice, with a landfill rate of 40% in most European countries.

Table 3-27: Landfill rate of plastic waste in Europe (2010)						
Country	Landfill Rate (%)	Country	Landfill Rate (%)			
Malta	90.1	Finland	55.3			
Cyprus	88.9	Czech Republic	55.0			
Bulgaria	83.5	Slovakia	50.2			
Greece	82.1	Italy	49.3			
Lithuania	80.5	France	42.2			
Latvia	75.6	Norway	8.6			
Romania	75.5	Netherlands <sup>(a)</sup>	7.9			
Poland	73.0	Luxemburg	7.5			
Slovenia	71.5	Belgium	5.2			
United Kingdom	69.0	Denmark	4.2			

Ireland	64.3	Sweden	1	3.7
Portugal	63.1	Austria		3.4
Estonia	61.2	Germar	ny	1.9
Hungary	60.8	Switzer	land	0.3
Spain	60.0			

<sup>(</sup>a): According to more recent information from consultation, no plastic waste is landfilled in Netherlands Source: Lindner (2012)

# 3.5.4 Waste textiles and furniture

The situation regarding the management of textile waste in Europe is uncertain. Textile and furniture waste is not explicitly covered by the current legislation on waste, therefore no consistent EU-wide monitoring takes place and statistics are not widely available. According to consultation, there is currently no mechanism to identify the upholstered items that contain DecaBDE in the UK. Regarding textiles, the main focus appears to be on clothes, which can be easily reused, especially if they are in good condition.

According to the Bureau of International Recycling (BIR), 50% of collected textiles are reused and 50% recycled. The textile recycling process includes sorting, shredding, cleaning of the fibres (carding) and spinning into new fabrics<sup>31</sup>. Unfortunately, it was not possible to find specific quantities for the total collected quantities of waste textiles in Europe.

Denmark has commented that textiles in their territory are mainly reused, while, on the other hand, furniture is incinerated. The Irish CA has commented that furniture waste is landfilled. Sweden has also reported a 20% reuse rate for textiles, with the rest being incinerated.

# 3.5.5 Special waste streams

#### **Construction and Demolition Waste**

Plastic forms only a small part of Construction and Demolition Waste. Sweden has commented that a very small percentage of plastic from construction waste was recycled in 2010, and it mainly came from packaging. The rest was incinerated. In total, plastic waste from the construction sector was estimated to be around 43,000 tonnes, but it was not known how much of this contained DecaBDE.

#### **End of Life Vehicles**

ElVs may contain

ELVs may contain DecaBDE in various components. Norway has identified DecaBDE in seat upholstery in cars from Asia, in levels of 1.5-2.5% w/w. The components are considered hazardous if they contain more than 0.25% DecaBDE. Such components are incinerated after shredding. An extended producer responsibility scheme and a scrap vehicle deposit are in place. Materials from ELVs under these are recycled, along with the majority of materials. The overall recycling rate reaches 90%.

Sweden reported in consultation that plastic from ELVs usually ends up in the Shredder Light Fraction (SLF), which is either landfilled (33%) or incinerated (67%).

Large plastic parts from ELV in Germany are mainly recycled but 10% are reused. The SLF with high calorific value is incinerated or used for energy recovery, while the low calorific value fraction, which has higher mineral content, can be used for landfill construction or the back-filling of mines. Out of

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<sup>31</sup> BIR, available online at: http://www.bir.org/industry/textiles/?locale=en US

roughly 135,000 tonnes of SLF from ELVs in 2010, roughly 37% is incinerated, 54% is recycled and the rest is landfilled (UBA, 2011).

# 3.5.6 Transboundary movements of waste

According to Basel Convention, hazardous waste generated in the EU-27 increased 28% between 1997 and 2009. Over the same period, the exported quantities from EU member-states more than doubled; however, the majority of the exports went to other EU countries or EFTA (Switzerland, Norway, Iceland and Liechtenstein) countries. Imports have nearly tripled, but again the majority of these came from EU countries. Non-EU countries enjoy a larger share of the imports (compared with the exports, specifically 1.3 Mt out of 8.9 Mt, but 75% of this came from EFTA countries. Discrepancies exist in this information, but they can be partly attributed to different classifications of certain wastes among the member states (e.g. an importing member state might consider non-hazardous a waste that the exporting member state shipped as hazardous) (EEA, 2012). Germany is the biggest net importer of hazardous waste in the EU. Based on the analysis of the 2009 data, wastes relevant to DecaBDE do not seem to be among those that were transported.

On the other hand, non-hazardous waste shipments to non-EU countries appear to have significantly increased in the previous decade. Plastic waste quantities exported from the EU have increased by a factor of five during the 1999 – 2011 period (from roughly 1 to roughly 5 Mt), with the majority of it sent to Asia.

The level of detail of the available information is not sufficient to estimate the exact amount of waste containing DecaBDE that is imported or exported and the related emissions. From the available information, however, it can be assumed that the emissions from waste containing DecaBDE are not expected to be impacted by imports of waste from (or exports to) third countries.

It was estimated that roughly 100,000 t of WEEE was exported legally from the EU in 2007. Half of this quantity was in the form of broken down components as opposed to whole appliances. It has also been noted that a large amount of generated WEEE remains unaccounted for, with indications that they are exported under a different label, as "used products", instead of WEEE.

# 3.6 Estimation of quantities of DecaBDE

As can be surmised from the presentation of the available data in the previous sections, data on quantities of DecaBDE that are imported and used in the EU comes from many different sources, which do not agree. In order to present information that can be effectively used for the estimation of the potential emissions, some assumptions must be made:

- The registration dossiers are considered the most reliable of the available sources, therefore, information found within those will be the starting point of the calculation. One of the three major importers has stopped supplying the substance in the EU in 2013
- Eurostat data seem to be lacking; this could be a result of unsent data or a lack of DecaBDE imports and exports from some Member States. Nevertheless, the data that is available can be used to observe trends in the EU market of DecaBDE
- It is expected that demand for DecaBDE from the plastics industry will have declined since 2008, while that from the textiles industry will have remained the same. Since 2012, it is expected that the demand for textiles will have fallen significantly, because, according to consultation, textile finishers in the UK are moving away from DecaBDE after its designation as a SVHC
- Another parameter that should be considered is that importers of chemical substances in the tonnage band of 1 – 100 t/y are not obliged to register DecaBDE with ECHA until 2018. During consultation, questionnaires from such importers were received at total quantities of < 100 t/y.</li>

There is a large number of companies that have submitted a C&L notification for DecaBDE to ECHA. These could be potential importers or users. A significant number of them commented that they are not currently importing or using DecaBDE when approached during consultation. A conservative estimation was made that a further 1,000 t/y can be added to the 2013 quantities, to account for unregistered quantities

• Stakeholders from the textile and furniture industry have commented that there has been a move away from DecaBDE in recent years, especially in the UK. This could mean that the actual quantities for textile use are much smaller than what is assumed for the calculations.

# 3.6.1 Estimation of imported quantities

Comparing the different sets of information collected, it was observed that they do not agree. In order to estimate the quantities of DecaBDE being imported in the EU, it was decided to examine different approaches, based on different starting points. Owing to the large uncertainty in the available information, it was decided to develop two scenarios, one high and one low.

## Approach 1 – Registration data

The information submitted by the registrants to ECHA is considered the most reliable regarding quantities. However, as it is bound by confidentiality issues, specific quantities are not going to be presented in the report. The quantities will be used in the calculations, but the results will be shown as a range and the exact numbers will be presented in the Confidential Annex.

As can be seen from **Table 3-7**, presented in Section 3.2.2, the most complete information for import quantities is for year 2009, but there have been significant fluctuations in the quantities for all registrants. It was decided to select a set of 'middle ground' values for 2010 and use this as the starting year and extrapolate to 2013. One of the major importers stopped importing DecaBDE in the EU in 2013. Before that, they were supplying Europe with DecaBDE. It was assumed that in 2013, the DecaBDE quantities were reduced by the amount supplied by this company owing to the withdrawal of this importer from the market. For the rest of the substances, the estimated quantities for 2010 were calculated by observing what was sold in previous years and assuming no significant changes in the market.

In this approach, the high scenario assumes that the volume of imports of DecaBDE in the EU has remained roughly the same, with the exception of the single non-EU manufacturer who has phased out DecaBDE production. The low scenario assumes a 50% fall in the consumption of DecaBDE, as a result of the RoHS restriction and the more recent move of the textile industry away from DecaBDE. This 50% reduction in the low volume scenario was assumed based on the trend observed by analysing the Eurostat data. The observed trend has a declining pattern in the later years. This is also confirmed by the annual VECAP reports, in which a sharp decline in DecaBDE quantities sold is reported in 2012.

For the exact quantities that were calculated for both scenarios, please refer to the Confidential Annex (Section 12).

# Approach 2 - VECAP data

VECAP's annual reports include information about the quantities of DecaBDE sold by the EFRA members. As shown in **Table 3-7**, the quantities sold in 2012 were between 2,500 and 5,000 t/y. EFRA members include most of the major manufacturers and importers of DecaBDE in the EU, but they do not cover all the quantities consumed in Europe. For example, one of the major

manufacturers, the Japanese company Tosoh, which is marketing DecaBDE in the EU, is not a member.

Considering this, and also that, in previous years, the quantities reported by VECAP members were lower than those in the registration dossiers, it can be assumed that these are underestimates. For that reason, the upper limit of the reported tonnage band (5,000 t/y) was selected as the starting point for the low volume scenario, according to this approach. To this quantity, a further 1,500 t/y were added, to account for quantities sold by other importers who have not yet registered their quantities to ECHA (as these can be <100 t/y, the registration deadline for which is in 2018).

For the high volume scenario, it was assumed that VECAP has underestimated the total quantities of DecaBDE sold, so the real quantities would be nearer to double the reported ones. However, since there is not sufficient evidence to support this assumption, only the low volume scenario of 6,500 t/y will be taken into account.

An alternative way of calculating the imported quantities has been based on the reported emissions from VECAP. In 2012, they reported specific environmental emissions of 60 g/t to soil, 25 g/t to water and 12 g/t to air, to give a total of 97 g/t. VECAP also reported total emissions of <300 kg/y. Taking the higher limit of the reported emissions, the quantities of DecaBDE responsible for the emissions were calculated at 3,093 t/y. Because the emissions were calculated for 84% of the quantities sold, the total quantity of DecaBDE is roughly 3,682 t/y. Taking into account imports from other companies (either registered or unregistered) that do not participate in VECAP, the actual imports in the EU could be 5,000–6,000 t/y.

## Selection of quantities

The results from the calculations in both approaches are presented in **Table 3-28**. A compilation approach, combining the numbers calculated in the other two approaches, is also included in the table and this one will be used for the estimation of the emissions.

Table 3-28: Estimated quantities of DecaBDE sold in the EU						
	Low Volume Scenario	Comments				
Approach 1	See Confidential See Confidential Annex Annex		The quantities have been removed to avoid disclosing registrants' confidential information			
Approach 2 (tonnages)	6,500 t/y	13,000 t/y	The high scenario in this approach is not robustly justified			
Approach 2 (emissions)	5,000 - 6	Calculated from reported emissions of VECAP				
Compilation	<10,000 t/y	10,000 - 15,000 t/y				
Note: The specific quantities for Approach 1 and the compilation can be found in the Confidential Annex						

# 3.6.2 Estimation of quantities per use

As was mentioned in the previous section, the proportion of DecaBDE use corresponding to plastics has decreased from 81.7% in 2002 (ECB, 2002) to roughly two thirds in 2010 (VECAP, 2010) (UK HSE, 2012). The latest VECAP report mentions that, at least among the cooperating companies, the share of textiles in the use of DecaBDE was slightly larger than that for plastics (VECAP, 2013). The reported breakdown was 52% for textiles and 48% for plastics, which is the share that will be used in this report.

In the USA, around 2010, the consumption of DecaBDE could be broken down as follows (excluding importing in articles): automotive and transportation 26%, building and construction 26%, textiles 26%, electrical and electronic equipment (EEE) 13% and others 9% (Danish EPA, 2013). Taking EEE out of scope, the new allocation would be: Automotive and transportation 30%, Building and construction 30%, Textiles 30% and others 10%. This would seem to agree with the situation in Europe at the time. As mentioned in the previous paragraph, however, this is not relevant any more.

# 3.6.3 Estimation of quantities imported in articles

The most recent information about the content of DecaBDE in imported articles comes from an RPA report (RPA, 2003). RPA estimated it at 1,300 t/y in 2003, of which 900 tonnes were in EEE and the rest in polystyrene. No information about content in imported textiles was available. The estimated imports of DecaBDE, from the same study, were 8,300 t/y. In total, 9,600 t/y of DecaBDE were imported in the EU, of which 14% was contained in imported articles.

For 2013, the EEE articles are no longer relevant, owing to the RoHS directive. Taking this into account, and allowing for DecaBDE treated textiles imported in the EU (albeit at a relatively higher price, as was suggested by a stakeholder from the textile industry), it will be assumed that the quantities of DecaBDE in imported articles are roughly 10% of the quantities imported as a substance. This number stemmed from the observation that, in 2003, the quantities of DecaBDE in imported articles (excluding EEE) was around 6% of total estimated imports. In order to take into account unidentified imports from Asian countries, as well as imports of DecaBDE in recycled plastic<sup>32</sup>, the relevant volume was increased to 10%. The same percentage was assumed for textiles as well. The quantities of flame retardant textiles (and more specifically those flame retardant with DecaBDE) that are imported in the EU cannot be estimated with any degree of certainty.

Summarising the information in the previous table, the imported quantities of DecaBDE used in plastics and textiles are below 2,000 t/y. Specific quantities are presented in the Confidential Annex.

For the purposes of the emission estimate, the imported substance quantities will be used for the emissions during industry use and the total substance quantities for the emissions during service life and the waste stage.

# 3.6.4 Estimation of quantities in waste

DecaBDE has been in use for many years, which means that a significant amount is present in articles still in circulation. Every year, a number of these articles become waste and they are replaced by new ones. In order to estimate the quantities of DecaBDE containing articles that become waste, it will be assumed that the new articles are replacing the old ones in a 1 to 1 basis, so the quantities in circulation remain constant. This probably does not reflect the current situation, as the imports of DecaBDE fluctuate and demand for FR products changes.

It should be noted that the quantities calculated below do not take into account the losses of DecaBDE during the service life of the articles.

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The presence of DecaBDE (among other Flame Retardants) was detected during routine control procedures by the Netherlands.

#### **Plastics**

Plastic articles that contain DecaBDE can be used in transport, building or other minor applications. In the absence of more specific information, it will be assumed that plastics containing DecaBDE are consumed uniformly across Europe.

The management of waste from transport, building and EEE is regulated by specific legislation around the EU that calls for their separate collection and treatment. The rate of collection and the methods of treatment vary from country to country. Plastic parts that are separately collected from these waste streams are mainly recycled or incinerated. Most plastics from transport applications (ELVs) are shredded and the SLF, in which the plastics end up, is then sent for recycling or energy recovery. Several MSCAs have responded that plastics collected from such waste are then exported to other countries for treatment and a small fraction is landfilled. In Germany, in 2010, around 60% of SLF was recycled and 40% was incinerated for energy recovery.

It was estimated that, EU-wide, around 40% of plastic waste was being landfilled, while the rest was either recycled or incinerated. The overall recycling rate for plastics in the EU in 2010 was 24.1%, with 35.9% being incinerated (calculated as balance) (Lindner, 2012).

Taking into account that many countries choose to export their plastic waste from certain waste streams for treatment in other countries (predominantly Germany), it can be safely assumed that the incineration rate will be somewhat higher, so a breakdown of 20:40:40 will be assumed for recycling, incineration and landfilling respectively.

#### **Textiles**

DecaBDE in textiles will mainly end up in draperies and upholstered furniture for domestic or contract use and in transport applications. The majority of these uses is expected to take place in the UK, where the fire safety regulations are the strictest, while the rest are probably spread around the rest of Europe. In the 2004 EU RAR, it was commented that around 50% of DecaBDE used in textiles was consumed in the UK (ECB, 2004). It is not known whether the situation has changed since then. Therefore, a breakdown of 50% UK to 50% rest of EU will be used in this report.

No specific collection scheme exists for textiles and furniture in the UK, so no detailed statistics about their treatment are kept. The Textile Recycling Association<sup>33</sup> appears to be mainly concerned with the collection and reuse or recycling of clothes. Therefore, it can be assumed that the vast majority of waste textiles and furniture are treated as mixed waste and are either landfilled or incinerated. According to the statistics for 2012/13 about waste managed by local authorities in England, 21% of household waste was incinerated and 32.6% was landfilled<sup>34</sup>. Therefore, assuming no (or insignificant) recycling of textiles or furniture takes place, waste from textiles and furniture will be allocated roughly 40/60 to incineration and landfill respectively.

In the rest of Europe, incineration of waste is practiced more in central and northern Europe, while eastern and southern Europe landfill more, as can be seen in **Table 3-26** above for plastic waste. Consultation with competent authorities from some of these countries also confirmed that landfilling only plays a minor part. It can thus be assumed that the situation is reversed, with incineration accounting for 60%, landfilling for 30% and recycling for 10%. Reused furniture or textiles are considered to be prolonging the service life of the articles; therefore, they are not

https://www.gov.uk/government/uploads/system/uploads/attachment\_data/file/255610/Statistics\_Notice\_1.pdf

TRA, available online at: http://www.textile-recycling.org.uk/index.html

DEFRA, report available online at:

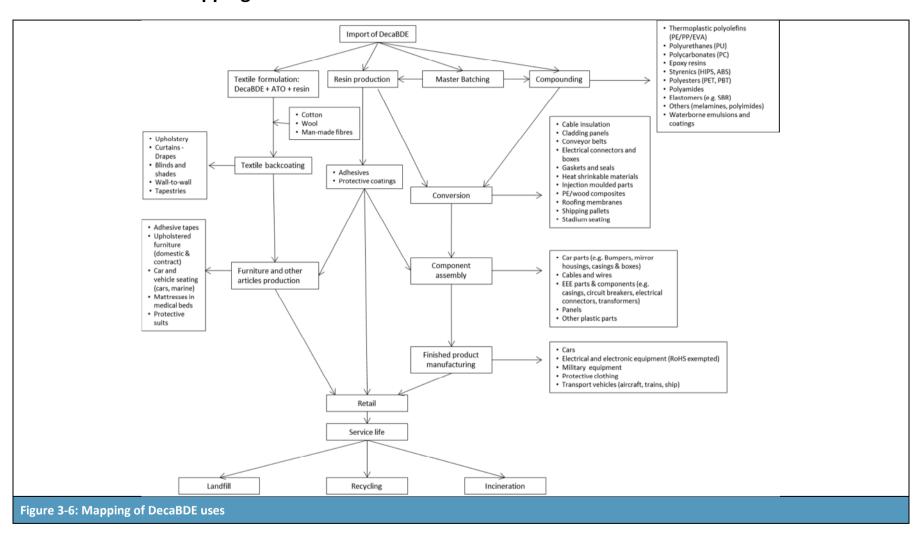
considered in the waste stage. The representative picture for the whole of the EU, after combining the situations in the UK and the rest of the EU, would be 50% incineration, 45% landfilling and 5% recycling.

# Overview

The following Table 3-29 presents an estimation of the breakdown of the treatment of plastic and textile waste containing DecaBDE, based on the methodology described above. The exact quantities are presented in the Confidential Annex.

Table 3-29: Treatment of waste containing DecaBDE							
Quantities Plastics Textiles Total						tal	
(t/y)	High volume	Low volume	High volume	Low volume	High volume	Low volume	
(41)	scenario	scenario	scenario	scenario	scenario	scenario	
Recycling	Soo	< 1,000	Ç o o	< 500	٠,٠	< 1,500	
Incineration	See Confidential	< 2,500	See Confidential	< 2,500	See Confidential	< 5,000	
Landfill	Annex	< 2,500	Annex	< 2,500	Annex	< 5,000	
Total	Aillex	< 5,000	Aillex	< 5,000	Aillex	< 10,000	

# 3.7 Overview – Mapping of uses



The mapping of the uses presents a general view of the flow of DecaBDE along the relevant supply chains and contains uses and applications that are in the process of substituting DecaBDE. It was not possible to collect sufficient information in order to bring more detail into it. Recent information from the VECAP report suggests a 52/48 split of DecaBDE between plastics and textiles (VECAP, 2013), but a more detailed breakdown could not be made. It was identified that DecaBDE is used in thermoplastics (e.g. PP, PE) and thermosets (e.g. polyurethanes) alike, however, no information on the related quantities was provided during consultation.

The number of actors in the different stages of the supply chain was not estimated, due to lack of sufficient feedback from consultation. The number of non-EU manufacturers and major importers is known from ECHA's dissemination portal, but the actual number of downstream users is unknown. In a previous study by RPA (2003), the number of textile finishers was stated, but the situation is bound to have changed since then.

In general, it seems that DecaBDE was still preferred until recently in several applications, both conventional, such as in textile backcoating or plastics and special, such as in protective clothing. The quantities used for special applications were small and did not particularly affect the total tonnage.

It was identified during consultation that the companies are moving away from DecaBDE and are experimenting with common or less common alternatives. The main reason, as has been frequently commented, is the inclusion of DecaBDE in the Annex XIV of REACH, as a candidate substance for Authorisation. Many downstream (or final) users of textiles or plastics request that the products they purchase do not contain SVHCs; therefore, the users of DecaBDE look for other solutions. It is possible that this move away from DecaBDE has resulted in a drop in the consumption as is indicated in the latest VECAP report, but this was not verified from the information that was received.

The MSCA were not able to provide meaningful information about imported quantities and uses of DecaBDE in their country, with some exceptions. Some potential uses were identified through the information provided but subsequent communication with the industry could not verify them.

In particular, the use in the adhesive layer in reflective tapes has been identified by Norway. Consultation with the relevant non-EU industries has shown that these companies have apparently ceased the use of DecaBDE, but not much more could be discerned.

The situation about imports from non-EU countries in manufactured articles is not clear. There is a hint, after a MSCA reported detection of DecaBDE in products made out of different recycled plastics (along with a number of other FRs such as HBCDD). These imports are, however, difficult to control or monitor.

# 4 Emission estimates

# 4.1 Introduction

DecaBDE releases can occur anywhere along the supply chain, including transport and storage. The following lifecycle stages have been identified as particularly relevant:

- 1. **Industrial use**. This stage includes all operations that take place in industrial settings and encompasses mixing DecaBDE with other substances, its application to textiles, the compounding of plastics and finally the manufacturing of components and articles. Such processes are described in detail in various studies (RPA, 2003).
- 2. **Service life**. Estimates of emissions during the service life of an article contain high uncertainty. Critical factors affecting the emissions of a substance are the concentration of the substance in the article, its bond to the substrate, the pattern and conditions of the use of the article and the product's length of life.
- 3. Waste (end-of-life) stage. After a product reaches the end of its service life and is discarded, it is considered waste. This waste will then be recycled, incinerated or landfilled, depending on the waste stream and on each MS's policy. The breakdown of the waste treatment for each of the product categories containing DecaBDE is not easy to determine due to the different waste management strategies in each MS and also due to the different legislation that may apply for each use (e.g. WEEE).

# 4.2 Existing legal requirements and implemented operational conditions and risk management measures

This information is addressed in Section 2.2.

# 4.2.1 Fire safety regulations and standards

# **Buildings and Construction**

Directive 89/106/EEC (Official Journal of the European Communities, 1989) on the approximation of laws, regulations and administrative provisions of the Member States relating to construction products, also known as the Construction Products Directive (CPD), was introduced in order to facilitate free trade of construction products in the EU, through the standardisation of their specifications. Products meeting the requirements described in the "interpretive documents" are awarded the CE-mark. There are six essential requirement categories and fire safety is among them. In order to prove compliance with these requirements, materials for construction must pass a series of fire resistance tests.

The CPD has now been replaced by the Construction Products Regulation 305/2011 (CPR), which brings a simplified harmonised legislative framework. It offers uniform methods of assessment of the (fire) performance of construction products, through harmonised European Standards and European Assessment Documents. It sets up the Euroclass system, which includes a set of different levels of fire safety requirements. However, each member state chooses for itself the four performance levels of the Euroclass system that a construction product needs to comply with.

Member States are also responsible for the assessment of products and award of the CE-mark and the specification of fire safety regulation and levels (Official Journal of the European Union, 2011).

DecaBDE is not mentioned explicitly in these specifications since they are focused on the fire safety performance of the material and not on the way that this is achieved. These specifications are relevant to DecaBDE in case it is used in construction materials such as in roofing applications and in wood-plastic composite panels (as mentioned elsewhere in this report).

#### **Transport**

Fire safety requirements for transport applications are mainly internationally established.

#### **Aircraft**

The International Civil Aviation Organization (ICAO)<sup>35</sup>, as a United Nations Specialized Agency, works, in close collaboration with the air transport community, to improve safety in the aviation industry. It does this through:

- 1. The Global Aviation Safety Plan (GASP) and the Global Air Navigation Plan (GANP), where new strategies are discussed
- 2. Standards, Recommended Practices and Procedures applicable to international civil aviation
- 3. The monitoring of safety trends and indicators. ICAO audits the implementation of its Standard, Recommended Practices and Procedures through its Universal Safety Oversight Audit Programme
- 4. Implementation of targeted safety programmes to address safety and infrastructure deficiencies
- 5. Effective response to disruption of the aviation system created by natural disasters, conflicts or other causes.

ICAO aims to implement practical and achievable measures that improve safety and efficiency in the air transport system. The most widely accepted regulations regarding fire safety in aircraft are the FAA regulations, which, in the EU are known as JAA (Joint Airworthiness Authorities). These include strict requirements to ensure airworthiness, among them specifications for protection from fire. Some large manufacturers have gone one step further and set up additional requirements for parts and materials used in their aircraft. During consultation, it was commented by major aerospace associations that the demanding requirements of these standards and the industry's commitment to airworthiness are the main reasons for which a complete move away from DecaBDE is not possible at this time.

#### Road transport

Road vehicles fire safety specifications are mainly developed in the US. The respective requirements for maritime transport, however, are developed by the International Maritime Organisation (IMO).

In the EU, Directive 95/28/EC sets specifications for the burning behaviour of materials used in mass transport road vehicles (buses, coaches). This is combined with the international FMVSS 302 (ISO

Available at: <a href="http://www.icao.int/safety/Pages/default.aspx">http://www.icao.int/safety/Pages/default.aspx</a>

3795) standard, which sets specific requirements for materials and components in the interior of cars, trucks and buses.

#### **Electrical and Electronic Equipment**

EEE is often used under high temperature conditions associated with high cost applications, meaning good fire safety performance is essential. Currently, there are some general safety requirements, as defined in the Low Voltage Directive and in the Electromagnetic Compatibility Directive, but the more specific ones, and those that are more frequently used, are either national or international fire safety standards.

The most common fire tests are the Underwriters Laboratories (UL) tests, and more specifically, the tests described by the UL-94 standard. This standard is transposed in Europe as harmonised EN standards, IEC/EN 60695-11-10 (HB, V2-V0), IEC/EN 60695-11-20 (5VA, 5VB), glow wire tests and the needle flame test. Most EEE are required to conform to the V0 level of the UL-94 standard. Before the RoHS directive, this was mainly achieved with brominated FRs, especially PBDEs. However, in recent years, developments in fire safety technology have led to successful implementation of alternatives. **Table 4-1** below shows the performance requirements for the V-0 to V-2 levels.

Table 4-1: Performance requirements according to UL94						
Requirement	UL94 V-0	UL94 V-1	UL94 V-2			
After flame time after each flame application	<10 s	<30 s	<30 s			
Total after flame time per set (10 flame applications)	<50 s	<250 s	<250 s			
Complete burn up	No	No	No			
After flame and afterglow time after each flame application	<30 s	<60 s	<60 s			
Ignition of cotton wool	No	No	Yes			

Another test mentioned is the "glow-wire test", described in the European Standard EN 60335"Household and similar electrical appliances – Safety – Part 1". Since, however DecaBDE is restricted from use in such appliances, it is not relevant to this report.

## Furniture and textiles

The legislation regarding furniture fire safety is not harmonised across Europe since different standard regulations can be used. Many countries use EN standards, such as EN 1021 and 597, to evaluate the ignitability of furniture by cigarette or match and EN 12952-1 and -2 for bedding. The UK and Ireland take into account cigarettes and matches but also other higher ignition sources with different levels depending on the hazards. One of the related regulations is the General Safety Product Directive (Official Journal of the European Parliament and of the Council, 2002), the objective of which is to ensure products placed on the market are safe and producers and distributors provide relevant information to consumers warning of any inherent risks involved and precautions to be taken.

A brief overview of the national regulation across Europe shows that France uses for domestic buildings Regulation No 200-164, and for public buildings U 23, Am 18 and GPEMD1-90 (Spain and Portugal follow the same regulations.) The UK and Ireland use for domestic regulation furniture and furnishing nº 1324, and for public buildings BS 7176. The equivalent Italian regulation is DM26/06/1984. Nordic countries, such as Finland, have Regulation No 743/1990 and No 479/96 for domestic buildings and fire safety guidelines for furnishing, published by the Ministry of interior

rescue Department Guideline A:56, 1988 for public buildings. Sweden has no regulation, only recommendations from the consumer agency. Norway has a regulation for the buildings that is Crown Prince Regent's Decree 07/09/1990. The remaining EU member States do not appear to have specific regulations.

## 4.2.2 International initiatives related to emissions

#### The Kiev Protocol on Pollutant Release and Transfer Registers

The Kiev Protocol (UNECE, 2014) became international law binding its Parties on October 2009, and the first meeting of the Parties was held on 2010. Its objective is to enhance public access to information through the establishment of coherent, nationwide pollutant release and transfer registers (PRTRs), so these registries are inventories of pollution from industrial sites and other sources.

Although regulating information on pollution, rather than pollution directly, the Protocol is expected to exert a significant downward pressure on levels of pollution, as probably no company wants to be identified among the biggest polluters.

The Protocol requires each Party to establish a PRTR which:

- Covers releases and transfers of at least 86 pollutants covered by the Protocol, such as greenhouses gases, acid rain pollutants, ozone-depleting substances, heavy metals and certain carcinogens, such as dioxins
- Covers releases and transfers from certain types of major point sources (e.g. thermal power stations, mining and metallurgical industries, chemical plants, waste and wastewater treatment plants, paper and timber industries).

The Protocol sets minimum requirements, which means that Parties are free to include additional pollutants and facilities and are required to work towards convergence between their PRTR systems.

Although the period for signature of the Protocol closed on 31<sup>st</sup> December 2003, the Protocol is open for accession (from 1<sup>st</sup> January 2004) by States and regional economic integration organizations by sovereign States Members of the United Nations to which their Member States have been transferred competence over matters governed by this Protocol.

On 7<sup>th</sup> January 2014, the Protocol has been ratified by 32 countries and the European Union.

With regard to DecaBDE, both the polymers and textiles finishing (pre-treatment) sectors are included in Annex 1 to the Protocol. The reporting threshold values for PBDEs included in Annex II to the Protocol are presented on **Table 4-2**.

Table 4-2: Threshold Values for Reporting of Emissions of PBDEs from Facilities – Annex II to the Kiev Protocol on PRTR (all values in kg/y)							
Threshold for Releases Threshold for Off-site Manufacture,							
Pollutant	To Air To Water To Land Transfers of Pollutants Process or use Threshold						
PBDEs - 1 1 5 10,000							
Source: UNECE (2014)							

# The Stockholm Convention

The Stockholm Convention on Persistent Organic Pollutants was adopted on 22<sup>nd</sup> May 2001 and entered into force on 17th May 2004 (Stockholm Convention, 2008).

The main objective of the Convention is to protect human health and the environment from the threats presented by persistent organic pollutants (POPs). So far, 179 Parties have ratified the Convention. The initial list of substances under the Convention consisted of 12 POPs introduced in Annex A (elimination), Annex B (restriction) and /or Annex C (unintentional emissions). In May 2009, the Convention was amended to introduce nine new POPs. These included FRs such as TetraBDE and PentaBDE (congeners forming commercial PentaBDE) and also HexaBDE and HeptaBDE (congeners forming commercial OctaBDE) in Annex A (elimination) to the Convention. In May 2013, Norway submitted a proposal to list DecaBDE as a POP under the Convention.

#### **OSPAR Convention**

BFRs (including DecaBDE) were identified as chemicals subject to priority action during the Ministerial Meeting of the OSPAR Commission of 1998 (Sintra) and were included in Annex 2 to the OSPAR Strategy with regard to the Hazardous Substances Strategy (OSPAR, 2014).

The EU Member States and, in some cases, the states of the European Economic Area (EEA) have obligations to implement measures under the EU Marine Strategy Framework Directive (2008/56/EC), the EU Water Framework Directive (2000/60/EC), and other relevant EU legislation to reduce nutrient discharges to water and emissions to air from point sources and diffuse sources (e.g. agriculture), including the National Emission Ceilings Directive (2001/81/EC), the Urban Waste Water Treatment Directive (91/271/EEC), the Nitrates Directive (91/676/EEC) and the Integrated Pollution Prevention Control (IPPC) Directive (2008/1/EC) and the Rural Development Regulation (EC) No 1698/2005.

The overall aim of OSPAR Commission for BFRs (and the other hazardous substances chosen for priority action) is to achieve by 2020 a "cessation of discharges, emission and losses [...] with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances" (OSPAR, 2014).

#### **OECD Voluntary Industry Commitment**

In 1991, OECD's Risk Reduction Programme began an investigation of BFRs to explore the possibility of taking further action to reduce risk. In 1994, an OECD monograph was published [OCDE/GD(94)96] which discussed the commercial and environmental life cycle of these substances as well as risk reduction measures implemented in Member countries and these countries' positions on the perceived risk from these substances (OECD, 1995).

Discussions were held in 1995 between Member countries and industry on possible activities that could be taken to further reduce risk. The result of these discussions was a proposed commitment, made by the major global producers of BFRs, to take certain risk management actions on tetrabromobisphenol-A, polybrominated biphenyls (PBBs), and PBDEs.

This commitment was formally presented to OECD's 23<sup>rd</sup> Joint Meeting of the Chemicals Group and Management Committee in June, 1995. The Joint Meeting agreed to oversee such actions and industry agreed to report to OECD every two years regarding their implementation of this initiative. At the 24th Joint Meeting in February 1996, a similar voluntary industry commitment, proposed by the Japanese manufacturers of these BFRs, was presented. The Joint Meeting agreed to incorporate this commitment with the one developed by the U.S. and European BFR manufacturers.

These voluntary measures have been undertaken by members of the US Chemical Manufacture Association (CMA), the Brominated Flame Retardant Industry Panel (BFRIP) and the CEFIC European Brominated Flame Retardant Industry Panel (EBFRIP).

The voluntary measures to be taken under this voluntary commitment relate to:

- Environmental exposure
- Toxicity studies to be undertaken
- Risk management measures.

Within this framework and with particular regard to DecaBDE, the BFRIP and EBFRIP committed to (OECD, 1995):

- Co-operate with polymer producers and end user manufactures (such as original equipment and textile manufacturers) on the safe disposal and recycling of polymers containing BFRs
- Co-ordinate toxicity studies
- Not manufacture or import/export the non-commercial brominated diphenyl oxide congeners as individual FRs, except when they are present as part of the commercial DecaBDE. The noncommercial congeners are Nona-, Hepta-, Hexa-, Tetra-, Tri-, Di- and MonoBDE
- Use BAT without incurring excessive costs, to improve the purity of DecaBDE, 97% or greater
- Minimise environmental exposure of BFRs through the appropriate treatment of effluents and emissions from the manufacturing process
- Continue to issue and regularly update product literature to educate customers on the safe use
  of DecaBDE. This includes the preparation of Material Data Sheets according to national
  standards, describing the product and its uses, and summaries of the toxicology data available
  on the product
- Use the best information available to regularly evaluate the risks of BFRs. Using any new information, BFRIP and EBFRIP member would seek to minimise risks that are identified by such evaluation.

#### **BSEF Product Stewardship Programme**

The Voluntary Emissions Control Action Programme (VECAP) is a voluntary initiative run by BSEF under the Responsible Care Initiative to set high standards for chemicals management in the workplace, both at manufacturing sites and along the value chain.

The aim of the programme is to reduce potential emissions of FRs to the environment through the promotion of manufacturing best practice among those involved along the value chain. This is achieved by increasing an understanding of chemicals management in the value chain, promoting dialogue between industry, regulators and stakeholders and by implementing best practices.

BSEF established the Product Stewardship Programme in 2002 which identified:

- The applications of concern
- The processes used by the downstream users
- The consumption patterns
- The geographical spread of the consumption of DecaBDE in the EU.

For the evaluation of the above parameters, a number of stakeholders were identified so as to cover all known applications and provide a sufficient coverage of consumption across the EU.

The scheme was initiated in 2004 by the UK textile coating industry that began to take action to reduce emissions of DecaBDE. Within three years, the programme had achieved a 97% reduction of DecaBDE emissions into water. Over the years, VECAP has extended its scope to include other FRs, namely HBCD and TBBPA.

VECAP currently operates under the European Flame Retardant Association (EFRA), a sector group of the European Chemical Industry Council (Cefic).

For the DecaBDE Stewardship Programme, nine companies (downstream users) from four countries (Belgium, Germany, Italy and the United Kingdom) agreed to participate including:

- Two textile formulations compounders
- One textile finisher
- Two producers of polymers (rubber foam insulation)
- Four polymers masterbatchers/compounders.

#### EU Ecolabel

The EU Ecolabel criteria indicate that no use of FRs or FR preparations is permitted where substances concerned are assigned one of a number of specified risk phrases and are present at more than 0.1% by weight.

Additionally, Green Public Procurement criteria have been developed for 20 product groups<sup>36</sup>, of which the following are relevant to DecaBDE:

- **Textiles**: DecaBDE (along with PentaBDE, OctaBDE and PBBs) should not be present in the textile. It is mentioned that if the product is certified according to a Type 1 ecolabel (e.g. EUecolabel), it is considered to comply with the criteria
- Furniture: They include the criteria for textiles as described above
- Transport: The criteria on passenger cars or public transport (bases) focus mainly on the
  emissions and fuel consumption of the vehicle. The main concern about materials is the share of
  recycled materials in the vehicle.

Other "green labels" such as the Japanese ECO Mark, Nordic Swan, German Blue Angel and Swedish TCO, had restricted halogenated FRs in IT products since early 1990's.

# 4.3 Information on environmental concentration and emissions

# 4.3.1 Introduction

Circultural 4000 th

Since the early 1980s, there have been several compilations and monitoring programs related to FRs, mainly associated with the aforementioned regulations and international initiatives. In this section, data are presented in two parts. The first part is "historical data", which refers to data from standardised sources of information or scientific data. The second part is "monitoring programs" that are continuing today.

Information included in the following section has been collected mainly from publicly available sources. These sources comprise internationally recognised research centres and projects, national organisations (e.g. US EPA, Danish EPA) and peer-reviewed publications related to the measurement, calculation and management of anthropogenic environmental pollutants, focusing on PBDEs or DecaBDE where possible.

# Congener specific estimations

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Depending on the location and number of Br atoms, there are 209 possible PBDE compounds, termed congeners. Each is assigned a specific brominated diphenyl ether (BDE) number (note: in

<sup>&</sup>lt;sup>36</sup> Available at: http://ec.europa.eu/environment/gpp/eu\_gpp\_criteria\_en.htm

this document, the abbreviation PBDE was used to denote the class of BFRs, while BDE was used in the context of PBDE congeners). For example, there are 42 TetraBDE congeners (PBDEs with four bromine atoms), but only a few of them, specifically BDE47 and occasionally BDE66, are found in the product formulations and in environmental or exposure media. Knowing that c-DecaBDE is a mixture with minor amounts of lower brominated diphenyl ether congeners (NonaBDE and OctaBDE), estimated emissions referring to the final product should take into account only DecaBDE (BDE-209).

## 4.3.2 Environmental fate

# Physico-chemical properties and environmental fate

The physical and chemical properties control the behaviour of DecaBDE in relation to air, soil, water and sediments, and to exchange among environmental compartments. They also indicate the physical form and phase of the chemical present in air and water. The physical and chemical properties influence the extent to which biotic and abiotic processes may transform or degrade DecaBDE in the environment, **Table 4-3**.

Table 4-3: Physico-chemical	properties of DecaBDE
Property	Value
Chemical formula	$C_{12}Br_{10}O$
Molecular weight	959.2
Melting point	300 – 310 °C
Boiling point	Decomposes at > 320 °C
Particle size	Typically < 5μm
Vapour pressure (at 21°C)	4.63 x 10 <sup>-6</sup> Pa
LogKow	6.27 (measured-generator column method); 6.625 in Registration dossier
Relative density	3.0
Flammability	Not applicable
Autoflammability	Not applicable
Explosive properties	None
Oxidising properties	None
Water solubility (at 25°C)	< 0.1μg/L (column elution method, GLP study)
Bromine content	About 83%
Henry's Law Constant (H)	1.20 x 10 <sup>-8</sup> atm-m <sup>3</sup> /mol (at 25 °C)
Log Koa	13.21
Source: ECB (2002), US EPA (2	2010), REACH Registration Dossier (ECHA Internet site)

# Significant data on environmental fate

PBDEs are ubiquitous environmental contaminants. Widespread dispersion of BDE congeners in the environment is governed by their respective physical and chemical properties. The atmosphere is the primary transport media, and soils and sediments are environmental sinks (US EPA, 2010).

Transport can occur over relatively long distances, perhaps over 1,000 km. Evidence for this comes from the presence of PBDEs in the polar environments, and in the tissues of deep ocean-dwelling whales and other marine mammals that spend a significant portion of their lives far from anthropogenic sources (US EPA, 2010).

PBDEs are lipophilic and hydrophobic compounds and readily bioaccumulate into terrestrial and aquatic food webs. This is shown in the detection of PBDEs in a wide variety of birds, fish, insects and aquatic and terrestrial mammals (US EPA, 2010), for example:

- 1. DecaBDE has been found in fish tissue, and in Peregrine falcon (*Falco peregrinus*) eggs, since their diet consists of medium sized birds such as doves, waterfowl, songbirds, waders and pigeons (US EPA, 2010).
- 2. Terrestrial mammals also tend to accumulate brominated PBDEs in relation with their diet. For example, the red fox (*Vulpes vulpes*) is a top terrestrial predator that mainly consumes voles, rabbits, squirrels and mice as prey (US EPA, 2010).Both bears eating maritime saltwater fish and meat-eating bears have displayed notable accumulation of also amount of DecaBDE as well as meat-eating bears (US EPA, 2010)

Once released into the air, the partition between vapour and particle phases in the atmosphere is in accordance with their vapour pressures. DecaBDE, owing to its high degree of bromination is primarily absorbed onto atmospheric particles. Photolysis (degradation by sunlight) in air is an important atmospheric removal mechanism but for DecaBDE the most important removal pathway is atmospheric wet and dry surface deposition, because DecaBDE primarily exists bound to particles in air (US EPA, 2010).

DecaBDE can be degraded by ultraviolet light (i.e. can undergo photolysis) to form lower-brominated PBDEs, and this may be an important degradation pathway in the environment (US EPA, 2010).

Overall, decay proceeded slowest with DecaBDE on soil exposed to UV light, showing a half-life of 150-200 hours. The researchers concluded that the photodegradation of DecaBDE, at least initially, follows a stepwise debromination process. They noted that as DecaBDE disappeared, lower brominated DEs (Nona- to HexaBDEs) were formed, but that after the maximum occurrence of HexaBDEs, only minor amounts of lesser brominated diphenyl ethers (Tetra- and PentaBDEs) were formed, resulting in a discontinued mass balance. This suggested that other unknown compounds were also being formed, but that these were lost during the sample clean-up. In addition to the identified PBDEs, Tetra- and PentaBDEs were also detected as transformation products of DecaBDE adsorbed to sand, sediment and soil.

Jafvert and Hua (2001) conducted photodegradation studies of DecaBDE adsorbed to solid matrices (sand and quartz surfaces) with water and humic acid and irradiated with natural or artificial sunlight. Their studies showed that some photodegradation of DecaBDE occurred under natural or artificial sunlight. Over time periods up to 240 h loss of DecaBDE varied up to 71%. Although they did not conclude that lower brominated diphenyl ethers were produced, the European Communities (2002) noted that there were indications that lower brominated DEs (particularly HexaBDE) were formed, based on their review of the DecaBDE humic acid coated sand exposure.

Palm et al. (2003) irradiated DecaBDE adsorbed onto silicon dioxide in aqueous suspension with artificial sunlight. They also found that approximately 50% of the initial DecaBDE concentration was lost after about 360 min. Details regarding the degradation products were not provided; however, Palm et al. (2004) notes that PBDFs were confirmed as short-lived trace intermediates.

Keum & Li (2005) investigated the debromination of PBDEs (including DecaBDE) in contact with several reducing agents; zerovalent iron, iron sulphide and sodium sulphide. In the experiments with zerovalent iron, DecaBDE was rapidly transformed to lower brominated diphenyl ethers. Approximately 90% of the parent was converted to Mono- to HexaBDEs after 40 d. During the initial reaction period (up to 5 d), DecaBDE was predominantly transformed into Hexa- and HeptaBDEs, but Tetra- and PentaBDEs were predominant after 14 d. The results demonstrated that DecaBDE undergoes reductive debromination in the presence of zerovalent iron. The experiments with sodium sulphide also showed transformation of DecaBDE to lower brominated DEs, but the rate was slower than that determined in the presence of zerovalent iron. A similar profile of transformation products was found to that determined in the experiment with zerovalent iron. Experiments were

also conducted with BDEs 28, 47, 66 and 100 in the presence of zerovalent iron. These also showed that debromination had occurred but that the rate of reaction decreased with a decreasing number of bromines. Although the conditions of this study are not directly related to those common in the natural environment, it is possible that similar reactions maybe taking place in the environment.

Several studies have shown that DecaBDE can also be degraded by biotic debromination. For example, *Sulfurospirillium multivorans* bacterium yielding OctaBDE and HeptaBDE after 2 months, other example is by using anaerobic mesophilic microorganisms indigenous to raw sewage sludge, DecaBDE was degraded by 30% and methane was produced as a result of microbial respiration (US EPA, 2010).

In addition, *in vivo* metabolic debromination can occur in fish, birds and mammals. Rainbow trout, lake trout and carp have shown accumulation of lower congeners not presented previously in their feed. An example with *Sprague-Dawley* rats also shows debromination of DecaBDE to lower congeners. Various examples for *in vivo* metabolic debromination were found for chickens, starlings, and even house cats.

Human exposure has increased rapidly since these chemicals came into use in the 1960s and 1970s. Environmental time-trends can be observed from lake sediment core studies and archived animal tissue samples.

# 4.3.3 Industrial emissions reporting

#### E-PRTR

The European Pollutant Release and Transfer Register (E-PRTR) is the EU registry for emissions of hazardous chemicals in air, water and soil. Emission data are reported annually by individual facilities across 65 different economic activities. These activities are grouped in nine industrial sectors:

- Energy
- Production and processing of metals
- Mineral industry
- Chemical industry
- Waste and wastewater management
- Paper and wood production and processing
- Intensive livestock production and aquaculture
- Animal and vegetable products from the food and beverage sector
- Other activities, including installations for the surface treatment of substances, objects or products using organic solvents, in particular for dressing, printing, coating, degreasing, waterproofing, sizing, painting, cleaning or impregnating.

DecaBDE releases are reported as total PBDEs, which includes PentaBDE and OctaBDE emissions, provided that the facility emits at least 1 kg/year of PBDEs to water or soil. Reporting of emissions to air is not common, probably due, as previously explained, to the low volatility of the substance.

The number of facilities that have reported PBDE emissions from 2007 to 2011, the number of countries they are located in and the total emissions are shown on **Table 4-4**. All the facilities that have reported PDBE emissions have done so for emissions to water, apart from one waste-water treatment plant (WWTP) in Norway, which has declared a very low emission (4.45 g/y) to air in 2011.

Table 4-4: Total reported	emissions of PBDEs to wate	r in E-PRTR	
Year	No of Facilities	No of Countries	Total emissions (kg/y)
2007	6	3	111
2008	7	3	151
2009	13	5	29.0
2010	13	3	39.7
2011	14	3	45.3
Source: E-PRTR (2014), acc	essed in February 2014		

**Table 4-5** contains the reported emissions each year from 2007 to 2011 by economic activity and **Table 4-6** contains the same information broken down by the country in which the facility is located.

Table 4-5: Reported emissions of I	PBDEs t	o water	in E-PR	TR by e	conomic	activity	/ (in kg/	'y)		
	2007		2008		2009		2010		2011	
Activity	No.	kg/y	No.	kg/y	No.	kg/y	No.	kg/y	No.	kg/y
Thermal power stations and other combustion installations	-	-	1	5.11	1	3.56	2	8.63	1	3.87
Ferrous metal foundries	-	-	-	-	-	-	-	-	1	18.0
Urban waste-water treatment plants	4	107	3	106	10	20.2	9	19.5	13*	23.4
Plants pre-treating or dyeing fibres or textiles	2	3.59	3	39.9	2	5.29	2	11.6	1	-
Total	6	111	7	151	13	29.0	13	39.7	15	45.3

<sup>\*:</sup> These numbers include one facility in Norway that reported emissions to air, but the quantities reported are too small (4.45 g/year) to be taken into account in the total quantities.

Source: E-PRTR (2014)

County	20	2007		2008		2009		2010		2011	
Country	No.	kg/y									
Belgium	1	2.49	2	38.8	2	5.29	2	11.6	-	-	
Czech Republic	-	-	-	-	1	7.10	-	-	-	-	
France	-	-	2	6.85	1	2.09	-	-	-	-	
Ireland	4	107	-	-	-	-	-	-	-	-	
Italy	1	1.10	3	106	1	3.56	1	7.28	1	3.87	
Serbia	-	-	-	-	-	-	-	-	1	18.0	
United Kingdom	-	-	-	-	8	11.0	10	20.8	12	23.4	
United Kingdom Source: E-PRTR (2014)	-	-	-	-	8	11.0	10	20.8	12		

Robust conclusions are difficult to form because of the small number of reporting facilities. However, some useful observations can be made:

- A significant reduction in the reported emissions is observed from 2009 onwards in waste-water treatment plants. The plants that reporting higher quantities were located in Ireland (2007 data) and in Italy and France (2008 data). After 2008, the majority of reporting wastewater treatment plants were located in the UK
- Emissions in Belgium can be safely correlated with textile treatment facilities, probably back-coating. In 2011, no Belgian textile industries have reported emissions of PBDEs that could indicate a switch to non-PBDE FRs, a decline in processing volume or better emission controls.

The Belgian CA has not completed a questionnaire, so it was not possible to discern the actual cause

- The reported quantities from the textile finishing facilities should be compared to the information that VECAP has published
- In 2011, a Serbian facility (CIMOS Livnica Kikinda<sup>37</sup>) that produces automotive parts reported emissions of PBDEs in water.

#### **VECAP**

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

According to the VECAP 2012 progress report, the total emission to land from all sources decreased from 575 g/t in 2008 to 60 g/t for DecaBDE in 2012 (VECAP, 2013).

**Table 4-7** presents a summary of the estimated emissions of VECAP from industrial activities involving BFRs, as published in VECAP's reports. It must be noted, however, that for DecaBDE the coverage of the used quantities is not complete. According to the 2013 annual report from VECAP, the calculated emissions accounted for roughly 84%<sup>38</sup> of the DecaBDE consumption in Europe in 2012. This would imply that there are users of DecaBDE that probably do not follow VECAP's code of practice, so they may have higher emissions of DecaBDE from their activities, although this is considered unlikely by VECAP. It has also commented in the report that the activities of 'second-line users' (e.g. back-coaters or those that buy DecaBDE through distributors) cannot be adequately monitored and controlled, meaning that the released quantities could be higher. The majority of these emissions occur on soil, which can be attributable to releases from the used DecaBDE packaging, which still contains small quantities of the substance (VECAP, 2013).

Table 4-7: Tot	tal emissions by me	mbers of the VECA	P Programme in the	EU (in t/y)	
Substance	2008	2009	2010	2011	2012
DecaBDE	3.4	1.2	1.4	<0.5	<0.3
HBCD	<2.5	<0.5	<0.65	<0.5	<0.25
TBBPA	<1	<0.15	<0.5	<0.005	<0.003
Source: VECA	P (2013)		•		

The England and Wales Environment Agency mentioned reported sewer emissions from a textile processing site in the UK from 2002 to 2007. These are shown in **Table 4-8**. These are high in comparison with quantities reported in E-PRTR. A decreasing trend is observed, but it is not known whether it has continued in later years (Environment Agency, 2009).

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Available at: http://www.cimos.eu/index.php?page=stebri&item=116

This percentage corresponds to the share of the companies who responded to the annual VECAP survey, by sending a completed questionnaire. The remaining 16% could not be surveyed, due to lack of participation of some companies mainly supplied through distribution channels.

Table 4-8: Emissions of bromine (or Do	ecaBDE) from a textile processing facility in the UK
Year	Reported emissions (kg/y)
2002	1,400
2003	2,440
2004	270
2005	86
2006	990
2007	554
Source: Environment Agency (2000)	

Source: Environment Agency (2009)

Note: The emissions are reported as bromine, not specifying if it refers to bromine or DecaBDE

The Risk Assessment Report from the Environment Agency (EA) also refers to a study of the emissions to wastewater from a Japanese textile processing factory. Each batch at the plant used 300 kg of textiles and 130 kg of DecaBDE and the process used 21,000 litres of liquid per batch. The concentration of DecaBDE in wastewater after treatment was reported as 6.2 mg/L. This would imply an emission factor of 0.1%, but the study does not give more details, according to the EA, and those numbers cannot be easily compared with other emission factors.

## 4.3.4 Emission estimations

#### Source Control of Priority Substances in Europe (SOCOPSE)

The SOCOPSE Project has estimated the emissions of DecaBDE to air, soil and water and has compared them with those calculated in the EU RAR. In many cases, the emissions from SOCOPSE are lower than those from the EU RAR (and its updates) and it is commented that the numbers from the latter are generally produced following a worst-case approach. However, as can be seen in Table 4-9, there are compartments for which SOCOPSE has calculated higher emissions than the EU RAR (SOCOPSE, 2009).

Environmental	Funitarious Courses	Emissions (kg/y)			
Compartment	Emission Source	SOCOPSE	EU RAR		
	Industrial processes (plastics)	<1	81		
\:	Industrial processes (textiles)	<1	4		
Air	Service life	138 – 465	1		
	Disposal	Insignificant	50		
Soil	Atmospheric deposition	?	0		
	Sludge application	900 – 1,500	0		
	Service life	0	107		
	Disposal	Significant	37,500		
	Atmospheric deposition	,	-		
	Surface runoff	Significant	-		
	Industrial processes (plastics)	<3,400	7		
Water	Industrial processes (textiles)	<1,300	166		
	Service life	0	60		
	Disposal	Significant	12,440		
	Waste treatment plants	50 - 320	0		

Note: Question marks (?) were present in the table of the source

No conclusion can be reached based on the information presented due to severe discrepancies between the numbers in the two studies. Additionally, in some cases, SOCOPSE describes the emissions qualitatively as significant or insignificant, without quantifying them. No further information is given in the report.

#### Control of hazardous substances in the Baltic Sea region (COHIBA)

Based on a substance flow analysis approach, sources of releases of PBDEs (all PBDEs taken together) in the Baltic Region have been estimated as part of the COHIBA regional project (COHIBA, 2012). The results presented in the study have shown that the highest emissions of DecaBDE in the Baltic Sea originate from Finland, Sweden and Poland. The authors do not mention concentrations of individual congeners, nor do they attempt to estimate them, but they comment that emissions of PentaBDE congeners are of the same order of magnitude as that of DecaBDE.

The main source of environmental contamination regarding PBDEs in the Baltic Sea region, according to the COHIBA project, seems to be the application of sewage sludge already containing PBDEs on soil, making sewage sludge the basic outflow route of PBDEs to the marine environment. The second most important factor considered are the releases of PBDEs during the service life of the products containing FRs, especially in the indoor environment. These emissions were calculated at 300-900 kg/y and they are estimated to be of a similar order of magnitude as the total emissions to the outdoor environment.

The modelling study performed as part of the COHIBA project indicates low potential for transport of PBDEs from inland soil to the Baltic, but it is possible that certain extreme conditions (e.g. flooding, erosion, etc.) not considered in the model scenarios could lead releases of this type (COHIBA, 2012).

According to HELCOM (2010), PBDEs mainly spread to the Baltic Sea environment by diffuse distribution via the atmosphere and rivers. Higher-brominated PBDEs have low water solubility and are mainly distributed in sediments. They are not easily transported from the sediment and suspended particulate material to marine organisms.

**Figure 4-1** presents schematically the flow of PBDEs during their life cycle, as described in the COHIBA report. It indicates the emissions from each life cycle stage to the various environmental compartments.

#### Other studies and projects

The Danish environmental monitoring programme, NOVANA, includes regular monitoring of the PBDEs only. A screening survey of 16 BFRs in the Nordic environment indicated that the concentrations of the "new" BFRs, with a few exceptions, were of the same order of magnitude or lower compared with the sum of BDE congeners included as priority substances under the Water Framework Directive. Available data indicate that BDE levels in the environment in the Nordic countries have approached the levels of DecaBDE, and that this contamination primarily occurs via the atmosphere.

Another study, by Sakai et al. (2006) performed an estimation of the emitted quantities of DecaBDE in Japan, based on their 2002 material flows and a series of field studies. The study estimated emission factors for various lifecycle stages, including plastics processing, textile processing, home appliance recycling and waste incineration. The estimated emissions of DecaBDE were  $170 - 1,800 \, \text{kg/y}$ . In general, the estimated emission factors in this study were smaller than their equivalents in other studies. The study did not estimate the environmental fate of the released DecaBDE.

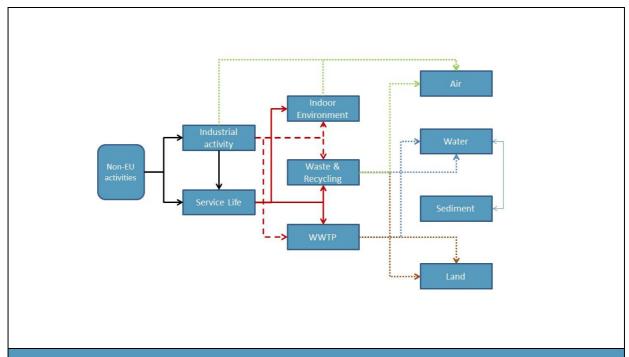


Figure 4-1: Simplified substance flow analysis (SFA) for PBDEs adapted from COHIBA (2012)

DecaBDE, as all PBDEs, has negligible solubility in water and low vapour pressure, but its Koc is relatively high, which means that DecaBDE is usually expected to be found adsorbed in soil, sediments and WWTP sludge. A calculation by Tissier et al. in 2005 (as referenced by Danish EPA, 2013) resulted in the vast majority of PBDEs in the environment being found in the soil (97.7%), while the rest is expected to be in sediments (2.2%) and a small quantity in the air compartment (0.1%). This view is confirmed more recently by the Annex XV dossier which refers to (not yet evaluated) QSAR-derived information from the registration dossier of DecaBDE (UK HSE, 2012).

The estimated emissions to air in the Baltic Region (4-100 kg) are significantly lower than the estimated atmospheric deposition in the area (approximately 100-700 kg/y for BDEs-47, -99, -100, -209). This could be an indication that long-range transport may be an important factor, but this difference could also be due to an underestimation of the transport rate of emissions from the indoor to the outdoor environment (as suggested by the authors of the Danish EPA report).

Estimates of Long Range Transport (LRT) of PBDEs show that the lower brominated BDEs had comparable LRT potential as their PCBs congeners (HexaCBs). Characteristic travel distances (CTDs) for TetraBDE were 1,113 and 2,483 km, and for DecaBDE 480 and 735 km. The models indicated that the higher brominated BDEs would not be subject to significant LRT and the process would be controlled by the transport of particulates, due to its low volatility (de Wit, et al., 2010).

#### 4.3.5 Emissions during service life

PBDE congener environmental distribution patterns are sometimes reported to resemble those of the PentaBDE and OctaBDE commercial products, leading some researchers, e.g. Song et al. (2004), to propose that these products are the primary sources of PBDEs into the environment.

A study performed by Rayne and Ikonomou (2002) consisted of semi-permeable membrane devices (SPMD) placed in the Fraser River in order to analyse the resultant SPMD samples for 36 PBDEs

(Mono- to Hexa- congeners). They found congener patterns differed significantly from those of the commercial PentaBDE and OctaBDE mixtures. They then applied modelling and calculation procedures and found that the reconstructed congener patterns more closely approximated those of the technical mixtures. These analyses lead the researchers to suggest that the PBDEs present in the region arose primarily from PentaBDE and OctaBDE mixtures.

# Releases from flame-retardant products

After manufacture, flame-retardant articles release the FR additive during their entire lifetime, since the additive is not chemically bound to the substrate. This means releases will occur during use and as waste after disposal. Thus, although other BDE congeners, like PentaBDE and OctaBDE have been banned or phased out, they may be present in products still in circulation and this will lead to their continued release from products and then from disposed waste for several decades to come (de Wit, et al., 2010).

At this stage, emissions can differ between plastic and textile products, as DecaBDE is incorporated in the substrate in different ways and the use pattern is different.

A study from Kajiwara et al. (2010) detected emissions of DecaBDE and other PBDE congeners from flame retardant polyester curtains to the indoor environment. It was also noted that, after exposure to sunlight, DecaBDE would decompose and produce less-brominated congeners and also polybrominated dibenzofurans (PBDFs). PBDEs with less bromine atoms were detected in the air even though they were below detection limits on the curtains. No quantitative information is available from this study.

The study by Sakai et al. (2006) estimated a release factor to indoor dust from electronic appliances (TV sets). The calculated emission during the service life of products containing DecaBDE was 54 kg/y, significantly lower than equivalent values from other studies. The corresponding emission factor was at least an order of magnitude lower than the ones in the other studies.

A study by Kajiwara et al. (2013) analysed textile samples intended for use in curtain manufacture and treated with either technical HBCD or technical DecaBDE. They concluded that there was emission of HBCDs and PBDEs, including DecaBDE, even at room temperature (20 °C), and the emission rates increased with increasing temperature. These results indicate that flame-retardant-treated upholstery textiles have the potential to be major sources of BFR contamination in indoor air and dust. At the higher test temperatures, the proportions of di- to Hexa-BDEs in the emissions were clearly larger than in the original sample, suggesting that the textile products treated with technical DecaBDE could be a source of environmentally relevant less brominated PBDE congeners such as BDE-47, 99, and 100.

According to the COHIBA project, the amount of released PBDEs transferred from the indoor environment to environmental compartments (air, sediment, water, soil), is estimated to be 3-60 kg and this is a result of dust transfer. There are studies, however, which state that indoor air may be responsible for as much as 86% of total releases of PBDEs to outdoor air (Danish EPA, 2013).

# 4.3.6 Emissions from the waste stage

Regarding plastic waste in particular, the Green Paper "On a European strategy on plastic waste in the Environment"<sup>39</sup> says that although plastic material is fully recyclable, only a small fraction of it is currently recycled in the EU. In 2008, out of the 25 million tonnes of plastic waste that was

<sup>&</sup>lt;sup>39</sup> Available at: http://eur-lex.europa.<u>eu/LexUriServ/LexUriServ.do?uri=COM:2013:0123:FIN:EN:PDF</u>

generated, roughly half of it (48.7%) was landfilled, 21.3% was recycled and the remaining 30% was incinerated.

According to the German competent authority, in a response to a consultation for waste management of POP substances (Stockholm Convention, 2012), potential sources of PBDE emissions to the environment are mechanical treatment of WEEE and waste sites. The consultation was about those PBDEs that are considered POPs, but the information may be applied for DecaBDE.

Most of the waste quantities, however, come from the use of plastic in packaging, which is not a relevant application for DecaBDE. The share of plastic packaging in the plastics market was 40.1% in 2008; construction sector had the second most important share with 20.4% (EC, 2013). The main source of plastic waste in Germany in 2010 was packaging (60.5%), while the rest came from building and construction (8.3%), EEE (5.5%), automotive (4.8%), etc.

Plastic waste is, in general, considered non-hazardous, therefore its transboundary movement is not heavily regulated, taking into account the provisions of the Basel Convention and EU Regulation 1013/2006 on shipments of waste. 'E-waste', on the other hand is considered hazardous, and therefore its shipping to non-OECD countries is forbidden.

The recast WEEE directive requires that waste containing PBDEs should be screened before treatment and taken to specially authorised facilities, separately from other waste streams (Official Journal of the European Union, 2012). Sweden sorts out bromine containing plastic waste manually or through X-ray diffraction analysis for bromine content and density separation (flotation). The flotation method, which consists of separating different fractions after they pass through tanks with water of different salinity levels, is also used in Switzerland for WEEE. These methods, however, do not distinguish between plastics containing different brominated substances, but mainly focus on the total bromine content (Stockholm Convention, 2012).

#### Recycling of DecaBDE-containing waste

The main focus of the studies on emissions of DecaBDE during the waste stage of materials is on WEEE. The identification and, most importantly, the separate collection of plastics containing PBDEs are difficult processes. As mentioned above, a flotation method of distinction between brominated and other FRs has been shown to work for styrenic polymers, while Schlummer et al. 2006, (referenced by (Environment Agency, 2009)) also examined two techniques that focus on the distinction between brominated and other FRs. As explained in this study, emissions of DecaBDE from waste can be generated during shredding of plastic waste. The detected concentrations in the waste varied in the various studies and were found to be as high as about 14%.

According to other available information shows that very small quantities of brominated dibenzo-p-dioxins and furans (PBDDs/PBDFs) have been detected after recycling HIPS containing DecaBDE. However, their concentrations were below the existing limit values. Analysis was also performed to detect the presence of less brominated PBDE congeners, but no PDBE were detected (Tange & Drohmann, undated).

Several techniques have been examined for the removal of bromine from waste plastics, in order to facilitate reuse of the plastics. These techniques mainly involved pyrolysis and had produced mixed results, according to the review by the UK EA (Environment Agency, 2009).

According to the European Commission Green Paper on plastic waste<sup>39</sup>, of the total 24.9 million t/y of plastic waste, 16 million t/y are covered by the existing legislation and could be recycled. This covers WEEE, construction and demolition waste, end-of-life vehicles, packaging, spent batteries and municipal solid waste. The Green Paper acknowledges that plastics in furniture and in equipment

other than EEE are not currently covered by the waste legislation. The fate of such waste is largely unknown, but it is expected that the largest portion is incinerated or landfilled.

The relevant waste legislation also sets specifications that must be met before a facility can accept certain wastes for recycling. The available recycling infrastructure is not at the same level across the EU member states, which, combined with the provisions of the legislation, leads to exports of waste. The demand of the Asian market for secondary raw materials has also contributed to the increased exports.

#### Landfilling (disposal) of DecaBDE-containing waste

The low volatility of DecaBDE limits its release to air, either by itself or on particles after deposition in landfill sites. This view is expressed in the OECD Emission Scenario Document for plastics as well as in ECHA's guidance for estimation of emissions in the waste stage (OECD, 2009), (ECHA, 2012c), where the emissions to air are considered to be practically zero for non-volatile substances.

Regarding emissions through leaching, according to OECD, these will depend on many factors relating to the type of landfill, the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal (OECD, 2009).

## Energy recovery from incineration of DecaBDE-containing waste

Incineration of solid municipal waste is a common practice in many countries of the EU. However, the rates of incineration of waste vary greatly across the EU, as can be seen in **Table 3-26**. If plastics containing DecaBDE are incinerated there is a potential risk (depending on the incineration temperature) that hazardous substances containing bromine would be produced and emitted. In general, bromine can be released as Br<sub>2</sub> or HBr, depending on the conditions during incineration (EBFRIP, 2002). However, it is possible that polybrominated dibenzo-p-dioxins (PBDDs) or polybrominated dibenzo furans (PBDFs), as well as mixed polybrominated and polychlorinated dioxins and furans could be formed if the temperature of the incineration process is not high enough.

According to the Danish EPA, PBDE-containing articles could be incinerated in municipal solid waste incinerators if the bromine concentration were not excessive (Danish EPA, 2013).

Currently, there are several techniques for thermal processing of waste. Owing to the prominent use of BFRs in WEEE, and owing to EU's focus on that particular waste stream, a number of studies have been performed on this type of waste. Co-combustion with municipal solid waste (MSW) has shown that the bromine levels in the exhaust gases are not affected, as long as the appropriate technical and health standards are followed (Tange & Drohman, 2005). PBDD/Fs have been associated with low temperatures and pyrolytic (oxygen-free) conditions according to laboratory testing, but most waste incinerators usually avoid these conditions. It is mentioned that in order to comply with the EU dioxin emission limits (<0.1 ng TCDD/m³), many smelters and incinerators have installed gas-cleaning equipment (e.g. alkali or acid scrubbers), which also affect bromine emissions (Tange & Drohman, 2005).

In trials run in a municipal solid waste plant by EBFRIP, in which WEEE was co-combusted with organic/green waste, it was found that bromine was produced during the combustion process. A significant amount of the total bromine (between 25 and 40%) stayed in the fly ashes, while the gas phase contained both HBr and, in higher loadings, Br<sub>2</sub>. The existing abatement systems could not always handle the bromine content in the gas phase, but after modifications the bromine removal efficiency increased considerably.

Several studies have examined the possibility of recycling bromine from the exhaust feed during an energy recovery process for WEEE. Thermal processing of waste (co-combustion, pyrolysis) produces bromine or hydrobromic acid in the exhaust gas, which can potentially be collected using scrubbers. These could then be used for the production of BFRs or other brominates substances (Tange & Drohmann, undated), (EBFRIP, 2002).

Production of PBDD/Fs during such processes is possible but can be avoided if proper procedures are followed Incineration of materials containing BFR does not contribute to the overall PBDD/Fs emissions (Tange & Drohman, 2005). Energy recovery processes that have been examined for materials containing brominated substances are pyrolysis, gasification and co-combustion. Other alternatives include combustion of the material in high temperature kilns or furnaces such as in cement kilns, which can reach temperatures up to 1,450°C.

# 4.3.7 Information from monitoring studies

#### Air

The DecaBDE monitoring programme undertook a study of measuring the concentration of DecaBDE (and other PBDEs such as Nona- and OctaBDEs) in outdoor air at a UK location. The measured concentrations were at the pg/m<sup>3</sup> level and they did not show a significant change from 2005 to 2007 (IVM, 2012).

BFRs in the Arctic are monitored within the framework of the Arctic Monitoring and Assessment Programme (AMAP). BDE-209 concentrations are increasing in the Arctic air. BDE-209 is shown to have either low or no bio-magnification potential (de Wit, et al., 2010). DecaBDE concentrations varied across the Arctic monitoring stations, with some showing it as the dominant PBDE congener and others not detecting it at all, probably due to the sampling technique and detection limit (Muir & de Wit, 2010). BDE-209 and other PBDEs were detected in moose and grouse in northern Norway providing evidence for entry of these BFRs into the terrestrial food web. However, the PBDE concentrations were low (probably in the ng/kg lipid weight range) (Muir & de Wit, 2010).

In a study by Moeller et al. (2011), in which the Long-Range Transport Potential (LRT) of PBDEs was examined, DecaBDE was not detected in significant quantities, but lower congeners which could have been produced through its photodegradation were detected.

Breivik et al. (2006) examined the Long-Range Atmospheric Transport Potential of DecaBDE using results from dated sediment cores along a latitudinal transect in North America to measure empirical half distances (EHDs). They saw an exponential decline in DecaBDE flux with latitude based on the seven lakes studied and this translated into an EHD of  $566 \pm 101 \, \mathrm{km}$ .

DecaBDE is not subject to photolysis in the atmosphere as it is almost entirely particulate bound and therefore shielded from sunlight, which in turn lengthens the lifetime of DecaBDE in the air. Wet deposition is the most important removal pathway for DecaBDE in air. This explains the observed depletion of lower brominated BDEs in e.g. Great Lakes sediments compared with DecaBDE. Thus, rain events and sunlight are important and as the daylight intensity declines or may be totally absent in some parts of the Arctic during winter, the lower brominated BDEs will be able to undergo LRT to a greater extent at that time.

The first evidence of DecaBDE in Arctic air samples comes from a study by Wang et al. (2005). High volume samplers were used to collect particulates on filters on a research cruise travelling from the Bohai Sea of China through the Bering Strait and into the Canada Basin of the Arctic Ocean from July to September 2003. DecaBDE concentrations were 3.01 pg/m³.

Compared to the samples from East Asia and the northern Pacific, the Arctic samples had a lower proportion of DecaBDE, and the authors speculate that this may be due to a combination of photodegradation during long-range transport and a higher deposition rate. They also speculate that the relatively high PBDE concentrations in the Arctic samples may be due to sampling near the North American continent, which may serve as a source of PBDEs to air in this area of the Arctic.

DecaBDE showed no seasonal trends at all but was episodic. Episodically elevated concentrations in wintertime are thought to be linked to Arctic haze, which is caused by inputs of aerosols and airborne contaminants from mid-latitude sources to the Arctic.

Deposition, particularly wet deposition, is a more important process of removal of DecaBDE from the atmosphere. However, during strong winds and periods of no precipitation, wet deposition of DecaBDE will be minimal, and consequently DecaBDE and other particle-bound PBDEs will be able to undergo long range transport to a greater extent than previously thought (Breivik et al., 2006). The results from actual air measurements support the theory that periods in the Arctic haze, when atmospheric conditions are stable with no precipitation, lead to long-range transport to the Arctic from more southerly source regions.

A study by Cincinelli et al. (2012) showed that the concentrations of DecaBDE in the air in and around WWTPs treating textile industry effluents in Italy, were higher than at a reference site. Additionally, this concentration had risen from 2004 to 2008, possibly as a result of the ban of PentaBDE and OctaBDE. The total measured PBDEs were in the range of 34 to 190 pg/m³, with DecaBDE accounting for a significant portion of these.

#### *Indoor atmosphere*

DecaBDE has also been detected in indoor environments, mainly in association with particulate matter produced through wear or tear of articles containing DecaBDE, but also to a lesser extent with particles in the vapour phase (Environment Agency, 2009).

Consumer products using PBDEs have been in use for a number of years. Despite the ban on the use of Penta- and OctaBDE in the EU in 2004, products that contain them may still be in circulation.

In a recent study by Watkins et al. (2011), DecaBDE was detected in samples of office dust and DecaBDE had the highest concentration of all the PBDEs that were measured, with a geometric mean of 4.2  $\mu$ g/g. However, it was not subsequently detected in serum samples with the same frequency.

# Surface water

PBDEs tend to associate highly to particulate matter in water, with only a small fraction actually dissolving in the water (to give the freely dissolved fraction). Filtering eliminates larger particles and suspended solids, and filtered water samples are thus more representative of the dissolved fraction of PBDEs, which is also the fraction that is bioavailable to water-breathing organisms (de Wit, et al., 2010).

Di- and tri-BDEs not found in the commercial mixtures were detected in all three regions in differing proportions relative to total PBDEs, indicating possible compositional changes via debromination of PBDEs during atmospheric transport (de Wit, et al., 2010).

A study performed by Wei et al. (2012) in South-central Arkansas, home to major manufacturing facilities for BFRs in the US, analysed sediment cores to address unintended release during production. Samples were collected from six water bodies in Arkansas including three located close

to the BFR manufacturing facilities in El Dorado and Magnolia, to investigate past and recent deposition histories. A total of 49 PBDEs and decabromodiphenyl ethane (DBDPE or EBP) were detected, with concentrations as high as 57,000 and 2,400 ng/g dw DecaBDE and EBP, respectively. The spatial distribution and temporal trend of the contamination indicate that manufacture of PBDEs and DBDPE is the primary source for these compounds in the environment of southern Arkansas. Interestingly, debromination of PBDEs in the sediments of a previously used wastewater sludge retention pond in Magnolia was indicated by the presence of congeners that had not been detected in any commercial PBDE mixtures and by increased fractions of lower brominated congeners relative to higher brominated congeners. Two other brominated compounds were detected in the sediments and identified as nonabromodiphenyl ethanes.

#### Sewage sludge

In general, WWTPs remove large proportions of biodegradable chemicals from the wastewater flow. However, PBDEs, as persistent chemicals, are more difficult to treat than most biodegradable chemicals and are therefore more often discharged through effluents, sewage sludge disposal or atmospheric emissions (Cincinelli et al., 2012).

As a result of the risk assessment of DecaBDE under the Existing Substances Regulation (ESR) (Official Journal of the European Union, 1993), a ten-year monitoring programme (known as the conclusion (i) monitoring programme) was requested by the EU Member States to investigate the long-term trends in the levels of DecaBDE in sewage sludge, sediment, air and bird eggs (Environment Agency, 2009). This programme is currently financed by BSEF and involves sampling sewage sludge (three samples from each site over a one week period of each sampling year) from a total of 12 sites in the EU over a 10-year period. Of these sites, seven are sewage treatment plants (STPs) with mainly domestic wastewater input.

According to the review of the DecaBDE monitoring programme, in the first two years of monitoring (2006 and 2007), the concentration of DecaBDE in wastewater varied among the different countries from 180 to 7,963 µg/kg dry weight. More specifically the levels of DecaBDE in the sludge from these STPs in 2007 were 3,810±2,580 µg/kg dw and 5,490±2,890 µg/kg dw in sewage from two STPs in UK, 5,170±989 µg/kg dw in one STP in Ireland and 248±145 µg/kg dw, 208±29 µg/kg dw, 353±28 µg/kg dw and 463±35 µg/kg dw in four STPs in The Netherlands (Environment Agency, 2009).

Compared with the levels found in the STPs in the Netherlands and other European countries, the levels in Ireland and the UK were an order of magnitude higher.

The most recent report on the project adds data collected in 2009 from the 12 sites in the UK, Ireland and the Netherlands. It is observed that samples collected in the UK and Ireland had significantly higher concentrations than those collected in the Netherlands (roughly an order of magnitude higher). Furthermore, in two of the UK sites a significant increase in the DecaBDE concentration was measured compared with 2007 sampling data, but no explanation could be given at the time of reporting. In the rest of the sampling sites, no discernible trend was visible (IVM, 2012).

A Danish Environmental Protection Agency study on the uses, exposure, risks and alternatives of over 40 hazardous chemicals, commented regarding emissions of DecaBDE in sewage sludge (Danish EPA, 2013):

"Consistently, BDE-209 (DecaBDE) accounts for more than 50% of the total PBDE concentration. The concentrations of DecaBDE in sludge from different countries (year of sampling) were: Germany 2002/3 (mean = 429  $\mu$ g/kg w.w.), Sweden 2002 (mean = 11  $\mu$ g/kg dw), Sweden 2007/8 (mean = 383  $\mu$ g/kg w.w.), Sweden (2007 (mean = 291)

 $\mu$ g/kg), Sweden (2008 (mean = 292  $\mu$ g/kg), and Switzerland 2003-5 (mean = 310  $\mu$ g/kg)."

Monitoring data from the Danish surveillance programme for the aquatic environment (NOVANA) showed very low emissions of DecaBDE from point sources (below detection limits), in levels of  $0.4 - 0.5 \, \mu g/l$  in Denmark. This Danish EPA study showed that available data for other BFRs that could substitute DecaBDE (such as EBP) are scarcer than equivalent data for DecaBDE (Danish EPA, 2013).

Alonso et al. (2007) estimated that the emissions of DecaBDE from urban sources to WWTP were roughly 6.16 mg per inhabitant per year in Spain. The emissions were calculated from the concentrations measured in 25 sewage treatment plants throughout Spain. The authors removed outlier measurements from their analysis in order to restrict them to emissions from municipal residues, mainly from houses. An extrapolation of the emissions to the whole EU would lead to total emissions from uncontrolled urban sources of 3.08 t/y.

#### Soil

Concentrations of DecaBDE in soil in the EU, as reported in a number of studies, reached up to 0.66 mg/kg dw, in samples collected from soil that receives WWTP effluents in Spain. Other, much higher, levels have also been reported near a WEEE recycling plant in China (up to 44 mg/kg dw), but its relevance to the EU is uncertain (Environment Agency, 2009). This study found high concentrations of PBDEs in soil near three e-waste disposal sites. DecaBDE had the highest concentration, in the range of 48.67 ng/g to 234.12 ng/g (Wang, 2009). In soil, DecaBDE was the predominant congener in all soil samples. Interestingly though, the soil concentrations were elevated in the samples taken within the Yellowknife landfill near some types of waste. For example, a soil sample taken near discarded refrigerators had 47 ng/g dw of DecaBDE, indicating that discarded consumer products that are flame retardant are leaching PBDEs into the surrounding environment (Wang, 2009). However, it should be noted that risk management measures and environmental controls in China are considered to be less strict compared to the EU this means that relevance of this study to the EU is uncertain (Environment Agency, 2009).

#### Sediment

The DecaBDE monitoring programme also monitors 10 (mostly estuarine) sites for contamination of sediment from DecaBDE. As with the water compartment, trends for the concentration of DecaBDE could not be drawn from the limited set of data. It can be noted, however, that the concentrations in Mersey (which crosses a heavily industrialised area) and in Belgium are significantly higher than in other collection points. The latest report of the monitoring programme comments that the concentrations of DecaBDE at the sampling points in Western Scheldt, Liverpool Bay and the River Mersey are consistently higher than the respective ones in Elbe, Ems, Seine and Outer Humber. At the moment, no clear conclusion can be derived, based on the available data. It is expected that a more reliable analysis will be feasible after the end of the project, in 2014, when data from the whole 10-year period will be available (IVM, 2012).

Other studies have given a wide range of values, which reached up to 12.5 mg/kg dry weight near one Spanish industrial park (Environment Agency, 2009).

Ranking the BDE congeners according to concentration in the Baltic Sea sediments yielded the following order: BDE-209 >> BDE-99 > BDE-47. In general, the levels in the sediment are low and do not exceed the PNEC level (Danish EPA, 2013).

#### Biota

DecaBDE has been detected in various animal and plant groups, both terrestrial and aquatic. It appears to be more frequently detected in birds and birds' eggs and in terrestrial mammals, although it has also been detected in plants and aquatic organisms (fish, shellfish and aquatic mammals).

The 10-year monitoring programme coordinated by the Institute of Environmental Studies (IVM) of the VU University of Amsterdam has identified no visible trends in the first 6 years of monitoring (2005 – 2010) in sparrow hawk and glaucous gull eggs. On average, sparrow hawk eggs contained higher concentrations of DecaBDE than gull eggs and this was attributed to the sampling points' proximity to the sources, albeit not with high certainty (IVM, 2012).

DecaBDE has generally not been analysed in fish from the Baltic Sea or has been found in low concentrations. However, relatively high levels (median 48  $\mu$ g/kg lw) in roach from the Archipelago Sea (Åland) have been reported (Danish EPA, 2013). DecaBDE was also found in perch (1.3  $\mu$ g/kg lw) and pike (1.7  $\mu$ g kg-1 lw) from the same area. However, the high BDE-209 levels found in roach muscle do present cause for concern.

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

DecaBDE concentrations ranged from 0.052 to 0.64 to ng/g dw (Mariussen, et al., 2008). This study shows that BDEs including DecaBDE can be spread into the terrestrial environment and food chains involving herbivores. The considerable presence of DecaBDE is probably a result of particle transport and deposition from the atmosphere. A significant decrease in the content of the lower brominated BDEs was seen with increasing latitude, and the concentrations of DecaBDE also decreased from south to north.

Concentrations of all PBDEs in terrestrial animals at lower trophic levels were found to be low in the previous review, whereas they were much higher in terrestrial birds of prey, particularly in peregrine falcons. Several, BDEs including DecaBDE showed increasing temporal trends in Greenland peregrine falcons.

#### **Humans**

BFRs are solids and have a very low vapour pressure (DecaBDE's vapour pressure is  $4.6 \cdot 10^{-6}$  Pa), therefore exposures through inhalation will mainly be to particle-bound substances, instead of DecaBDE vapours.

Another important parameter for human exposure is water solubility, which, in the case of DecaBDE is also low. However, PBDEs are persistent and lipophilic and can therefore be accumulated and magnified through the aquatic food chains. DecaBDE in particular is considered very Persistent and Bioaccumulative (vP, B), according to its PBT assessment.

Humans may be directly exposed to BFRs in occupational settings that involve handling these chemicals, or materials containing these chemicals. Consumers may be directly exposed to these chemicals through exposure to consumer products. Releases from such products may also cause

elevated levels in indoor air and dusts. The general population may further be potentially exposed to BFRs in polluted ambient air, soil and drinking water.

Non-dietary human exposure to PBDEs and other BFRs can occur via inhalation of gas-phase PBDEs and PBDEs on particles, as well as oral intake of house dust. Such exposure can occur in homes as well as in the workplace. Dermal exposure is not considered to be of any importance for the total human exposure (EFSA, 2011).

The estimated occupational exposure to the main BFRs is described in the EU Risk Assessments. However, the occupational exposure has likely decreased as a consequence of the activities under VECAP and based on the information they include in their annual reports. It should be noted that the emission reduction programme of VECAP does not specifically target occupational exposure, but it includes the issuing of good practices in handling DecaBDE and contaminated materials (e.g. empty packaging).

According to the EU Risk Assessment, the main occupational exposures to DecaBDE are by handling of the substance such as filling or emptying bags, adding the substance by formulation processes (e.g. hot-melt adhesives) or sewing DecaBDE treated textiles. The occupational exposure from the end-use of FR products is considered negligible (ECB, 2002).

The dominating source of BFRs in arable soil is via application of sludge from sewage treatment plants (EFSA, 2011). According to the EFSA reviews, the general population is mainly exposed to BFRs through the food chain.

#### **Food**

The European Food Safety Authority (EFSA) has published a scientific opinion on PBDEs in food in 2011, analysing the information on these PBDEs in food samples provided by 11 Member states (EFSA, 2011) from 2001 to 2009. In this opinion, EFSA (2011) underlines the analytical difficulties which remain for congeners Hepta- (BDE-183) and DecaBDE (BDE-209).

It was proposed to limit the list of indicators proposed by EFSA to six congeners: TriBDE (BDE-28), TetraBDE (BDE-47), PentaBDE (BDE-99) and (BDE-100), HexaBDE (BDE-153) and (BDE-154), while DecaBDE was not prioritised. Therefore, it was proposed to derive in this fact sheet a unique Environmental Quality Standard (EQS) for the PentaBDE and OctaBDE, including data on their main components which are Tetra-, Penta-, Hexa- and HeptaBDE where appropriate.

This EQS value, expressed in  $\mu g.kg^{-1}$  of food and proposed for compliance check with biota concentrations, will apply in monitoring terms to the sum of the following six indicator congeners in fish: TriBDE (BDE-28), TetraBDE (BDE-47), PentaBDE (BDE-99) and (BDE-100), HexaBDE (BDE-153) and (BDE-154).

During the review process, it was underlined that the current proposal might, in some cases, be less conservative than an approach where the sum of all BDEs would have been considered. It is noted that this would be the case in sampling sites where the six indicators are not the main contributors to the BDEs concentration.

EFSA provided a scientific opinion about Polybrominated Diphenyl Ethers (PBDEs) in food as requested by the European Commission. They concluded that the chemical stability of the PBDEs congeners varies with the individual structure but a general rule is that PBDE congeners with up to three bromine substituents and those with nine and ten bromine substituents are more susceptible to abiotic transformation. PBDE congeners with four to eight bromine substituents show the highest stability (EFSA, 2011).

PBDE congeners are susceptible to photolysis, reductive debromination and radical reactions while they are less susceptible to oxidation and hydrolysis. In general, PBDE congeners are persistent and bioaccumulative. Bioaccumulation is congener- and species- dependent. The technical mixture DecaBDE has different physico-chemical properties compared to the PBDE congeners making up the PentaBDE and OctaBDE mixtures (EFSA, 2011).

Occurrence of DecaBDE shows that this is present ubiquitously in biota and likewise in food and feed (EFSA, 2011). Degradation in water shows hydroxyl-PBDEs from the biosynthesis by marine organisms or from metabolic transformation of PBDEs in wildlife and humans. Information on occurrence and toxicity of these is scarce (EFSA, 2011).

The food category "fish and other seafood" dominated the total samples, followed by "meat and meat products" and "animal and vegetable fats and oils", "milk and dairy product" and "eggs and egg products", to examined DecaBDE content. In a specific study of a sub-category of "fish meat", the results indicate a relationship between the PBDEs levels and the fat content of the different fish (EFSA, 2011).

DecaBDE was determined in human milk at mean concentrations between 0.21 and 2.9 ng/g fat. In addition, in serum or blood samples (0.77-37 ng/g fat) was the most predominant congener. The human exposure from diet is highest for DecaBDE showing an average of 0.35 and 2.82 ng/kg bw for minimum lower bound and maximum upper bound, respectively. The range of estimated dietary exposure for high consumers (95<sup>th</sup> percentiles) across European surveys is 0.7 and 4.58 ng/kg bw (EFSA, 2011).

Supplements, such as fish oil, e.g. cod liver oil, are another source of DecaBDE exposure, at around 4.27 ng/kg bw per day (maximum upper bound across European surveys) (EFSA, 2011).

As contamination of food samples of plant origin is generally lower than that of food samples of animal origin, it can be assumed that the dietary exposure to PBDEs for vegetarians is lower than that for people consuming mixed diet (EFSA, 2011).

A survey on the PBDE content of food in Denmark has shown that all measured substances in the samples were present at below the tolerable level of 100 ng/g fat, in 2009 and 2010 (Danish EPA, 2013).

The European monitoring programme by EFSA which begun in 2006 has shown that:

"The levels of BDE-209 were the highest in almost all of the food categories except for "Fish and other seafood (including amphibians, reptiles, snails and insects)" and "Food for infants and small children""

The estimated mean chronic dietary exposure for average consumers across the dietary surveys in European countries can be up to 2.82 (maximum UB) ng/kg bw per day for DecaBDE. For high consumers, the minimum LB and maximum UB dietary exposure estimates of DecaBDE is 4.58 ng/kg bw per day (EFSA, 2011).

For children from 1 to 3 years old the dietary intake of DecaBDE is about 3-6 times higher than for adults. PBDEs are biotransformed in mammals. Debromination and hydroxylation are the major metabolic pathways. The estimated elimination half-life of PDBEs in human serum varies from 1 to 2 weeks. Intake associated with the body burden at BDML10 and the estimated dietary intake for the different population groups indicate that current dietary exposure to these PBDEs is unlikely to raise a health concern (EFSA, 2011).

# Overview of the current monitoring programs

Table 4-10:	Plans, programmes and	studies on monitoring of PBDEs	
Matrix	Authority	Program	Reference
Air	European	Action Plan on Environment and	
	Commission	Health, 2006-2010	
Ambient	Federal Environment	Sampling and analysis of PBDE and	(Knoth, et al., 2010)
Air	Agency (UBA)	HBB in air samples in the Rhine	
A	NAi-richus of	Main Area, Germany	(CE- 0 Hadr- KO Hd 2010)
Articles	Ministry of	Investigation of BFRs present in	(GEo & Hydro -K8 Ltd, 2010)
	Environment, New Zealand	articles being used, recycled and	
Bream	Federal Environment	disposed of in New Zealand  BFRs in bream ( <i>Abramis Brama L</i> .)	(Sawal, et al., 2009)
muscle	Agency, Laboratory	from six rivers and a lake in	(Sawai, et al., 2009)
muscie	for Water Analysis	Germany	
Breast milk	WHO	Action Plan on Health and	http://www.who.int/foodsafety/c
Di Cast IIIIK	WIIO	Environment	hem/pops biomonitoring/en/
Breast milk	Centre for Public	Current concentrations, temporal	(Mannetje, et al., 2013)
	Health Research	trends and determinants of	( 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
	(CPHR), Massey	persistent organic pollutants in	
	University, New	breast milk of New Zealand women	
	Zealand		
Breast milk	Centre for Public	Concentrations of polybrominated	(Coakley, et al., 2013)
	Health Research	diphenyl ethers in matched	
	(CPHR), Massey	samples of indoor dust and breast	
	University, New	milk in New Zealand	
	Zealand		
Breast milk	National Food	Levels of persistent halogenated	
	Agency	organic pollutants (POP) in	
		mother's milk from first-time	
Breast milk	Federal Environment	mothers in Uppsala, Sweden FRs in breast milk	(Durkon et al. 2005)
DI EdSt IIIIK	Agency (UBA)	FRS III DI EdSt IIIIK	(Durkop, et al., 2005)
Breast milk	Swedish EPA (the	Levels of persistent halogenated	
	Health related	organic pollutants (POP) in mothers	
	Environmental	milk from first-time mothers in	
	Monitoring Program)	Uppsala, Sweden-results from	
		2008/2010 and temporal trends	
Deer liver	Eurofins GfA GmbH	Analytical experience with the	(Paepke, et al., 2011)
		German Environmental Specimen	
		Bank: polybrominated diphenyl	
		ethers in deer liver samples and	
F!	For only of a to attract.	corresponding soils	(Fliada an at al. 2042)
Eggs in	Fraunhofer Institute	Levels and trends of industrial	(Fliedner, et al., 2012)
herring seagulls	for Molecular Biology and Applied	chemicals (PCBs, PFCs, PBDEs) in archived herring gull eggs from	
scaguiis	Ecology (Fraunhofer	German coastal regions	
	IME)	German coastal regions	
Eggs	Department of	Polybrominated diphenyl ether	(Johansson, et al., 2009)
peregrine	Applied	congener patterns,	, 22 2, 23 2,
falcon	Environmental	hexabromocyclododecane, and	
	Science (ITM),	brominated biphenyl 153 in eggs of	
	Stockholm	peregrine falcons (Falco	
	University,	peregrinus) breeding in Sweden	
	Stockholm, Sweden		

Table 4-10:	Plans, programmes and	studies on monitoring of PBDEs	
Matrix	Authority	Program	Reference
ELV and WEEE waste streams	IVM/IVAM	POP-BDE waste streams in the Netherlands: analysis and inventory.	Report R13-16 (in preparation)
Food	EFSA	PBDE in food	EFSA Journal 2011; 9(5):2156 Scientific Opinion on Polybrominated Diphenyls Ethers (PBDEs) in Food.
Forest top soil		N. B. data analysis in progress, German forest soil status report	
Human serum	Centre for Public Health Research (CPHR), Massey University, New Zealand	Concentrations of Selected Persistent Organic Pollutants (POPs) in the Serum of New Zealanders	(Centre for Public Health Research (CPHR), 2013)
Humus layers from Alpine forest			(MONARPOP Technical Report, 2009)
Indoor air	Federal Environment Agency (UBA)	Sampling and analysis of PBDE and HBB in air samples in the Rhine Main Area, Germany	(Knoth, et al., 2010)
Indoor air and dust	MTM-research centre, Örebro University, Örebro, Sweden	Levels of BFRs in blood in relation to levels in household air and dust	(Karlsson, et al., 2007)
Indoor dust	Centre for Public Health Research (CPHR), Massey University, New Zealand	Concentrations of polybrominated diphenyl ethers in matched samples of indoor dust and breast milk in New Zealand	(Coakley, et al., 2013)
Indoor dust in cars	University of Birmingham, UK	Concentrations of organophosphate esters and BFRs in German indoor dust samples	(Brommer, et al., 2012)
Indoor dust in housing	University of Birmingham, UK	Concentrations of organophosphate esters and BFRs in German indoor dust samples	(Brommer, et al., 2012)
Indoor dust in offices	University of Birmingham, UK	Concentrations of organophosphate esters and BFRs in German indoor dust samples	(Brommer, et al., 2012)
Landfills Marine environ- ment	Kemikalinspektionen OSPAR Convention	Landfill leachates Environmental monitoring	Keml Report 1/9 CEMP Assessment report: 2008/2009. Assessment of trends and concentrations of selected hazardous substances in sediments and biota. OSPAR Commission. 2009.
Municipal waste	North Rhine- Westphalia State Environment Agency 2006	Waste composition and characterisation	ABANDA Database

Table 4-10: Plans, programmes and studies on monitoring of PBDEs						
Matrix	Authority	Program	Reference			
Sewage sludge	Federal Environment Agency (UBA)	Polybrominated diphenyl ether in sewage sludge in Germany	(Knoth, et al., 2007)			
Sewage treatment	Department of Applied Environmental Science (ITM), Stockholm University, Stockholm, Sweden	Mass balance of decabromodiphenyl ethane and decabromodiphenyl ether in a WWTP	(Ricklund, et al., 2009)			
Slurry from municipal waste water	North Rhine- Westphalia State Environment Agency 2006	Waste composition and characterisation	ABANDA-Database			
Wastes	Ministry of Environment, New Zealand	Brominated Flame Retardant Research: A pilot study of e-waste plastic sorting in New Zealand	(Environ Australia Pty Ltd, 2014)			

# 4.3.8 DecaBDE (or PBDE) concentration data submitted by MSCA during consultation

The following **Table 4-11** summarises the monitoring information on DecaBDE that was submitted by the MSCAs during consultation. As can be seen, most of the information comes from Central European or Nordic countries. Furthermore, monitoring data from some major importing countries, such as Belgium and Italy are missing. Most of the member states have not reported any observable trends during their measurements.

Compartment	Austria <sup>(a)</sup>	Germany	Netherlands	Norway	Sweden
Ambient air	Rural-urban: n.d. – 100 pg/m³ (2011) Alpine: n.d 73 pg/m³ (2005 - 2007)	0.97 – 56 pg/m <sup>3</sup> (2002 - 2009)		<0.01 – 2.409 pg/m <sup>3</sup> (2010 – 2012)	0.2 pg/m <sup>3</sup> (2009 - 2010)
Deposition	Rural-urban: n.d. – <45 ng/m³ (2011) Alpine: n.d 232 ng/m³ (2005 - 2007)				
Surface water	n.d. – 0.24 μg/L (2011) n.d <18 μg/L (2012)	-		<20 ng/l (2012)	-
Groundwater	n.d <18 μg/L (2012)	-		-	-
Sediments	-	-		Salt water: 0.25 – 1,555 μg/kg dw (mean 110) (2003 – 2012) Fresh water: 0.04 – 415 μg/kg dw (mean 15) (2003 – 2008)	
Sewage sludge		Sewage sludge: 97 – 2,200 ng/g dm (2002 – 2003)		44 – 2,000 μg/kg dw (mean 269) (2006 – 2011)	
Indoor air	House dust: 3.8 – 170 μg/kg (2003)	Air: 0.66 – 190 pg/m³ (2002 – 2009) Dust: 19 – 19,000 ng/g (2001 – 2003) Dust (12 cars): 220 – 3,100 ng/g (2010 - 11) Dust (12 offices): 28 – 310 ng/g (2010 – 11) Dust (1 home): 21 – 72 ng/g (2010 – 11)			
Soil	Mineral, rural: n.d. – 2.3 μg/kg dw (2008) Mineral, rural: n.d. – 1.7 μg/kg dw (2011) Humus layer: 0.6 – 11	Humus *: 0.35 – 8.9 ng/g dw (2002) Humus *: <0.01 – 81 ng/g dm (2006) Humus (alpine) *: 0.61 – 11		Soil: 0.17 – 4.34 ng/g dw (2005) Moss (wet): 0.03 – 0.66 ng/g ww (2002) Moss (dry): 0.43 – 8.64	

Compartment	Austria <sup>(a)</sup>	Germany	Netherlands	Norway	Sweden
	μg/kg dw (2004)	ng/g dw (2004) Forest top soil*: "Some to several 10" ng/g dw (2006 – 2007)		ng/g dw (2005)	
Solid waste		Parts of used devices: 100 – 7,800 mg/kg Municipal sewage sludge: 0.012 – 8.5 mg/kg SLF: 0.76 – 75 mg/kg Municipal solid waste: 0.008 – 0.13 mg/kg		Landfill leachate: 0.09 μg/l (2006 – 2010) Landfill (sediment): 0.05 μg/l (2006 – 2010)	
Biota	Spruce needles: n.d. – 1.2 ng/kg dm (2004)	Eggs of herring seagulls: 3 – 198 ng/g lw (1998 – 2008) Bream muscle: 0.46 – 663 ng/g lw (1995 – 2009) Deer liver*: 0.47 – 29 ng/g lw (2001 – 2007)		0.01 – 10.51 μg/kg w/w (1993 – 2012)	2 eggs of herring seagulls: 0.21; 0.28 ng/g fw
Food			<1 – 311 pg/g (2006)	(c)	Fats: 89 pg/g fat (2010)
Human tissue				(c)	Serum (1 <sup>st</sup> time mothers): 0.95 ng/g lw (2010)
Maternal milk	n.d. – 13 ng/g fat (2008)	0.1 – 4.5 ng/g milk fat (2001 – 2004)		(c)	1.5 ng/g lw (2007)

<sup>\*:</sup> It was mentioned that the numbers reflect total PBDE concentration

<sup>(</sup>a): A total of 14 grassland sites under extensive use were selected in the federal provinces of Burgenland (BGL), Carinthia (KTN), Upper Austria (OÖ) and Styria (STM), and soil samples were taken at depths of 0–5 cm and 5–10 cm. The contents of 25 congeners of the possible 209 PBDE compounds were analysed within the framework of this study. It appears that the verifiability and magnitude of PBDE levels vary considerably in the congeners. Highest levels (up to 3,900 ng/kg DS) have been found for DecaBDE (BDE-209). The total values from the sum of all 25 analysed PBDEs are between 14.3 and 5,283.9 ng/kg DS.

<sup>(</sup>b): Monitoring information from Denmark has been submitted through (Danish EPA, 2013) and was incorporated in the main body of this report.

<sup>(</sup>c): These will be described by the Norwegian CA in the chapter on human biomonitoring data in Part B of the restriction dossier. Source: Consultation (specific sources can be found in the respective questionnaire)

## 4.4 Estimation of releases from the lifecycle of the substance

## 4.4.1 Introduction

Calculation of the emissions to the environment is usually done at two scales: locally, which reflects emissions from point sources (such as a representative plastic processing site); and regionally, which includes all sources and wide dispersive (e.g. consumer) uses in an area of Europe (usually assumed to be 10% of total emissions) (OECD, 2009). In this study, the aim is to calculate the total emissions (100%) to the environment, so no other scale will be shown. The aim of the release estimation is to calculate the rate of total release of a certain substance to the relevant environmental compartments (air, water, soil, waste water) for each life cycle stage (ECHA, 2012b). To achieve this, information on the following should be collected:

- Life cycle stage
- Supplied tonnage for each use or group of uses per life cycle stage
- Operational conditions (OC) and Risk management measures (RMMs)
- Release or Emission factors (usually expressed in kg/kg or %).

## Life cycle stage

The term life cycle (LC) refers to the notion that a fair, holistic assessment requires the assessment of raw-material manufacture, article production, distribution, use and disposal including all intervening transportation steps necessary or caused by the product's existence. In this case, we should refer to the production (not anymore in Europe), manufacture, distribution, use and disposal of articles or products containing DecaBDE.

To develop a Life Cycle Assessment it is necessary to have a previous Life Cycle Inventory (LCI) that involves the creation of an inventory of flows from and to nature for a product system. Inventory flows include inputs of water, energy, and raw materials, and releases to air, land, and water. To develop the inventory, a flow model of the technical system is constructed using data on inputs and outputs. The input and output data needed for the construction of the model are collected for all activities within the system boundary, including from the supply chain.

When estimating the emissions of a substance, all stages in the life cycle of it have to be covered, especially if it is ultimately intended for consumer use, as is the case with DecaBDE.

The various life cycle stages affect the release of a substance during use, as they determine the general conditions and the users of a substance or mixture. ECHA has determined some discrete life cycle stages that can be used to divide the life cycle of DecaBDE, namely:

- Manufacture: This refers to the manufacture of DecaBDE and is not relevant to this assessment.
- **Formulation**: It corresponds to the mixing and blending of the substance in a mixture. In the case of DecaBDE, this is the compounding process for plastics (where it is mixed with plastic and other additives) and the formulation of the coating mixture for textiles.
- **Industrial use**: This refers to the use of the mixture or substance in an industrial context. In the case of DecaBDE, it is intended to be included in or on the article matrix. Conversion of plastic compounds in semi-finished or finished articles and coating of textiles fall in this category.

- **Wide dispersive use**: This life cycle stage concerns use by a large number of users (e.g. professionals in gas stations or consumers). This could include the use of textiles as upholstery by professionals.
- **Service life**: It concerns the use of articles containing the substance for periods longer than one year. This is relevant to the use of all articles containing DecaBDE.
- **Waste treatment**: This is the final stage, when the used articles are treated as waste (recycling, incineration or landfill). Reuse of the article can be considered as part of its service life.

ECHA has established a harmonised system of use description in the framework of the REACH Regulation, in order to promote a uniform and standardised way of describing the uses along the life cycle and for calculating emissions during the use of a substance. This covers the whole length of its lifecycle, including manufacturing, formulation, industrial, professional and consumer use and facilitates better communication along the supply chain.

It is based on five descriptors:

- **SU**: sector of use, which describes the industry sector in which the use applies (or the professional or consumer use) and it can also utilise the NACE codes
- **PC**: (chemical) product category, which indicates the category of the chemical according to its function and is relevant only for substances or mixtures, not articles
- **PROC**: process category, which refers to the process that is involved in the use of the chemical and is mainly required for determining occupational exposure
- AC: article category, refers to the category in which the final article belongs
- **ERC**: environmental release category, which refers to the mode of potential release of the substance to the environment and is relevant to the environmental exposure.

The complete descriptors related to DecaBDE for the identified uses of the substance, as submitted by the registrants, are shown in Section 8.

## Supplied tonnage

The tonnage of the substance used in each application is the starting point for estimating the releases of DecaBDE during its life cycle.

As mentioned earlier in this report, conflicting information from available sources and an absence of meaningful information from the consultation procedure did not make it possible to derive accurate numbers for the quantities of DecaBDE imported and used in the EU, as well as for the breakdown of these quantities along the supply chain. In order to produce this information, conservative educated assumptions had to be made, based on the available information.

The calculations are described in detail in Section 3.6 above and the results are going to be used for the purposes of the emissions' estimation. Regarding the consumption, a low volume (LV) and a high volume (HC) scenario were developed. The breakdown of these quantities in plastics and textiles uses was calculated according to the breakdown mentioned in the latest VECAP report, i.e. 52/48 for textiles and plastics respectively. The quantities that will be used are shown in **Table 4-12** below. Exact quantities can be found in the Confidential Annex to this report.

To protect registrants' confidential data, all information on quantities and emissions in the high volume scenario have been moved to the Confidential Annex.

Table 4-12: DecaBDE use allocation scenarios (quantities in t/γ)							
	High volun	Low volume scenario					
	Plastics	Textiles	Plastics	Textiles			
Imported as substance (t/y)	0 0 0	See Confidential	<5,000	<5,000			
Imported in articles (t/y)	See Confidential Annex	Annex	<500	<500			
Total imports (t/y)			<5,000	<5,000			

The quantities imported as substance are relevant for the industrial use of DecaBDE, while the total imports are relevant for the service life and waste stage. It was considered, for the sake of simplicity, that the imported articles enter the market directly and do not participate in industrial processes such as in the manufacture of a more complex product (e.g. cars).

## **Operational conditions and risk management**

The released quantities of DecaBDE are also affected by the processes in which it participates. Operational conditions, such as content in the mixture, process temperature, indoor or outdoor use, open or closed process and whether it is a continuous or batch process, may affect the emissions. Technologies and procedures intended for controlling the emissions of the substance (e.g. use of filters, or the passage of the effluent through a WWTP) also affect the emissions to the atmosphere, and it should be specified whether the calculated emissions are before or after abatement.

## Release / Emission factors

The approach to estimate the emissions of DecaBDE to the environment is based on the use of release (or emission) factors. These permit to address the fraction of the used quantities of the specific substance that is being released to the environment during its lifecycle. They are usually expressed as percentages. In this approach the documents provided for OECD regarding plastic and textile sector will be used as a starting point to address the emission of DecaBDE to the environment all throughout its life cycle (OECD, 2009), (OECD, 2004).

These sources do not provide emission factors for some life cycle stages. To fill these gaps, emission factors found in the ECHA Guidance documents (ECHA, 2012b), (ECHA, 2012c) and the EU Risk Assessment Report (ECB, 2002) and the study by Earnshaw et al. (2013) were used.

The release factors usually describe the initial release from the process (before application of risk management measures). However, in some cases the release factors apply only under the condition that RMMs are in place and in other cases it is not clear if RMMs are included or not. It would be optimal if the release factors to air, water and soil would always relate to the emission before RMMs, as this would provide for a direct relationship between release factor and operational conditions, enable the registrant to iterate the assessment only on the side of risk management measures and avoid any misunderstandings of how the factors should be interpreted (Umwelt Bundes Amt - UBA, 2011). The quantities that will be calculated for the industrial emissions in this report are expected to be before abatement or waste treatment, because this is what is calculated with the available models / equations. After that, an abatement factor will be applied, based on the assumed efficiency of possible Risk Management Measures (RMMs), taken mainly from the CEFIC RMM Library (CEFIC).

Although DecaBDE has been studied extensively for its environmental properties, the literature is severely lacking emission factor (EF) data specific to DecaBDE (PBDEs), so estimation methods or generic EF have to be used instead (Prevedouros, et al., 2004). Most generic emission factors found in literature in guidance documents are derived using conservative approaches and refer to worst case scenarios. DecaBDE is a non-volatile and poorly water soluble substance, having a lower release potential than other organic plastic additives, such as DEHP (OECD, 2009).

Estimation of emissions is often subject to very large uncertainties because:

- There can be a lack of good quality EF measurements
- EFs are often highly variable, depending on conditions, compounds, etc.

Many release factors have been derived from existing literature, such as the TGD and the OECD Emission Scenario Documents (ESDs). This approach is useful and regarded as valid in principle; however, in most cases, neither the TGD nor the ESDs specify the operational conditions underlying the emission factors and it is frequently not clear, if they integrate the use of risk management measures (Umwelt Bundes Amt - UBA, 2011).

Emissions of a substance to the environment depend on its physicochemical properties, among other factors.

The standard technique used by the EU risk assessment to calculate emissions from products in service is based on using vapour pressure (Vp) as the controlling factor. The following equation has been used to calculate the % of loss by volatilisation:

Emission by volatilisation per year = 
$$1.1 \times 10^6 \times Vp$$
 (%) [1]

Where Vp is the Vapour Pressure of the substance (in mmHg at  $20^{\circ}$ C). Equation [1] is used to describe the loss of plasticiser additives in different plastics films. This equation can be used to calculate the emissions due to volatilisation of a substance, such as liquid plasticisers. DecaBDE has very low vapour pressure ( $4.63 \cdot 10^{-6}$  Pa at  $21^{\circ}$ C), so it is unlikely that its emissions to air will be due to that mechanism.

Equation [1] can be modified to calculate the total emissions across the service life of the product by simply multiplying by its lifetime.

Another equation that can be used to calculate the Emission Factor to air is Equation [2]. This involves the use of the octanol-air partition coefficient  $(K_{OA})$ , a physicochemical parameter often reported for POPs and used to describe their environmental partitioning.

$$\log EF = -0.839 \, x \log K_{OA} \, (20^{\circ} \, C) + 4.83$$
 [2]

It should be noted that  $K_{OA}$  data are also subject to variability and this equation is not necessarily fully applicable for DecaBDE.

The implications of this emission approach for explaining the ambient air levels are very important. If DecaBDE is emitted in function of its Vp values, then their presence in the air should follow similar patterns for each PBDE congener, but this is inconsistent compared to monitoring data (Prevedouros, et al., 2004). When using the EF  $K_{OA}$  approach (low emission and high emission scenario) it seems that the estimated emissions for all congeners are lower than the ones obtained using EF Vp one (Prevedouros, et al., 2004).

According to the US EPA (2010), it is consistent with chamber studies in that the greater the vapour pressure, and the lower the octanol-air partition coefficient ( $K_{OA}$ ), the more likely it is that the substance will volatilise from the product into the air.

Another approach for selecting emission factors is through the use of Environmental Release Categories (ERCs), as discussed by ECHA in their guidance document on environmental exposure estimation (ECHA, 2012b).

The Environmental Release Category (ERC) is the set of use descriptors relevant to the potential emissions to the environment during the use of the substance in an industrial, professional or consumer setting. They reflect the general characteristics of the use, in respect to the potential for emission. Such characteristics are the life cycle stage, whether it is used in an open or closed process, whether it is used by a few (e.g. industrial) or many (wide dispersive consumer use), indoors or outdoors and also the technical fate of the substance in that use (reaction, inclusion into or onto a matrix, use as a processing aid, intended release).

They can be used to describe the broad conditions of use and as a basis to define default release factors for emission to water, air and soil. The ECHA Guidance on emission estimation includes a link between these general ERCs and some worst case scenario emission factors, taken from the literature (ECHA, 2012b). The ERCs are thus designed to be conservative.

In determining the appropriate emission factors for the estimation of the emissions of DecaBDE to the environment throughout its life cycle, it is possible to assign these ERCs to identified uses of DecaBDE. This has already been done during registration by the registrants of the substance and they can be found in Section 8 of this report.

#### **Emission Scenario for plastics**

Many different types of substances are added to plastics depending on:

- The polymer from which it is made
- The form (pipe, sheet, film, etc.) of the finished plastic material.

These two factors determine:

- The substances added to the polymer to produce a plastics material of the expected performance for that end use and the additives used as processing aids
- The properties and fractional content of the particular additives used
- The likely service life of the plastics material.

From an emission scenario point of view, and taking into account that FRs may act as additives, it would be useful to know the polymer to which a FR is added, and the type of process used in the conversion of the plastics material, i.e. closed, open or partially-open, and possibly the industry sector or sectors in which the resulting product will be used. **Table 4-13** presents a list of plastics that have been associated with DecaBDE, based on literature review and information from consultation. It was not possible to derive the share of DecaBDE for each of these plastics, as quantitative information was scarce.

If we presume the process is using masterbatches, then the masterbatches could be thus made up to contain high concentrations of specific additives. These are then supplied to processors who disperse them into the main polymer matrix by simply mixing.

The volatility of DecaBDE is nonetheless limited and will be taken to be similar to that of the least volatile of plasticiser and antioxidant groups.

**Table 4-13** presents the situation regarding the types of processes associated with different plastics in the UK, according to 1994 data. Closed processes are those that take place in an enclosed system, with minimal exposure of the environment. They include injection and compression moulding of thermoplastics and thermosets, as well as sheet and profile extrusion. Partially open systems include extrusion coating and film extrusion, while open processes include calendering (OECD, 2009).

Table 4-13: Indicative breakdown of type of processes relevant to different types of plastics					
Plastic	% Closed	% Partially Open	% Open		
LDPE	12%	88%	0%		
HDPE	86%	14%	0%		
PP	52%	48%	0%		
Flex PVC	25%	49%	26%		
PS	62%	7%	31%		
EPS	100%	0%	0%		
ABS	92%	0%	8%		
PET	90%	0%	10%		
PA	90%	0%	10%		
Acrylics	30%	40%	30%		
PC	86%	14%	0%		
PU	100%	0%	0%		
UPR	41%	0%	59%		
Source: OECD (2009)					

## 4.4.2 Emissions from manufacturing process

No manufacturing of DecaBDE takes place in the EU; therefore, the estimation of emissions for this section is not relevant to this study. Calculation of emissions will begin at the formulation life cycle stage.

## 4.4.3 Processing (Industrial use)

## **Plastics - General information**

This stage includes the industrial processing of DecaBDE for plastics, and more specifically the handling, compounding (formulation and inclusion in the polymer matrix) and conversion (manufacturing of semi-finished or finished article) of plastics. These can be undertaken in separate facilities, but there are also some sites that perform both of them. The OECD ESD suggests adding the EF for compounding and conversion together for sites where compounding and conversion both take place (OECD, 2009). This gives the same result as calculating the emissions separately and then adding them together. Therefore, it will be assumed in this report that the compounding and the processing take place at distinct facilities and stages.

The major properties considered for the determination of the emission factors are particle size and volatility. The particle size affects the loss of solids, and the threshold value is 40  $\mu$ m. Volatile losses can be related to the vapour pressure, ideally at the temperature of the operation being considered.

## Equations for estimating emissions

The total EU wide emission from formulation (compounding) and processing (conversion) of plastics can be estimated using the following equations:

$$RELEASEtot_{polymer, \frac{for}{proc}, air} = \frac{F_{\underbrace{form}}}{100} \times Qtot_{polymer} \times 1000$$
[3]

$$RELEASEtot_{polymer, \frac{for}{proc}, water} = \frac{F_{form}}{100} x \ Qtot_{polymer} \ x \ 1000$$
 [4]

#### Where:

 $RELEASEtot_{polymer, \frac{for}{proc}, air}$  = total emission to air from the formulation or conversion (processing)

lifecycle stages (kg/y)

 $RELEASEtot_{polymer, for \ proc}$  = total emission to water from the formulation or processing lifecycle stages (kg/v)

 $F_{rac{form}{proc},air}$  = emission factor to air for the formulation and processing lifecycle stages (%)

 $F_{\frac{form}{proc},water}$  = emission factor to water for the formulation and processing lifecycle stages (%)

 $Qtot_{polymer}$  = total amount of additive used in a polymer type in the EU each year (t/y)

There are three possibilities in the emission scenarios that can be explained as follows:

Processing (compounding) only site:

$$F_{formulation,air} = F_{handling,air} + F_{compounding,air}$$
 [5]

$$F_{formulation,water} = F_{handling,water} + F_{compounding,water}$$
 [6]

Processing (conversion) only site:

$$F_{processing,air} = F_{conversion,air}$$
 [7]

$$F_{processing,water} = F_{conversion,water}$$
 [8]

Combined formulation/processing site:

$$F_{\underline{form}, air} = F_{handling, air} + F_{compounding, air} + F_{conversion, air}$$
 [9]

$$F_{\frac{form}{proc},air} = F_{handling,water} + F_{compounding,water} + F_{conversion,water}$$
[10]

Where:

 $F_{handling,air}$  = emission factor to air for materials handling (%)

 $F_{handling,water}$  = emission factor to water for materials handling (%)

 $F_{compounding,air}$  = emission factor to air for compounding (%)

 $F_{compounding,water}$ = emission factor to water for compounding (%)

 $F_{conversion,air}$  = emission factor to air for conversion (%)

 $F_{conversion,water}$  = emission factor to water for conversion (%)

 $F_{formulation,air}$  = emission factor to air for formulation (%)

 $F_{formulation.water}$  = emission factor to water for formulation (%)

 $F_{processing,air}$  = emission factor to air for processing (%)

 $F_{processing,water}$  = emission factor to water for processing (%)

 $F_{rac{form}{proc},air}$  = emission factor to air for combined formulation and processing (%)

 $F_{\frac{form}{proc},water}$  = emission factor to water for combined formulation and processing (%)

## Emission factors for handling and plastics compounding

Initially some emissions will be to the atmosphere, but ultimately all particulates will be removed or settled, and vapours will condense to some extent resulting in losses to both solid waste and waste water (via aqueous washing). It will be assumed that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

Physicochemical properties of DecaBDE show a particle size < 5  $\mu$ m (ECB, 2002), which is less than 40  $\mu$ m. This implies that there is increased potential for solid loss. Based on the vapour pressure of the substance (4.63·10<sup>-6</sup> Pa), it is classified in the low volatility group. Therefore, the Emission Factors that will be given, according to the OECD ESD (OECD, 2009) for plastics (FRs) are:

 $F_{handling,air} = 0\%$ 

 $F_{handling,water} = 0.6\%$ 

 $F_{compounding,air} = 0.001\%$ 

 $F_{compounding,water} = 0.051\%$ .

## Emission factors for plastics conversion process

These losses will initially be to air at elevated temperature. However, subsequent condensation could result in losses to liquid waste. As a worst case, it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

For an open process-solid articles, low volatility:

$$F_{conversion,water} = F_{conversion,air} = 0.005\%$$

For an open process-foam articles, low volatility:

$$F_{conversion,water} = F_{conversion,air} = 0.01\%$$

For a partially open processes, low volatility:

$$F_{conversion,water} = F_{conversion,air} = 0.003\%$$

For a closed process, low volatility:

$$F_{conversion,water} = F_{conversion,air} = 0.001\%$$

For processing significantly in excess of 200°C, the above emission factors should be increased by a factor of 10 (OECD, 2009). Conversion of plastics frequently requires temperatures in excess of 200°C, depending on the melting point of the plastic (RIKZ, 2000). The OECD ESD does not specify what "significantly in excess" means and the melting points of various plastics can range from around 100°C (for PE) to over 200°C (nylon). As a conservative approach, it will be assumed that all plastics conversion takes place at temperatures above 200 °C. Therefore, the emission factors mentioned above will be:

For an open process-solid articles, low volatility:

$$F_{conversion,water} = F_{conversion,air} = 0.05\%$$

For an open process-foam articles, low volatility:

$$F_{conversion,water} = F_{conversion,air} = 0.1\%$$

For a partially open processes, low volatility:

$$F_{conversion,water} = F_{conversion,air} = 0.03\%$$

For a closed process, low volatility:

$$F_{conversion.water} = F_{conversion.air} = 0.01\%$$

## Calculation of emissions

Detailed results of the estimation of potential releases of DecaBDE during industrial processes can be found in the relevant tables in the Confidential Annex.

As expected, the total emissions to water are higher than those to air. The total quantities released to water during compounding are < 3 t/y in the low volume scenario. This quantity is equivalent to that reported by VECAP before 2008 for all its applications (including textiles).

The calculated emissions to water during handling of the substance are higher than those from the actual compounding process and are < 20 t/y in the low volume scenario. This is calculated on the basis of no RMMs being in place.

To estimate the total emissions to air and water during the production of plastic articles for the low volume and the high volume scenario, it was decided to calculate the total emissions, as if all DecaBDE was treated in a single type of process. The exact breakdown of plastics to specific process types is unknown. In reality, based on the description of the processes, it seems that 'open' and 'open foam' processes are not too relevant to DecaBDE, with 'closed' and 'partially open' having a higher share. According to the OECD ESD, thermoplastics may be treated in closed, partially open or open processes, while thermosetting resins are mainly treated in closed ones (OECD, 2009). In a 2000 report for the Dutch Ministry of Transport (RIKZ, 2000) it is mentioned that all processing of plastics takes place in closed systems.

The emissions to both air and water during conversion have been calculated between 1 and 5 t/y for the low volume scenario.

#### Textiles - General information

Information coming from (OECD, 2004) describes the emission scenario document on the textile processing industry. It describes the processes of the life cycles stages "industrial and professional use" for all types of chemicals, and the emission estimations to local surface water and air.

Finishing agents such as coating and carpet backing and binders remain on textiles substrates. Air emissions are a minor but not negligible source of pollution. Most of the chemicals and auxiliaries are released to waste water. Some chemicals and auxiliaries (such as DecaBDE) create an effect on the textile and are fixed in a physical way on the fibres. Only a small amount of these substances will be found in the effluent or off-gas.

Total emission of the substance to water in EU level

The ESD on textiles does not mention calculation of losses during handling of the material. However, since the handling stage is the same in textiles as in plastics (i.e. opening and emptying of bags), the same emission factors used for plastics are going to be used in order to estimate emissions during handling of DecaBDE for textile use. It is assumed that workers with the same skill would perform the task and that similar technology is used. Emissions to water during handling of DecaBDE can be found in the Confidential Annex.

For estimation of the releases during the coating process, the following equation can be used.

```
Elocal_{water} = \{Q_{textile} \ x \ F_{product} \ x \ Q_{product} \ x \ C_{substance} \ (1 - F_{fixation})\} + \{Q_{textile} \ x \ F_{product} \ x \ Q_{product} \ x \ C_{substance} \ x \ F_{residual \ liquor}\} [11]
```

#### Where:

 $Q_{textile}$  = mass of textile processed per day (t/d<sup>1</sup>)

 $F_{product}$  = Fraction of fabric treated with one auxiliary, basic chemical or dyestuff

 $Q_{product}$  = mass of auxiliary/basic chemical/dyestuff preparation per mass of fabric (kg/t)

 $C_{substance}$  = content of active substance in preparation of auxiliary, basic chemical or dyestuff

 $F_{fixation}$  = degree of fixation

 $F_{residual\ liquor}$  = amount of residual liquors

 $Elocal_{water}$  = local emission of substance per day to waste water

For coating, approximately 99% of coating liquors remains on the textile.

The degree of fixation in this case is  $F_{fixation} = 1$  (OECD, 2004).

The quantities of DecaBDE used annually in textiles have been estimated in Section 3.6. The term  $\{Q_{textile} \ x \ Q_{product} \ x \ C_{substance}\}$  in Equation [11] actually calculates that quantity. The Emission Factor  $F_{product}$  in the OECD ESD is considered to be 1, because the whole fabric is treated with DecaBDE.

The most important parameters seem to be the degree of fixation and the amount of residual liquors. These depend on the affinity of the chemical to the fibre, liquor ratio, temperature, time, pH, additives, kind and quantity of rinsing processes, etc. Therefore, thorough knowledge about optimum conditions is necessary to minimise losses to the wastewater. In any case, since the formulation is expected to remain on the fabric, in order to perform its function, the degree of fixation is 1, meaning that the first term of Equation [11] is zero. For a realistic worst case estimation,  $F_{residual \, liquor} = 0.01$  would be a default value (assuming that this 1% corresponds to the loss of formulation due to residual liquors).

Detailed results on the releases of DecaBDE to waste water during finishing of textiles, using coating processes, can be found in the Confidential Annex.

The total annual releases to waste water from textile finishing facilities, are, therefore < 40 t/y for the low volume scenario. These quantities are much higher than those reported by VECAP, but it must be noted that they are calculated before wastewater treatment (or other RMMs) takes place.

Total emission of the substance to air in EU level

Equation [12], taken from the OECD ESD for textiles (OECD, 2004), was used to calculate emissions to air from textile finishing processes.

$$Etotal_{air} = Q_{textile} x Q_{product} x F_{product} x fs$$
 [12]

Where:

 $Q_{textile}$  = mass of textile processed per day (t/d)

 $Q_{product}$  = mass of auxiliary/basic chemical/dyestuff preparation per mass of fabric (kg/t)

 $F_{product}$  = fraction of fabric treated with one auxiliary, basic chemical or dyestuff

fs = substance emission factor of auxiliary/basis chemical/dyestuff

 $Etotal_{air}$  = total emission of substance per day to air

Detailed results of the calculations can be found in the Confidential Annex. Total annual emissions to air, before abatement measures are taken into account, have been estimated on <20 t/y for the low volume scenario. These emissions are considered high, especially taking into account that DecaBDE is applied on the textile in an emulsion, therefore no dust generation is expected. Furthermore, the low volatility of the substance means that releases due to volatilisation are minimal. It is more probable, therefore, that emissions to air would be much lower than those calculated here, probably in the order of a few kg/y.

#### Overall emissions during industry use

The following table summarises the calculations for the releases during industrial use of DecaBDE. For confidentiality reasons, the releases are presented as ranges. The exact quantities can be found in the Confidential Annex.

Table 4-14: Emissions to the environment during industrial use of DecaBDE							
	Emissions	to air (t/y)	Emissions to	water (t/y)			
	High volume scenario	Low volume scenario	High volume scenario	Low volume scenario			
Handling of DecaBDE	See Confidential	0	See Confidential	< 50			
Plastics compounding	Annex	< 0.1	Annex	< 3			
Plastics conversion		< 3		< 3			
Total plastics (excl. handling)		< 3		< 5			
Textile finishing		< 15		< 40			
Total		< 20		< 100			

## **Application of Risk Management Measures**

The total emitted quantities of DecaBDE during industrial use are higher than what has been reported by industry, mainly because in this report the presence of RMMs was not taken into account. The efficiency of such measures is what will determine the actual amount of DecaBDE that actually reaches the environment. A mathematical model capable of taking RMMs into account in order to calculate DecaBDE emissions to the environment would be desirable.

In order to have an idea of the RMMs that the formulator/compounder companies could already be carrying out, a description of the main individual RMMs is presented. It is assumed that substitution by less hazardous substances has been considered before starting the risk assessment process. General categories of RMMs, as described in CEFIC's RMM Library are (CEFIC, undated):

- Product-substance related; measures changing the chemical or physical profile of the substance or adapting the packaging
- Product safety / advice; changing appearance, colour, odour or providing safety advice
- Process control /change; e.g. technical solutions to control exposure
- Ventilation control;
- General dilution ventilation;
- Organisational; e.g. management systems, training, supervision
- Good hygiene practices and housekeeping;
- Personal protection equipment, e.g. gloves, goggles, respirators
- First aid measures.

It is important that these are used from the top down, so as not to create confusion when carrying out occupational risk assessments. Within this overall structure, it is believed that all RMMs (and OCs) for the control of exposure to consumers and the environment will fit (CEFIC, undated).

The RMMs applied by the industry were not specified during consultation. In order to calculate emissions to the environment after abatement, appropriate RMMs found in CEFIC's RMM Library were selected. For airborne emissions high efficiency air filters with an efficiency of 99% are expected to be used. Filtration is expected to be used on the industrial site to control emissions to water. This method has a minimum efficiency of 50% and a maximum of 99.99%, according to the CEFIC Library (CEFIC, undated). It is possible that a combination of RMMs is being applied, thus increasing the overall efficiency. A guidance published by VECAP on how to minimise losses from the handling of DecaBDE proposes a number of 'good practices' that should be followed, including the use of filters when emptying the packages, clean-up methods and general operational conditions (VECAP, undated). This brochure expects that RMM efficiency for both air and waste water streams

is 99% and is the value that will be used for the treatment of emissions to water. Some examples of such good practices are (VECAP, undated):

- Focus on empty packaging and make sure that collected solid wastes are sent to controlled chemical landfills, while waste water should be treated in an appropriate facility
- Use of local exhaust ventilation when emptying polymer additives. Filters should be disposed of as chemical waste
- Dry cleaning is the preferred way for cleaning since most additives are insoluble to water
- Maintain training programmes for workers.

The resulting effluent is then led to an industrial waste water treatment plant. The reported degree of PBDE removal in an Australian WWTP is 99% (Eljarrat & Barcelo, 2011). It can be assumed that this would be the efficiency of WWTP in Europe. PBDEs are removed through sedimentation, so are expected to be present in the sewage sludge. A fraction of the sewage sludge may be deposited to agricultural soil. The percentage of sewage sludge that was used in agriculture was 39%, using data from years 2003 – 2007 (Milieu Ltd., WRc and RPA , 2009). This could mean that there is a potential of releasing DecaBDE to agricultural soil.

**Table 4-15** presents the final emissions of DecaBDE from industrial processes, after the application of RMMs and compares them to the estimated emissions reported by VECAP (VECAP, 2013). For confidentiality reasons, the releases are presented as ranges. The exact quantities can be found in the Confidential Annex.

Table 4-15: Emissions to the environment during industrial use of DecaBDE after application of RMMs							
	Emissions to air (t/y)			Emissions to water (t/y)			
	High volume scenario	Low volume scenario	VECAP	High volume scenario	Low volume scenario	VECAP	
RMM efficiency	See	0.99	Unknown	See	0.99	Unknown	
Emissions before RMM	Confidential	< 20	Unknown	Confidential	< 100	Unknown	
Emissions after RMM	Annex	< 0.2	*	Annex	< 1	*	
Specific emissions (g/t)	< 50	g/t	12 g/t	< 150 g/t		25 g/t	

<sup>\*:</sup> Total VECAP emissions for 2012 include emissions to air, water and soil and were estimated as <0.3 t/y Source: (CEFIC, undated), (VECAP, 2013)

The specific emission would then be < 150 g/t, which is higher than the emission factor from VECAP's estimations (VECAP, 2013). If DecaBDE emissions to waste water were treated at a WWTP, 99% of them are expected to exit in the sewage sludge. Assuming a 39% usage of sludge in agricultural soil, it is possible that < 0.5 t/y of DecaBDE are ultimately emitted to soil in the low volume scenario.

Comparing the specific emissions (i.e. the emissions of DecaBDE per imported tonne) calculated in this report and those estimated by VECAP, the specific emission to air that was calculated in this report is higher than what was reported by VECAP and the same applies to the specific emission to water.

The reasons for this discrepancy can be:

- Different RMMs applied. For the estimation of the abatement achieved through RMMs, individual technical RMMs were used, without taking into account combinations of RMMs or other measures (such as good manufacturing practices). This might result in a higher efficiency of the RMMs that were used by VECAP. It must be noted that VECAP claims that participating companies in this voluntary agreement (which in 2012 accounted for 84% of the total quantities sold by its members) are committed to following "best practices" in their operations (e.g. dry cleaning instead of rinsing of spilled powder), meaning that they probably use very low emission factors in their calculations and higher RMM efficiency coefficients
- The emission factors used in this report were the default ones proposed in the OECD ESD for plastics and for textile finishing. They have not been modified to be specific for DecaBDE

## 4.4.4 Article service life

#### **Plastics**

It depends on the additive whether during the service life it is destroyed or entirely released. DecaBDE is a functional additive, which means that it will have to remain in the material in order to provide the desired effect. Therefore, it should not be completely destroyed or released.

Loss of additives over the service life of polymers can be considered to occur through volatilisation to air and leaching to water.

Due to the fact that polymers are used widely the life emissions are considered on a regional basis rather than a local basis. Some of the emission factors also include particulates caused by abrasion/degradation of the plastic. Ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down; therefore, this will be assumed to be released to water. For the outdoor use of plastics, emissions to soil have to be taken into account.

The yearly emissions of additives during the service life of plastics can be estimated from the following equations (OECD, 2009):

$$RELEASEtot\_STST_{polymer,air} = \frac{F_{servicelife,air}}{100} x Qtot_{polymer} x 1000$$
[13]
$$RELEASEtot\_STST_{polymer,water} = \frac{F_{servicelife,water}}{100} x Qtot_{polymer} x 1000$$
[14]
$$RELEASEtot\_STST_{polymer,soil} = \frac{F_{servicelife,soil}}{100} x Qtot_{polymer} x 1000$$
[15]

#### Where:

 $RELEASEtot\_STST_{polymer,air}$  = annual total release of the substance to air over the service life of the product at steady state (kg/y)

 $RELEASEtot\_STST_{polymer,water}$  = annual total release of the substance to water over the service life of the product at steady state (kg/y)

 $RELEASEtot\_STST_{polymer,soil}$  = annual total release of the substance to soil over the service life of the product at steady state (kg/y)

 $F_{servicelife,air}$  = emission factor to air over service life of the polymer product (%)

 $F_{servicelife,water}$  = emission factor to water over service life of the polymer product (%)

 $Qtot_{polymer}$  = annual total input of the substance into the polymer product (tonnes/y) Indoor service, leaching to liquid waste  $F_{servicelife,water}$  = **0.05%** over lifetime Indoor service, volatility to atmosphere  $F_{servicelife,air}$  = **0.05%** over lifetime

Outdoor service, leaching to waste water  $F_{servicelife,water} =$ **0.16%** x Tservice Outdoor service, volatility to atmosphere  $F_{servicelife,air} =$ **0.05%** over lifetime Outdoor service, leaching to soil  $F_{servicelife,soil} =$ **0.16%** x Tservice (ECHA, 2012b)

The breakdown of DecaBDE in the various plastics and the relevant applications is not known. The indoor applications are clearly relevant to DecaBDE and some quantities might be released to the indoor environment. During the literature review, some outdoor applications were also identified (see **Table 3-22**), but consultation did not confirm the use or provide any information on how much DecaBDE is used in these applications. The EU RAR estimated that the share of plastics containing DecaBDE which was used outdoors was less than 0.1% (ECB, 2004), but a 'worst case' of 10% outdoor use was also considered (ECB, 2002). This document was published before the restriction of the use of DecaBDE in EEE by the RoHS Directive. Electrical and Electronic Equipment are mainly used indoors. It is expected that, after the restriction, the share of outdoor uses has increased. The available information does not allow for the estimation of an exact number, but the 'worst case' of 10% outdoor use from the initial EU RAR will be used, even though the update used a much smaller number.

It could be argued that, due to the low volatility of DecaBDE at ambient temperature, releases to air through volatilisation are insignificant. The only expected emissions to air should be in particulate form after wear of the plastic article. In that case, they would be expected to mostly deposit on surfaces and then rinsed to wastewater. The calculations in the current report did not take this into account, presenting a conservative approach. The estimated emissions were < 5 t/y.

The estimated emissions to air during service life of plastic articles are < 3 t for the low volume scenario. The estimated emissions to waste water are < 10 t for the low volume scenario. Finally, the estimated emissions to soil are < 10 t for the low volume scenario. These emissions are the total emissions over the whole service life of the plastic articles. For an assumed service life of 10 years, one tenth of these will be emitted each year. In a steady state, however, during which the quantities in circulation remain constant, the calculated numbers are equal to the annual emissions of DecaBDE from plastic articles in the market.

Outdoor applications are responsible for more than 75% of emissions to waste water and for all the emissions to soil. If the share of outdoor applications is lower than the assumed 10%, the total emissions will be lower.

An alternative method for calculating the releases of DecaBDE from plastic articles is based on the area of the article containing it and the article's lifetime. This is described in Annex IV of the OECD ESD for plastics. Emission factors for this method were not found, so no calculations were made with it (OECD, 2009).

Detailed results for the emissions of DecaBDE from plastic articles to air and water during its service life can be found in the Confidential Annex.

## **Textiles**

The estimation of emissions from the entire service life of textiles can be calculated using the following equation.

## Where:

 $Qtot_k$  = annual input of the substance in article k (t/y)  $Tservice \ k$  = service life of article k (y)  $F_j$  = fraction of substance emitted over one year during service life to compartment j Nd = emission duration per year  $Etot_{k,j}$  = local emission to compartment j

The most important distinction (for environmental release) among the applications of textiles treated with DecaBDE is whether they are used indoors or outdoors, as the outdoor emissions cannot be easily contained and may also end up in the soil or water, without necessarily passing through an abatement system such as a municipal WWTP.

The majority of the applications for textiles that may be treated with DecaBDE are indoor uses, e.g. upholstered furniture, contract furniture (e.g. seating for public buildings), curtains, etc. The only identified outdoor application is in transportation. The confirmed quantities in this use are small compared to the total consumption of DecaBDE (<200 t/y which account for less than 10% of the total use of DecaBDE in textiles in the low volume scenario). Other objects (e.g. furniture) can also be used outdoors, either continually or intermittently. For that reason, a 'worst case' scenario uses the assumption that 90% of articles containing DecaBDE are used indoors, while the remaining 10% are used outdoors.

The OECD ESD for textiles does not have default EFs for emissions during service life. The EFs proposed by ECHA in the guidance for environmental exposure estimation were used instead. The most appropriate ERC for indoor uses of textiles containing DecaBDE is ERC 11a which, according to ECHA's Guidance for environmental exposure estimation corresponds to an emission factor of 0.05% (or 0.0005) to air and water (ECHA, 2012b). Similarly, for wide dispersive outdoor use, ERC 10a is the most appropriate. ERC 11b is not considered relevant because it presents an unrealistic situation. Most of the textile products associated with DecaBDE are not washable, in the way that clothes are (i.e. they are not normally put in a washing machine). Furthermore, identified applications (e.g. furniture, curtains) are mentioned in the description of ERC 11a, as examples. In addition, the release factor of 100% for ERC 11b indicates that all the quantity of DecaBDE is released during service life. This conflicts with the function of the substance, since it has to remain in the substrate in order to be effective in case of a fire (ECHA, 2012b). However, some articles might still be washed, albeit in a much lower frequency than typical textile products. The EU RAR estimates that only 2% of the textiles containing DecaBDE are subject to washing and assumes an emission factor to waste water of maximum 0.05% over the service life (ECB, 2004).

The following values have been selected for the parameters of Equation [16]:

- $F_{qir}$  = **0.005**% for both indoor and outdoor use
- $F_{water}$  = **0.005**% for indoor and **0.16**% for outdoor use
- $F_{soil}$  = **0%** for indoor and **0.16%** for outdoor use
- $Qtot_k$  = variable. This depends on the quantities of DecaBDE in textile articles, as have been estimated earlier and the breakdown of these quantities in indoor and outdoor applications
- y = 10
- Nd = 365. However, it will not be used in the calculations, as this will give a daily emission, while the annual emissions are suitable for the purposes of this study.

It is mentioned in the ECHA Guidance document R.16 (2012b) that the proposed emission factors represent a worst case scenario and have been taken from the OECD ESD on plastic additives.

The estimated emissions to air during service life of textile articles are < 3 t for the low volume scenario. As commented in the previous section on plastic articles, it could be argued that, due to the low volatility of DecaBDE at ambient temperature, releases to air through volatilisation are insignificant. The only expected emissions to air should be in particulate form after wear of the plastic article. In that case, they would be expected to mostly deposit on surfaces and then rinsed to wastewater. The calculations in the current report did not take this into account, presenting a conservative approach.

The estimated emissions to waste water are < 10 t for the low volume scenario. Emissions to water due to washing of textiles are < 0.1 t for the low volume scenario. Finally, the estimated emissions to soil are < 10 t for the low volume scenario. Outdoor applications are responsible for more than 75% of emissions to waste water and for all the emissions to soil. These are the total emissions over the whole service life of the textile articles. For an assumed service life of 10 years, one tenth of these will be emitted each year. In a steady state, however, during which the quantities in circulation remain constant, the calculated numbers are equal to the annual emissions of DecaBDE from textile articles in the market.

Exact results of the calculations for the emissions during the service life of textile articles containing DecaBDE can be found in the Confidential Annex.

#### **Overall** emissions

The following **Table 4-16** presents the calculated annual emissions of DecaBDE to air and water during the service life of the articles that contain it. They are shown in ranges but exact numbers can be found in the Confidential Annex.

Table 4-16: Emissions to all the environmental compartments during service life of DecaBDE							
		Emissions to air (t/y)		Releases to	water (t/y)	Emissions to	o soil (t/y)
		High volume scenario	Low volume scenario	High volume scenario	Low volume scenario	High volume scenario	Low volume scenario
Dia ati a	EU manufactured		< 3		< 10	See Confidential Annex	< 10
Plastics	Imported articles	See	< 0.5	See	<1		< 1
	Total plastics		< 3		< 10		< 10
Tautilaa	EU manufactured		< 3		< 10		< 10
Textiles	Imported articles	Confidential Annex	< 0.5	Confidential Annex	< 1		< 1
	Total textiles	Aillex	< 3	Aillex	< 10		< 10
	EU manufactured		< 5		< 20		< 20
Total	Imported articles		< 0.5		< 2		< 2
	Total		< 5		< 20		< 20

The above figures present the estimated annual emissions of DecaBDE from products containing it during their service life. They account for the total stock of DecaBDE in the society at any given time,

assuming a steady state. The following **Table 4-17** presents the total emissions to all environmental compartments.

Table 4-1	Table 4-17: Total emissions to the environment during the service life of DecaBDE					
		Emissions (t/y)				
		High volume scenario	Low volume scenario			
	EU manufactured	See Confidential Annex	< 20			
Plastics	Imported articles	1	< 2			
	Total plastics		< 20			
	EU manufactured		< 20			
Textiles	Imported articles		< 2			
	Total textiles		< 20			
	EU manufactured		< 40			
Total	Imported articles		< 4			
	Total		< 40			

A study by Alonso et al. (2007) (mentioned in Section 4.2.7) estimated the emissions of DecaBDE from urban sources based on measured concentrations of the substance in sewage sludge from 25 WWTP in Spain. Their result of 6.16 mg per inhabitant per year for DecaBDE could be extrapolated for the whole EU (population calculated 500 million). The outcome is roughly 3.08 t/y. This is lower than the total calculated emissions in this report, which could be attributed to the conservative approach followed in this study regarding the quantities and the use of default (worst-case) emission factors instead of tailoring them to DecaBDE.

## 4.4.5 Waste stage

The emissions during the waste stage of DecaBDE are subject to a lot of uncertainty, even more than in the previous life stages. Apart from the uncertainties regarding the actual imported quantities and the breakdown to the various uses, further uncertainties are the breakdown of waste to different treatment methods (recycling, incineration or disposal) and also the selection of the proper emission factors and equations. The OECD ESD document for plastics does not consider emissions of FRs from the waste stage to be significant, while there is no mention of such a model to the OECD ESD document for textiles. Furthermore, there are different emission factors found in the literature and they vary significantly, as will be discussed below (ECB, 2004; ECHA, 2012c; Earnshaw, et al., 2013).

#### Loss in waste during package emptying

The OECD Emission Scenario Document on plastics assumes a 1% loss of solid additives, that remain in the packaging after emptying (OECD, 2009). These quantities may enter the solid waste stream, according to VECAP. However, the same source comments that the industry which uses DecaBDE has taken action to minimise losses during handling of the product, in order to also avoid high emissions to the environment. According to their latest report, the quantities of DecaBDE disposed of along with the empty packaging were in the range of 60 g/t in 2012 (an emission factor of 0.06%) (VECAP, 2013). This corresponds to roughly <500 kg/y for the low volume scenario, taking into account all the quantities of DecaBDE, since handling of packages of the substance are part of all uses, regardless of the substrate (plastic or textile). If the 1% loss is assumed, then between 10 - 250 t/y would be lost in that stage. In either case, the collected packaging waste is treated as hazardous waste in special facilities, so no emissions to the environment are envisaged.

## Waste disposal practices

The plastics industry uses little, if any, process water. Its use is predominantly for cooling equipment when it is used in closed water systems, recirculating between chillers and the processing equipment. The only other use of water, of significance in this context, is for rinsing of plant surfaces.

Additives are expensive in the plastic industry, and cost many times more than the matrix polymers. Users of such additives are therefore very careful to minimize any waste. Residues in the delivery containers generally join the general waste stream and are most likely to be disposed of to landfill.

The situation regarding the disposal and recycling of plastics is currently in a state of flux. New legislation with respect to plastics recycling is proposed throughout the European Union. Consequently, the current waste streams do not necessarily reflect the future situation.

As mentioned earlier, the quantities of textiles recycled are relatively small, with the vast majority of textile waste being incinerated or landfilled. In that case, the situation would probably be similar to that for plastics.

## Recycling

Mechanical recovery of plastic waste may take one of several forms but this is an evolving situation, which is likely to change in the future:

- a) The articles may be sold to specialist companies which clean, grind and market them as clean low grade plastics material. The material may be classified into polymer type and, at the highest level, the materials may be compounded into other polymers/plastics materials and sold as well specified materials which compete against virgin plastics.
- b) The articles may be collected by a specialist manufacturer of plastics products who, after cleaning and compounding, processes them into a particular product. Examples of this include the conversion of some waste from large distributors into plastic film and the use of spent PET bottles to produce polyester staple fibre for use as an insulating filler for clothing, duvets and pillows, etc.
- c) Certain industries, notably the automotive sector, are being encouraged to take back their post-consumer waste and reuse the materials within the same industry.

In many of these processes, the thermoplastic material is melted and reused. The release of additives would be expected to be similar to that which results from the conversion of plastics compounds made from virgin polymers. It is not known whether additional additives are used when recovered plastics articles are used as the feedstock for particular products. Plastic articles from recycled plastic have been found to contain several different FRs, which were probably originally present in the waste plastic.

Information available from ECHA Guidance, shows that it is possible that a relatively large amount of additive could be released during a shredding process, showing a release factor from shredding to air of  $F_{shredding,air}=0.1$  for plastics and 0.05 for rubber. This EF was derived from expert judgement. On the other hand, the shredding can be described by ERC 12a, namely "Industrial processing of articles with abrasive techniques (low release)". The default emission factor to air for this category of operations, which includes cutting or grinding of textiles and plastics, is 2.5% (or 0.025). This emission factor is considered conservative and it also does not take the presence of RMMs into account.

The final amount of DecaBDE released during shredding across Europe recyclers' installations is difficult to estimate but it cannot be considered negligible. Assuming the 10% emission factor mentioned by the Guidance document, the emissions of DecaBDE to air from plastics and textiles in recycling facilities is between 10 - 250 t/y. Assuming the use of dust filters, with an efficiency of 99%, the actual emissions are between 0.1 and 2.5 t/y. If a 2.5% EF is used, initial releases are 2.5 - 100 t/y and the emissions after abatement would be 0.025 - 1.0 t/y. For the calculation of total emissions, and since a conservative approach has been followed for the most part of this report, the higher emissions from recycling will be used.

Exact results of the calculations for the emissions during shredding of plastic and textile waste containing DecaBDE can be found in the Confidential Annex.

The EU RAR (based on monitoring data and expert judgement) calculated an upper limit of emissions to air from recycling of plastics from EEE equal to 8.8 kg/y (ECB, 2004). These numbers cannot be readily compared because each study used different starting quantities. Nevertheless, the starting quantity used in the EU RAR (4,615 t/y) was higher than what was used in this report. The effective emission factor used in the EU RAR is  $1.9 \cdot 10^{-4}$ %. The final EFs used in this report (after abatement) are 0.1% and  $2.5 \cdot 10^{-2}\%$  which are both much higher (two to three orders of magnitude) than the one used by the EU RAR.

## Landfilling

A study on European starling (*Sturnus Vulgaris*) eggs collected in 2009, 2010 and 2011 in Canada, has reported the concentrations on PBDEs in these eggs from birds in urban industrial areas, landfills and rural areas located at different distances from urban centres. The date reveal that PBDE median concentrations for landfills was 28-280 ng/g ww in eggs; there was a strong correlation in eggs from landfill sites and the human population density of the metropolitan region that the landfill served. This supports the hypothesis that landfills are not only a sink of PBDEs but also a source (Chen, et al., 2013).

In this context, estimates are made of possible releases of an additive in a landfill. It is possible that, ultimately, degradation of the plastic material leads to the release of the remaining additives contained within it. A prediction whether or not this breakdown will occur cannot be made because it depends on the conditions in the landfill as well as the properties of the plastic material. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount will be released. ECHA's guidance document for the estimation of emissions from the waste stage mentions an emission factor of 3.2% of loss to water over 20 years due to leaching (which corresponds to a 0.16% annual EF). This release factor is the highest one for plastic additives, taken from the OECD ESD. This is high, considering that DecaBDE is practically insoluble to water.

The following equations and the emission factors found in ECHA's R.18 guidance document can be used (ECHA, 2012c):

$$RELEASEtot\_Landfill_{air} = \frac{F_{disposal,air}}{100} x Qtot_{landfill waste}$$
[17]
$$RELEASEtot\_Lanfill_{water} = \frac{F_{disposal,water}}{100} x Qtot_{landfill waste}$$
[18]
$$RELEASEtot\_Landfill_{soil} = \frac{F_{disposal,soil}}{100} x Qtot_{landfill waste}$$
[19]

#### Where:

 $RELEASEtot\_Landfill_{air} =$ annual total release of the substance to air from landfill over the waste stage (t/y)

 $RELEASEtot\_Landfill_{water} =$ annual total release of the substance to water from landfill over the waste stage (t/y)

 $RELEASEtot\_Landfill_{soil} =$ annual total release of the substance to soil from landfill over the waste stage (t/y)

 $F_{disposal,air}$  = emission factor to air from landfill (%)

 $F_{disposal,water}$  = emission factor to water from landfill (%)

 $F_{disposal,soil}$  = emission factor to soil from landfill (%)

 $Qtot_{landfill\ waste}$  = annual waste quantities (t/y)

The values of the emission factors are (ECHA, 2012c):

 $F_{disposal,air} = 0\%$ 

 $F_{disposal.water} = 3.2\%$  over 20 years

 $F_{disposal,soil}$  = **1.6**% over 20 years

It should be noted that the same ECHA guidance contains an illustrative example for the calculation of emissions of a plastic additive. The additive is of similar volatility to DecaBDE but has higher water solubility. The emission factor to the leachate of the landfill was 2.8·10<sup>-5</sup>%, based on a model using measured data of related substances (ECHA, 2012c). No such model is available for DecaBDE. However, use of the generic EF proposed in the guidance document (3.2% over 20 years) will grossly overestimate the emissions to water due to leaching.

The 2002 EU RAR on DecaBDE comments that leaching from plastics in landfills is not likely to take place, but erosion and wear of particles containing DecaBDE could constitute another transportation pathway for DecaBDE to the leachate. It was commented, however, that the release of DecaBDE through that route could not be calculated. The EU RAR has made some rough calculations regarding the releases from textiles that have been disposed, assuming an overall 2% particulate loss per year due to wear and tear, which is considerably higher than the other emission factors mentioned above. The report also comments that this calculation contains a high degree of uncertainty (ECB, 2002).

Sakai et al. (2006) state that atmospheric emissions from landfill are attributed to fugitive emissions of dust during transport, unloading and disturbance of waste. In general, there is no substance specific model for emissions from landfills. In the case of DecaBDE, which is insoluble to water, a lower emission factor would be more suitable.

Earnshaw et al. (2013) say that emissions of DecaBDE are mainly in particles, owing to the processes of physical abrasion, disintegration and weathering of c-DecaBDE containing products during their lifetime. BDE-209 has high LogKow ( $\approx$  9) and LogKoa ( $\approx$  17) values, so any gaseous emissions will likely partition to available particles.

Earnshaw et al. collected emission factors from various studies, for use in their model. The EF that was used in the worst case scenario was 0.1%. On the other hand, a  $10^{-4}$ % for emissions of DecaBDE in particles was used in the so called "realistic scenario". The study also considered one-off losses due to unloading of waste in the landfill and assigns an EF of  $10^{-3}$ %. Volatilisation loss from landfill is

likely to be limited. No emission factors for emission of DecaBDE to the leachate or to soil were provided (Earnshaw, et al., 2013). For that purpose, the "realistic" emission factor of 10<sup>-4</sup>% from Earnshaw will be used.

Using the "realistic" emission factors from Earnshaw et al. mentioned above, the one-off emissions to air from plastic and textile waste containing DecaBDE are < 0.05 t/y for the low volume scenario. The annual particulate emissions of DecaBDE to air from landfilled waste are < 0.005 t/y for the low volume scenario. The quantities are the same for emissions to water and soil, as the same emission factor is used.

If the conservative emission factor of 0.1% is used, the annual emissions to air would be d < 5 t/y for the low volume scenario. ECHA's 1.6% over 20 years can be used as a conservative emission factor for soil. This would give an annual emission to soil of < 5 t/y for the low volume scenario.

Exact results of the calculations can be found in the Confidential Annex.

## Incineration of waste

For incineration, following best environmental practices (BEP) organic substances will be destroyed so  $F_{disposal,air} = F_{disposal,water} = 0\%$ . There may still be residues of inorganic materials left in the ash, which will be disposed of as solid waste, but this is not relevant to DecaBDE. ECHA's guidance suggests an emission factor of 0.01% to air and water from incineration facilities for organic waste (ECHA, 2012c). It is also mentioned in the guidance that emissions from pre-treatment operations, such as shredding, are very small, compared to overall incinerator emissions, so they need not be calculated separately. The major concern in these processes, however, seems to be the formation of other hazardous substances such as PBDDs or PBDFs.

## 4.4.6 Other sources of release

Releases to the environment of additive in polymeric particulates caused by wear/weathering of polymers could also occur over the service life and at disposal of a product, but these releases are not considered further here.

# 4.5 Summary of estimated DecaBDE emissions

The calculated emissions, before emission abatement measures, are presented in the following table. The results are in ranges, but they can be viewed with more detail in the Confidential Annex.

Table 4-18: Emissions to the environment during the life cycle of DecaBDE after RMMs								
	Emissions	Emissions to air (t/y)		water (t/y)	Releases t	o soil (t/y)		
	High volume scenario	Low volume scenario	High volume scenario	Low volume scenario	High volume scenario	Low volume scenario		
Handling (textiles and plastics)		-		< 1		-		
Plastics compounding		< 0.001		< 0.1	See Confidentia I Annex	-		
Plastics conversion		< 0.05		< 0.1		-		
Textile finishing	See	< 0.5	See	< 1		-		
Service life - plastics articles	Confidentia I Annex	< 2.5	Confidentia I Annex	< 10		< 10		
Service life - textile articles		< 2.5		< 10		< 10		
Waste stage		< 1		< 0.1		< 0.1		
Total		< 5		< 20		< 20		

**Table 4-19** presents the emissions during manufacturing and service life, divided between quantities that have been imported in the EU in articles and quantities that have been imported in the EU as a substance. The former take only service life emissions into account and the latter both the manufacturing and the service life emissions.

Table 4-19: Imported quantities of DecaBDE and emissions to the environment (t/y)							
	High volume scenario			Low volume scenario			
	Textiles	Plastics	Total	Textiles	Plastics	Total	
Imported DecaBDE as substance	See Confidential Annex			< 5,000	< 5,000	< 10,000	
Imported DecaBDE in articles				< 500	< 500	< 1,000	
Emissions from manufacturing				<1	<1	< 2	
Emissions from service life of EU manufactured articles	See Confidential Annex			< 20	< 20	< 40	
Emissions from service life of imported articles				< 2	< 2	< 4	
Emissions from waste stage				< 0.5	< 1	< 1.5	
Total emissions				< 25	< 25	< 50	

The sources of the emissions are split almost evenly between plastics and textiles, with textiles contributing slightly more. The degree of uncertainty in these numbers is high, however.

## 4.6 Discussion

The releases calculated in the previous sections have a very high degree of uncertainty. They were made in order to create a possible picture, assuming "worst case" conditions, on what the releases of DecaBDE may be. The actual situation can be different than what is presented here for a number

of reasons. The findings of this study on emissions should be used with care to assess the effectiveness of a restriction. These reasons / the uncertainties in this report are:

- The quantities of DecaBDE currently imported and consumed in the EU. Information coming from official sources (e.g. EUROSTAT) does not agree with that reported by the industry (VECAP, registration dossiers). This is not something that is particular to this substance, but has been observed to occur in other cases as well
- The breakdown of DecaBDE to its identified uses. The most recent information for the split between plastics and textiles is roughly 50/50. Further breakdown among specific uses was not possible with the information collected during the project. This may affect the calculations for several reasons (e.g. whether DecaBDE is used in indoor or outdoor applications, what the lifetimes of the different articles are and how they are treated when they become waste)
- During consultation, it was discovered that downstream users of DecaBDE were moving away from the substance, both in the EU and in North America. The extent to which this phase out has affected the quantities used and the breakdown among the different uses is not known. It is expected that the actual quantities will be lower than what was assumed in this study
- Based on the previous point, the situation in Asia is not clear, but so far no phase out has been
  declared for DecaBDE. It is therefore possible that Asian companies continue to use DecaBDE in
  their articles, some of which may be sold in the EU. The quantities and DecaBDE content of such
  articles was not known and a future trend in the use of DecaBDE by Asian companies could not
  be identified
- Conservative assumptions were made for the estimation of emissions during service life of
  plastics and textiles containing DecaBDE. The share of articles used outdoors is unknown, so for
  textiles a 10% share was assumed, based on information received through consultation. For
  plastics a less informed assumption was made and a 10:90 split was decided as well. The EU RAR
  assumed that, in 2004, 0.1% of plastic articles containing DecaBDE was used outdoors, but this
  was before the RoHS directive took effect for DecaBDE
- Precise information on the fate of waste containing DecaBDE is not available. Assumptions were made based on the general situation for plastic and textile waste in Europe
- The emission factors that were used for the estimation of the releases of DecaBDE were mostly generic ones and not tailored to the substance, so they represent a worst case scenario. They are representative for more water soluble and volatile plastics additives than DecaBDE. It is very probable, therefore, that the estimated emissions in this report are overestimations
- There has been large variation in the emission factors during the waste stage, particularly for emissions during landfill
- No information was received by the industry regarding the Risk Management Measures that are applied during the processes involving DecaBDE. Based on RPA's experience and information found in the EU RAR, RMMs were selected for the purpose of estimating the final emitted quantities to the environment from industrial processes. These RMMs are probably used in the industrial facilities, but there may also be other measures in place, contributing to higher abatement efficiency

•	The study only discusses the emissions from use of DecaBDE from its use in plastics and textiles. Other uses that have been mentioned are in adhesives, coatings and inks. Current levels of use in these applications has not been confirmed through consultation.



## 5 Alternatives for DecaBDE

## 5.1 Overview of alternatives for DecaBDE

## **5.1.1** Alternatives for DecaBDE in plastics

## **Potential substitution strategies**

#### Overview

Past research into alternatives for DecaBDE in polymers provides useful insights into strategies that may be followed for the replacement of DecaBDE in plastics; nevertheless, previous research has largely focused on the use of the substance in plastics for E&E enclosures, which has now been addressed under the RoHS Directive.

Given the wide range of polymer materials that may currently be flame-retardant with DecaBDE (e.g. styrenics, polyamide, polyester, epoxy, PVC and polyolefin-based plastics), it has been asserted in the past that a universal FR solution cannot be assumed to be available, and the selection of the FR strategy has to be considered individually for each polymeric component (JRC, 2007). The UK HSE agrees in the Annex XV dossier for nominating DecaBDE as a PBT substance that the fire performance of polymers is the result of the particular combination of chemical FRs and other components of the polymer matrix such as fillers and plasticisers. Moving from one combination to another will have to be performed on a case-by-case basis meaning that plastic/polymer producers, compounders and masterbatchers will need to engage in R&D for the development of alternative combinations of FRs and additives that provide the required technical properties and fire performance for their product (UK HSE, 2012).

The Lowell Center for Sustainable Production (2005) recalls information from a 2003 Oeko Institute report that identified which complex products such as the plastic-based articles containing DecaBDE lend themselves to the following general substitution options.

## Replacement of DecaBDE at the substance level

There are a variety of substances that could theoretically be considered as alternatives to DecaBDE. The following categories of alternative FRs may be considered (Troitzsch, 2011) (Keml, 2005):

- Brominated FRs (BFRs): e.g. brominated epoxies, brominated polystyrene, decabromodiphenyl ethane (EBP), ethylene bis(tetrabromophthalimide), poly(pentabromobenzyl acrylate), tetrabromobisphenol-A (TBBPA), TBBPA carbonate oligomer, tris(bromoneopentyl) phosphate, TBBPA (2,3-dibromopropyl ether)
- **Chlorinated FRs**: e.g. chloroparaffins, hexachloroendomethylene tetrahydrophthalic acid, tris(chloropropyl) phosphate
- Organophosphorous FRs: these may include phosphines, phosphine oxides, phosphonium compounds, elemental red phosphorous and phosphates, e.g. bisphenol-A bis(diphenyl phosphate), cresyl diphenyl phosphate, dimethylpropane phosphonate, polyphosphonates, metal phosphinate, phosphorous polyol, resorcinol bis(diphenyl phosphate), tricresyl phosphate,

triphenyl phosphate. It is noted that in some cases phosphorous/halogen compounds are used to increase the effectiveness of the FR or act (in parallel) as plasticisers

#### **Substance**

Replacement with another FR substance

#### Substance + material

Replacement with another FR substance which can meet FR standards, if used with an inherently more FR resin

#### **Material**

Replacement of polymer with an inherently flame retardant material

#### **Article**

Fundamental changes to the characteristics of articles (e.g. separation of high-voltage components that need greater ignition protection from low-voltage components, or reduction of operating voltage requirements and therefore reduction of the need for FR enclosures)

Figure 5-1: Substitution strategies for DecaBDE in polymers (increasing complexity towards foot of pyramid) Source: Adapted from Lowell Center for Sustainable Production (2005)

- **Nitrogen-containing FRs**: e.g. ammonium polyphosphate, melamine cyanurate, melamine, melamine poly aluminium and zinc phosphates
- Inorganic FRs: e.g. aluminium hydroxide, magnesium hydroxide, red phosphorous (also in combination with a halogen-free FR (HFFR))
- Other: sulphonate salts, boron compounds, silicates, etc.

Replacement of DecaBDE might not necessarily mean a 1:1 replacement of the substance by an alternative FR substance. JRC explains that re-formulation strategies may involve the use of combinations of FRs with synergistic FR mechanisms and minimised smoke generation during the fire (JRC, 2007).

Some less conventional FR solutions can be found in the literature:

• Intumescent systems: these may often be allocated under the nitrogen-containing FRs or organophosphorous FRs or be described under a variety of names (e.g. "intumescent systems based on phosphorous/nitrogen compounds", "intumescent system based on ethylenediamino phosphate"). The mechanism of FRs based on intumescent technologies is to cause the plastic, when heated, to swell (intumesce) into a thick, insulating char that protects the underlying material from burning, by providing a physical barrier to heat and mass transfer. For

intumescent technologies, the Danish EPA suggests that solutions for polypropylene (PP) have been commercially available for many years, but they face both technical and economic viability challenges (Danish EPA, 2006)

• Nanocomposites: mesoporous silicate particles (MSP) are porous silica beads, which, when in use, interact with both the internal surfaces of the pores and the external surfaces of the particle due to the large size of the pores, thereby forming a physically cross-linked polymer-particle network. The network created by the MSP provides a char barrier during combustion that reduces flame intensity while simultaneously improving the mechanical performance of the polymer into which they are compounded. When used on their own, they will not typically achieve flame retardancy, but by replacing a portion of the FR loading with about 2 to 8% by weight MSPs, flame retardancy may be reached (US EPA, 2014).

According to the UK HSE, research into the use of nanocomposites has focused on plastics like polymethyl-methacrylate (PMMA), polypropylene, polystyrene, and polyamides (UK HSE, 2012)

• Expandable graphite: expandable graphite is an option that has been used for aircraft carpets. On exposure to fire, the graphite expands to over 100 times its original size producing a barrier effect. It has been used in thermoplastics and can be used in polyolefins in combination with another FR such as ammonium polyphosphate, magnesium hydroxide, chloroparaffins or red phosphorous (UK HSE, 2012).

Finally, another category of substances that work alongside FRs are **smoke suppressants**. These are generally systems that lead to the formation of glassy coatings or intumescent foams or dilution of the combustible material, which prevents further formation of pyrolysis products and hence smoke (Keml, 2005). Such systems are of particular relevance to transportation applications of DecaBDE. Molybdic oxide is one such substance and common FRs used alongside include aluminium hydroxide and magnesium hydroxide (Keml, 2005).

Replacement of DecaBDE at the substance and material level

Past research has demonstrated that drop-in replacement of DecaBDE by certain alternative FRs may be difficult and a simple reformulation may not be possible to allow the new compound to meet the required standards. Therefore, a more radical reformulation is needed, one where the substrate (polymer resin) needs to be changed for the new FR compound to meet the specifications of the final product.

Example replacement strategies include the following:

• Polymer blends: the replacement of DecaBDE in E&E enclosures stipulated by the RoHS Directive provides examples of such replacement strategies. Readily flammable polymers (e.g. HIPS or ABS) may be blended with less readily flammable polymers such as PC, PPO (also referred to as PPE) or polyphenylene sulphide (PPS). This enables lower FR loadings to be used with limited impact on other technical properties (UK HSE, 2012). The JRC also confirms that more expensive polymers such as PC, PPO and PPS (possibly in the presence of a fluorinated polymer (as synergist) so that halogen-free FR options also become possible) may indeed be used as substitutes to the combination of HIPS/DecaBDE/ATO or ABS/DecaBDE/ATO while achieving an acceptable processability and recycling properties (JRC, 2007).

Another option is layering where an article is produced using layers of highly FR filled polymer and low or non-flame retardant polymer. This apparently gives a similar level of fire performance as would be achieved if the entire polymer had been treated, while helping to retain the mechanical properties of the polymer (UK HSE, 2012)

• Use of inherently flame-retardant matrices: in its 2006 report, the Danish EPA confirms that the properties of the thermoplastic PES and PA cannot easily be obtained by use of other resins and so they may need to look into their replacement with matrices that are inherently flame-retardant (Danish EPA, 2006). Halogenated polymers such as PVC have FR properties because they release halogen radicals, which have the same effect during combustion as halogen radicals released from halogenated FRs. This effect can be enhanced by the addition of synergists such as ATO to halogenated polymer blends. Polymers that char, such as polyimides, polyaramides, liquid crystal polyesters, polyphenylene sulphide, polyarylenes and many thermosets also tend to have a greater resistance to fire. Where the base polymer has FR properties, depending on the end use, a sufficient level of fire performance may be achieved without the need for chemical FRs or much lower loadings may be required (UK HSE, 2012). KemI also mentions that systems, such as phenolics, have been developed without smoke suppressants additives, which practically do not release any smoke (KemI, 2005).

The Danish EPA (2006) mentions polymer materials that are inherently flame-retardant and which might be considered as a substitute to DecaBDE-based polymers (e.g. PBTE or PA) that cannot be replaced by polymer blends that can be combined with alternative FRs. Examples mentioned by the Danish EPA include:

- Halogen-free polyketone (this is considerably more costly than PBTE or PA), or
- High performance thermoplastics such as polysulphone, polyaryletherketone (PAEK) or polyethersulphone (PES).

According to the UK HSE, implementation of these options will require a higher level of research and development activities than the substitution of DecaBDE with an alternative FR. These options may be pursued by companies bringing new products to the market but are unlikely to be considered for existing products (UK HSE, 2012). Some examples of new inherently FR materials are mentioned in literature, such as GreenArmor, GreenCrest, Emerald 1000 and Polyquel and these are often promoted as replacements for DecaBDE (UK HSE, 2012; Albemarle, 2013; Great Lakes, 2013; PR Newswire, 2010).

Replacement of DecaBDE at the article level

The Lowell Center for Sustainable Production report offers examples of options that may be classed under 'product redesign', such as the following which are specifically relevant to EEE (Lowell Center for Sustainable Production, 2005):

- Replacement of the original polymer material with another in combination with shielding of power supplies (this has been the case with a move from HIPS to ABS and additional shielding in printers and related equipment)
- Removal of the power supply from the product thus reducing the fire retardancy requirements of the electronic enclosure.

### 5.1.2 Alternatives for DecaBDE in textiles

#### **Potential substitution strategies**

Overview

Two basic market segments exist for the use of DecaBDE in textiles:

- Contract textiles (such as curtain, blinds, textile wall coverings and seating fabrics)
- Domestic furniture textiles (primarily driven by the stringent fire safety regulations in the UK), a number of alternatives may be considered for the replacement of DecaBDE.

For all these applications, a variety of natural (essentially, cotton) and man-made fibres can be used as a substrate for the DecaBDE-based coatings.

There are a number of possible DecaBDE substitution strategies ranging from direct substitution of the FR to complete redesign of the textile product. The Lowell Center for Sustainable Production (2005) recalls information presented in a 2003 Oeko Institute report according to which DecaBDE applications in textiles lend themselves to the following substitution options (this overview has been informed with data from other sources).

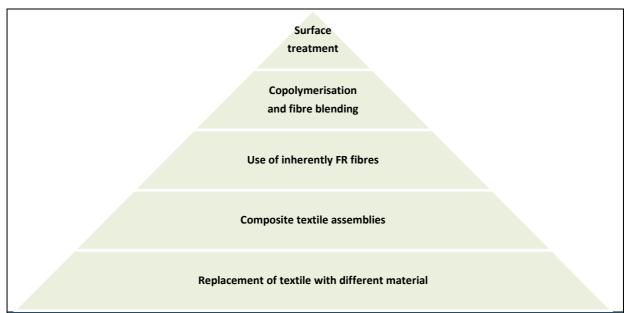


Figure 5-2: Substitution strategies for DecaBDE in textiles (increasing complexity towards foot of pyramid) Source: Adapted from Lowell Center for Sustainable Production (2005) and Gnosy et al. (2010)

### Replacement surface treatments

There are two types of surface treatments – finishes and coatings. A finish is applied by impregnating the fabrics in an aqueous solution of the chemical. A coating, on the other hand, is the application of a continuous or discontinuous layer on the surface of the fabric generating a heterogeneous fabric/polymer composite (Gnosys, et al., 2010).

There are established FR substances and potential new variants based on different synergistic combinations as possible substitutes for DecaBDE/ATO. These may be (KemI, 2004):

- Organic phosphorous compounds or phosphorous chlorine compounds
- Aluminium and zinc hydrate
- Swelling (intumescent) systems
- New synergistic combinations, for example antimony bromine/phosphorous silicon
- Surface-active fibre systems
- Systems with graft copolymers.

A summary of potentially relevant treatments are shown in **Table 5-1**.

FR options	Examples			
Chemical	Phosphates			
finishes	Polyphosphates			
	Phosphorous amides			
	-	Phosphonium derivatives		
	Borax and boric			
	Halogenated FRs			
Chemical	Triaryl phosphat			
coatings		phosphate or phosphinate		
	•	dodecane (HBCD)		
		entabromophenyl)		
		Ethylene bis(tetrabromophthalimide)		
	Alumina trihydrate Exfoliating graphite containing coatings			
Other	Swelling (intumescent) systems			
	Plasma-induced-graft-polymerisation:			
	Phosphorous-containing acrylate monomers(diethyl(acryloyloxyethyl)phosphate (DEAEP)			
	Diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP)			
	Diethyl (acryloyloxymethyl)phosphonate (DEAMP)			
	Dimethyl (acryloyloxymethyl)phosphonate (DMAMP))			
	Nanocomposites	(see below)		
	Cotton	MMT clay in a 50% solution of 4-methylmorpholine N-oxide (MMNO)		
	Polylactic acid	Organomodified (OM)-MMT with PLA		
	Polyester	Montmorillonite clay in PET		
	Polypropylene	Clays with maleic anhydride - grafted polypropylene as a compatabiliser		
		Poly(vinylsilsesquioxane) (POSS)		
		Multi-walled carbon nanotubes (MWNT)		
	Polyamides	Nylon 6 and nylon 6.6 / clay hybrid fibres made by melt blending and by melt		
		spinning to increase the effectiveness of more normal FRs and thus enable lower quantities to be used in synthetic fibres		

FR chemicals are of little use unless they stay on the fabric throughout its life, so durability is a requirement for their selection. A FR treatment that wears off easily, washes off, or evaporates form the fabric is less suitable, and might actually fail any prescribed durability test-performance requirements (National Research Council, 2000).

Improvement of FR properties of synthetic fibres by copolymerisation and fibre blending

Copolymerisation refers to the inclusion of an additive in the fibre melt spinning process; FRs are added into the molten plastic during the spinning process and become physically part of the fibre matrix (e.g. organophosphorous added to viscose fibres). This approach is applicable to synthetic fibres only where either one of the monomer/homopolymer can be fire retardant or the FR molecules can be attached to the polymer chain during polymerisation, or FR additives can be in the polymer melt or in solution prior to extrusion (Gnosys, et al., 2010). Some examples are provided in **Table 5-2.** 

Table 5-2: Example	Table 5-2: Examples of FR copolymerisation treatments for textile fibres				
Fibre type	Examples				
Viscose or rayon	Bis(2-thio-5,5-dimethyl-1,3,2-dioxaphosphorinyl)oxide - Viscose FR Polysilicic acid (Visil®) and aluminium (Visil AP®)				
Polyester	Comonomeric phosphinic acid in PET – Trevira Bisphenol-S-oligomer derivatives -Toyobo GH Cyclic phosphonates - Antiblaze CU and 1010 Phosphinate salts				
Polypropylene	Phosphorous-containing Halogen-containing Silicon-containing Metal hydrate and oxide (effective but required in high levels, typically >20% w/w) Tris(tribomoneopentyl) phosphate (FR 372, ICL)				
Source: Gnosys et a	I. (2010)				

Furthermore, fibre blending is a very common method of reducing the flammability of flammable fibres. Polyester is usually blended with cotton and this 'poly-cotton', if it has lower than 50% polyester content, can pass the simple vertical strip flammability test. With higher polyester content, sometimes the blended fibre is more flammable than the individual components. This is called a wicking effect where the cotton acts like a wick, holding the polyester component together, which burns. Cotton-nylon blends are also quite commonly used to reduce flammability of cotton (Gnosys, et al., 2010).

Wool and Visil fibre are blended to improve the latter's fibre properties, but the flammability of the blend is also reduced (Visil rayon is a FR form of viscose which has silica embedded in the fibre during manufacturing, see above table). Cotton-wool blends are quite common as well. Aramids are blended with many fibres for different applications. Nomex® can be blended with FR viscose and FR wool to produce fire blocking fabric, e.g. for aircraft seats. Nomex® blended with Kevlar® shows better performance than 100% Nomex® in firefighters' outer protective garments. Various blends of glass fibres with aramids, melamine fibres, PVC fibres and polyester have been reported for use in fire-protective non-woven veils for upholstery and mattresses (Gnosys, et al., 2010).

Finally, Albemarle notes that its proprietary GreenArmor brominated polymer can be used as an alternative to DecaBDE-based backcoating (Albemarle, 2013).

Use of inherently heat resistant and FR fibres

Natural cellulosic fibres such as cotton and linen can ignite readily whereas some synthetic fibres such as aramids actually self-extinguish, as shown in **Table 5-3.** 

Table 5-3: Fire characteristics of different textile fibres				
Fibre	Fire characteristics			
Cotton/linen Silk	Burns with a hot vigorous flame and high smoke.  Does not melt or draw away from the flames			
Rayon/Lyocell	Burns similarly to cotton and linen, except that it may shrink up			
Acetate	Burns with a rapid flame and melts when burning. May melt and pull away from small flames without igniting. Melted fabric may drip carrying flames to other surfaces. After burning, leaves a hot molten residue difficult to remove from any surface			
Acrylic	Burns similarly to acetate, except that it burns with a very heavy, dense, black smoke. It drips excessively			
Nylon, polypropylene, polyester, spandex	Burns slowly and melts when burning. May melt and pull away from small flames without igniting. May self-extinguish			
Wool	Burns slowly and is difficult to ignite. May self-extinguish			
Modacrylic and saran	Burns very slowly with melting. May melt and pull away from small flames without igniting. Self-extinguishes			
Aramid, novoloid, vinyon	Chars, does not burn			
Source: Gnosys et al. (2010), EFF	Source: Gnosys et al. (2010), EFRA (2012)			

Other fibre types referred to in the literature include oxidised polyacrylonitrile, polyphenylene sulphide and polybenimidazoline fibres. Such inherently fire-resistant fibres generally have applications for firefighters, racecar drivers, industrial workers and in the military (UK HSE, 2012).

Design and inherent FR materials approaches to fire retardancy are possible for several textile products; however, they lead to the restriction of choice for the consumer in some way, usually limiting the choice of covering or filling materials, or may produce an inferior, less durable product in the case of personal protective equipment (Gnosys, et al., 2010).

Comments received by industry during the preparation of the Risk Reduction Strategy for DecaBDE in 2003 had suggested that inherently fire-resistant fibres find applications mainly in polyester materials and to a lesser extent in polypropylene and acrylic fabrics. They have poor aesthetics (they are difficult to dye) and are not relevant to the uses of DecaBDE but are excellent in technical textiles. Such inherently fire-resistant textiles were believed by industry not to be able to meet the requirement of the UK Fire Safety Regulations 1988 applied to domestic upholstery. In a fire test, designed to simulate actual usage of the upholstery, their thermoplastic nature was believed to be a considerable disadvantage and the flame retarding effect not sufficient. Industry claims that the application of an additional fabric finish often completely negates their flame retarding effects depending on defined circumstances. Trials had been made with inherently fire-resistant acrylics and a phosphorous-based backcoat. These showed that it might be necessary to use around three times as much FR (for instance, microencapsulated ammonium polyphosphate) to achieve the same flame retardancy as with DecaBDE (RPA, 2003).

## Fire barriers and composite textile assemblies

Fire barriers are fire-resistant materials placed either between the exterior cover fabric of the product and the first layer of cushioning materials, or beneath one or more "sacrificial layers" of cushioning. These sacrificial layers are close to the product's exterior surface and provide a desirable aesthetic feel or look (Lowell Center for Sustainable Production, 2005). Fire barriers are made from inherently fire-resistant fibres such as para-aramids, melamines, modacrylics, or glass,

and, therefore, do not rely on the use of FR chemicals (Lowell Center for Sustainable Production, 2005).

Barrier materials used in soft furnishing applications have several forms, as shown in **Table 5-4**. Generally, highloft, nonwoven fibre battings are used in residential mattress applications, whereas coated or laminated textiles are more common in institutional and upholstered furnishing applications. Types of barrier fabrics used in soft furnishings are mainly influenced by end user applications and cost (Nazare & Davis, 2012).

Barrier materials created by bonding a highly fire-resistant "layer" to one of the textile components to give composite barrier fabrics are also used in upholstered furniture. Bonding is generally accomplished by mechanical processes such as stitch bonding or needle punching, or thermal (heat bonding) processes. Adhesives can also be used for laminating various layers of barrier fabrics. Examples of composite barrier materials include a glass fibre fabric coated with PVC, or a very thin layer of aluminium sandwiched between a woven fibreglass and spun fibreglass for upholstery, or thin layers of FR polyurethane foam laminated or backcoated onto various textile substrates in mattresses and upholstered furniture. Composite barrier systems are particularly costly as they can be an order of magnitude more expensive than other FR technologies (Nazare & Davis, 2012).

Table 5-4: So	Table 5-4: Soft furnishing barrier types				
Barrier type	Structure	Constituent fibres			
Non-woven	Thermally bonded highloft	FR rayon/polyester			
		Basalt-based fibre/FR treated cotton/polyester			
	Needlepunched stratified	Inherent FR fibres			
	Needlepunched	FR rayon/polyester low melt synthetic fibre			
		Boric acid treated cotton			
	Needlepunched stratified	Boric acid treated cotton/polyester fibre + FR rayon/polyester			
	Needlepunched stitchbond	FR rayon			
	Non-woven	Glass fibre			
Woven	Woven	Glass fibre			
		Core spun yarn with glass fibre core and FR modacrylic sheath			
Knitted	Knitted	Core spun yarn with glass fibre core and FR			
	Double face knit				
Source: Nazar	e & Davis (2012)				

#### Replacement of textiles by alternative materials

There are certain materials that could be used instead of textiles, such as natural leather, which is inherently fire-resistant and artificial leather FR with borates<sup>40</sup> (Gnosys, et al., 2010).

It is noted that some of the borates have a harmonised classification for their CMR properties, thus making this alternative technology not ideal for the replacement of DecaBDE.

### Overview of alternatives for different textile fibres

The table overleaf summarises the availability of alternatives for different textile substrates, as presented in the open literature. The table does not present the alternatives in any particular order (of importance or popularity).

#### Discussion on alternatives to DecaBDE for specific textile applications

#### Upholstery coverings

A known alternative to DecaBDE/ATO systems for upholstery outer coverings of all material types is HBCD with ATO as synergist. For specific substrates, other FR systems may be considered (mainly taken from Gnosys et al, 2010):

- **Polypropylene**: usually halogenated fire retardants (e.g., tris(tribomoneopentyl) phosphate (FR 372, *ICL*) are used, introduced into the polymer by melt blending, prior to extrusion into fibres. These have been traditionally used in the presence of ATO as a synergist although more recently this has been replaced by the novel hindered amine stabiliser such as NOR116 (*Ciba*)
- **Polyester**: cyclic oligomeric phosphonate (e.g., Antiblaze CU, *Rhodia Specialities Ltd*; Aflammit PE, *Thor*) is applied as a chemical finish by pad-dry-cure method. A US company has also been noted in literature as using a blend of polyphosphonophosphates (Flamex PF) for a product intended for applications on upholstered furniture in restaurants, nightclubs, high-rise hotels, apartments, nursing homes, schools, theatres, etc. (Lowell Center for Sustainable Production, 2005)
- Cotton rich fabrics (>80% cotton): ammonium polyphosphate (APP) based products may be
  used, which on curing can provide soak durable treatments. The use of modified acrylic/cotton
  blends or polyester in coverings may be seen as limited within the current vast range of
  materials and constructions currently available
- Cotton and cotton/polyester fabrics: on cotton, durable phosphorous and nitrogen based chemical finishes are applied, such as Pyrovatex (*Huntsman*) or Proban (*Rhodia*) are applied. These finishes are phosphorous and nitrogen based. While Pyrovatex is covalently bonded to cellulose structure, the Proban-type finish is a highly cross-linked three-dimensional polymer network, enclosing the fibrillar structures. Traditionally the use of chlorinated paraffin wax-based coatings have been used because they confer water repellence
- **Wool**: Zirpro is used by an exhaustion method often simultaneous with the application of dye in the dyebath, where negatively charged complexes of zirconium or titanium are ionically bonded to positively charged wool fibres. Literature suggests that DecaBDE may have been used in wool (Lowell Center for Sustainable Production, 2005; National Research Council, 2000) but this has not been confirmed as a current use
- Artificial leather (PUR-based): inorganic fire retardants such as borates are used as additives
- Artificial leather (PVC-based): this does not require fire retardant treatment for domestic furniture, but may require other fire retardant additives to pass specific tests, depending upon specific end uses
- Polyester inherently FR version: Trevira CS polyester is used.
- Other inherently FR fibres: inherently FR materials such as aramid would be possible, but would be considerably more costly. Glass fibre wrapped in inherently FR fibres could also theoretically be a solution. Aramid, novoloid and melamine are claimed to find increasing uses in furniture upholstery and mattresses (Lowell Center for Sustainable Production, 2005).

Fibre	FR systems used	Example products (Company)
Natural fibres		
Cotton (and cotton-rich poly-cotton)	Organophosphorous and nitrogen- containing monomers or reactive groups	Proban CC ( <i>Albright &amp; Wilson</i> ), Pyrovatex CP ( <i>Huntsman</i> ), Aflammit P and KWB ( <i>Thor</i> ), Flacavon WP ( <i>Schill &amp; Seilacher</i> ), Flammentin® FMB ( <i>Thor</i> ), Pyrovatim® PBS ( <i>Huntsman</i> )
	Other	Fyroltex® HP (Akzo Nobel), Noflan® (Firestop)
Wool	Antimony-organohalogen systems	Flacavon F12/97 (Schill & Seilacher), Myflam (BF Goodrich) These products were DecaBDE -based
	Ammonium phosphates and polyphosphate	Pyrovatex CP (Huntsman)
	Boric acid-borax	
	Ammonium bromide	
	Zirconium hexafluoride complex	Zipro (IWS), Aflammit ZR (Thor)
Regenerated fibres		
Viscose	Organophosphorous and nitrogen/sulphur-containing species	Sandoflam 5060 ( <i>Clariant</i> )
	Polysilicic acid complex	Visil AP (Sateri)
Synthetic fibres		
Polyester	Organophosphorous components (e.g. phosphinic acidic comonomers and phosphorous additives)	Trevira CS ( <i>Trevira</i> ), Fidion FR ( <i>Montefiber</i> ), Amgard CU ( <i>Rhodia</i> ), SMC 688 ( <i>Special Materials</i> ), Afflamit® PE ( <i>Thor</i> ), Flammex® DS ( <i>Zschimmer &amp; Scharz Mohsdorf</i> )
	Brominated FR (HBCD)	CD-75PM® (Chemtura)
Modacrylic	Acrylic/halogenated co-monomer: e.g., Vinyl bromide (VBr) at 35-50 % w/w plus antimony compounds	Velicren (Montefiber), Kanecaron (Kaneka Corp.)
Polypropylene	Both halogen and non-halogen additives incorporated into the melt spinning process  Brominated FRs	Sandoflam 5072 ( <i>Clariant</i> ), Ciba® Flamestab® NORTM 116, Tris(tribromomoneopentyl) phosphate (FR 372, <i>ICL</i> ) Brominated epoxy (FR-2400), Brominated polystyrene (FR-803P)
Nylon	Intumescent coatings for nylon carpets for airlines	

Fibre	FR systems used	Example products (Company)
Nylon, PP, polyester-nylon blends, acrylics, etc.	Brominated FR (HBCD)	
Inherently fire-resistant fibres		
Melamine	Melamine units joined by methylene and dimethylene ether linkages	Basofil (BASF)
Polyhaloalkenes	Polyvinyl chloride Polyvinylidene chloride	Clevyl (Rhone-Poulenc) Saran (Saran Corp.)
Polyaramides	Poly(m-phenylene isophthalamide) Poly(p-phenylene terephthalamide)	Nomex ( <i>DuPont</i> ) & Conex ( <i>Teijin</i> ), Kevlar ( <i>DuPont</i> ), Twaron ( <i>Acordis</i> ) & Technora ( <i>Teijin</i> )
Poly (aramide-arimide)		Kermel (Rhone-Poulenc)
Glass fibres		
Polybenzimidazole		PBI (Hoechst-Celanese)
Carbonised acrylic	Carbon fibres from polyacrylonitrile	Pyron (Zoltek)

Finally, another solution is the use of fire barriers to protect the interior cushioning fire load in upholstered furniture (Lowell Center for Sustainable Production, 2005).

#### Drapery

There are three main strategies to replacing DecaBDE (Lowell Center for Sustainable Production, 2005):

- **Alternative backcoating treatments**: where synthetic fibres are used, substitutes for DecaBDE for polyester, polypropylene and rayon fibres involve the use of phosphate-type additives in the polymer/fibre manufacturing process
- Use of natural fibres: literature suggests that natural fibre fabrics are the best choice when choosing a drapery fabric to flame retard with chemicals. Cotton, silk, linen, wool, etc. absorb the FR readily and can be treated with non-halogen phosphate type treatments (e.g. phosphonates) to meet the relevant flammability standards
- Use of inherently flame-resistant fibres: Internet searches for suppliers of inherently flameresistant draperies reveal, for example, the use of modacrylic fibres<sup>41</sup> and polyesters<sup>42</sup>.

#### Mattresses

The Lowell Center for Sustainable Production (2005) suggests that alternatives to the use of DecaBDE in mattresses include the use of non-halogenated phosphate type coatings for backcoating mattress fabrics (e.g. phosphate-based intumescent systems) or the use of fire barrier materials (as discussed above). These barriers protect the mattress and fully encapsulate the interior materials and must be combined with fire-resistant border seams, tape, and threads.

### **Tenting**

A UK publication argues that light tentings are now being replaced by nylons that require no fire retarding because of their thermoplasticity, which enables them to pass any required fire test (Gnosys, et al., 2010). Earlier in this document, it was discussed that military tents may be coated with a PVC layer for water-proofing and it is possible that the canvas is also backcoated. The US EPA also mentions the use of inherently fire-resistant materials such as Nomex® and Teflon in soldier protection fabric and FR tents (US EPA, 2014).

### Transportation and aviation seating

According to Gnosys et al. (2010), for seats in transportation, interior materials are sometimes used beneath the covering fabric for more comfort. In some cases, barrier materials, such as oxidised acrylics and aramids, are used between the face fabric and the foam, as explained earlier. These were first used for aircraft seats and now being increasingly used on trains, buses and coaches. In the USA, such barriers may also comprise glass-cored yarns about which are wrapped with inherently fire resistant fibres. This reduces the overall costs of fabrics because of the relatively low costs of glass filament yarn components (Gnosys, et al., 2010).

See <a href="http://www.sewwhatinc.com/fr">http://www.sewwhatinc.com/fr</a> flammability.php or

See http://www.rajvirindustrieslimited.com/flame.htm (accessed on 22 April 2014).

http://www.profoundit.com/product::4237::Flame-resistant-cubicle-curtains (accessed on 22 April 2014).

#### Realistic substitution strategies for DecaBDE in textiles

Consultation with industry reveals some elements of a realistic substitution strategy for DecaBDE in textile applications. The analysis here has been informed by the findings of the detailed consultation that had been undertaken by RPA for the preparation of the 2003 Risk Reduction Strategy and considers recent consultation findings for this restrictions proposal.

#### Flame retardants for natural fibres

Cotton and cotton-rich blends are best protected with phosphorus-based systems, which may be classified as reactive 'durable' FR treatments or 'semi-durable' treatments. Cotton and cotton-rich fabrics can also be treated by backcoating. Such systems can be made to react with themselves to become insoluble or with the fibre itself to resist washing treatment; however, in order for such an approach to be taken, the textile should be very rich in natural fibre content (the best is 100% cotton). Such treatments with phosphorus may prove to be considerably cheaper than BFR systems on a per unit cost basis, but may require larger quantities than brominated FRs in order to achieve the required levels of fire safety (RPA, 2003).

For durable treatments, there are two modes of using phosphorus treatments (RPA, 2003):

- By incorporating an insoluble compound into the fibre (for example, by using tetrakis hydroxymethyl phosphonate, also known as Proban, used for bed sheets, quilts and workwear), or
- By a reaction of the fibre material with N-hydroxymethyl-3-dimethyl phosphonpropionamide in the presence of a phosphoric acid catalyst (commonly used in the UK before the introduction of the national Fire Safety Regulations in 1988).

These two methods are rather expensive and the latter in particular requires a complicated application process and a considerable amount of washing to remove the excess material, resulting in only around 50% of the flame retarding material remaining fixed on the fibre. Generally, the main phosphorous alternative systems are of a very different (lower) order of insolubility when compared to DecaBDE. One trial on an upholstery fabric in the early 2000s required the addition of 250 grams of phosphorus-based FR formulation per square metre instead of 80 grams when using a brominated FR system (RPA, 2003). Phosphorus compounds, even when used with micro-encapsulation techniques, cannot achieve resistance to washing or wetting to the standards achieved by brominated FRs (RPA, 2003).

### Flame retardants for man-made fibres

For the majority of man-made fibres, FR systems reportedly need to act in the vapour phase, which requires the presence of a halogen. The most effective means of applying such FR systems is by backcoating the synthetic fibre. In theory, it is possible to use synthetic fibres such as polyester for blinds which are flame retardant by an alternative system. Alternative FRs include aluminium trihydroxide, chlorinated paraffins, chlorophosphate esters (e.g. triaryl phosphates), although they may be accompanied by a BFR in order to achieve the desired fire safety standards (RPA, 2003).

In the past, the most prominent of the alternative BFR for (synthetic) textiles was HBCD. HBCD had the advantage that it could be used in low-pigmenting systems which are important for lighter, more open weave fabrics. It was generally used where a DecaBDE-free system was required but was

considered as being less effective on man-made fibres compared to DecaBDE. Therefore, larger quantities would have to be used in order for the desired fire safety standards to be met.

#### Realistic strategy for substitution

At the time of preparing the 2003 Risk Reduction Strategy, the situation with alternatives was somewhat different to the current situation. DecaBDE was (and still is) a very effective and reasonably inexpensive FR. In 2003, the UK textile finishing industry had suggested that the only successful alternative commercial system was based on limiting the fabrics treated to those that contain at least 75% cotton fibre. In other words, only if there was a switch from man-made textiles to cotton or cotton-rich textiles would an alternative emerge and take the place of DecaBDE. The relevant alternatives would be phosphorous-based substances through the use of higher loads, as shown in **Table 9-1** (Annex 3 to this document). Any such move would exclude the major proportion of fabrics that were treated with DecaBDE at the time, especially in the contract textiles area (RPA, 2003). Industry had claimed that a market review had revealed that alternative systems used by retailers were predominantly based on cotton fabrics (or fabrics with a significant cellulosic content, in general) and semi-durable phosphorus FR systems (for instance, microencapsulated APP) (RPA, 2003).

Arguments had been made at the time about whether such a switch between fibres would be appropriate. Industry had argued the following:

- Man-made fabrics produce lighter fabrics of good strength that are a good substrate for coating to produce modern textiles with improved performance
- Man-made fabrics have generally better wear properties than cotton
- Cotton and cotton-rich fabrics were processed through traditional textile processors i.e. wet
  processing. FR treatments (such as those with N-hydroxymethyl-3dimethylphosphonpropionamide (DMPP)) that are durable would also need to be made through
  a processor with wet processing as they require specialised equipment and washing facilities.

There are certainly differences between now and ten years ago. As shown in **Table 9-1**, technically, brominated alternative substances were the most promising. Their fates though have been diverse: HBCD is under regulatory pressure and its use as a FR in textiles has been impacted. It can no longer be considered a promising or indeed a suitable alternative. On the other hand, ethane-1,2-bis(pentabromophenyl) (EBP, also referred to as DecaBDE ethane) still remains a 'drop-in' replacement and is still promoted as such, with one key difference: while it was twice as costly as DecaBDE in 2003, the price difference has significantly reduced. It will be explained later in this document that EBP may now be only 5-20% more costly than DecaBDE and this is why it is now generally accepted as a feasible drop-in replacement for DecaBDE in textile applications.

## 5.1.3 Alternatives for DecaBDE in coatings, adhesives and sealants

The analysis presented above explains that the use of DecaBDE in coatings, adhesives and sealants has been suggested, by REACH registration data and by certain authorities (Norway and Finland), although certain industry stakeholders have not identified these areas as particularly relevant to DecaBDE in the course of the consultation for this analysis.

With particular regard to **coatings**, some literature sources do refer to the potential use of certain alternatives as replacements for DecaBDE in coatings. The available information is summarised in **Table 5-6**.

Table 5-6: Overview of substances of relevance to the replacement of DecaBDE in coatings						
Potential alternative	CAS No.	Source				
Magnesium hydroxide (MDH)	1309-42-8	US EPA (2014)				
Dodecachloro dodecahydro dimethano dibenzocyclooctene	13560-89-9	US EPA (2014)				
Ammonium polyphosphate (APP)	14728-39-9; 68333-79-9	US EPA (2014), PINFA (2010b)				
Aluminium trihydroxide (ATH)	21645-51-2; 8064-00-4	Albemarle (2013), US EPA (2014), PINFA (2010b)				
Ethylene bis(tetrabromophthalimide)	32588-76-4	Albemarle (2013), US EPA (2014)				
Red phosphorous	7723-14-0	US EPA (2014)				
Ethane-1,2-bis(pentabromophenyl) (EBP)	84852-53-9	Albemarle (2013), US EPA (2014)				

Furthermore, three of the above substances (APP, MDH and ATH) have been identified by EFRA, alongside ATO, as FRs used in adhesives, sealants and coatings for building and construction applications (EFRA, 2012b). ICL, a manufacturer of DecaBDE, also mentions the following FRs as feasible for use in latex/adhesive formulations:

- Tris(tribromoneopentyl) phosphate, CAS No. 19186-97-1 (product name: FR-370)
- Tributyl phosphate, CAS No. 126-73-8 (product name: Phosflex 4)
- Tris(butoxyethyl) phosphate, CAS No. 78-51-3 (product name: Phosflex T-BEP).

The Annex XV dossier for DecaBDE further refers to TBBPA as a FR occasionally used in **adhesives** (UK HSE, 2012). Other literature provides further possibilities for FR use. A 1998 patent discussed FRs for adhesives applied on carpets and referred to ATJ, bromine or chlorine FRs enhanced by ATO (such chlorinated paraffins, DecaBDE or TBBPA), zinc borate, MDH or magnesium carbonate, melamine phosphates and pyrophosphates, molybdenum trioxide or ammonium octamolybdate, triaryl phosphate esters or other organophosphorous compounds, zinc oxide or combinations or mixtures of the above (Drake & Herrin, 1998).

Finally, PINFA has provided a list of substances that are used as FRs in **sealants** and this includes (PINFA, 2010b):

- Aluminium trihydroxide (ATH)
- Ammonium polyphosphate (APP)
- Red phosphorous
- Melamine phosphate and pyrophosphate
- Melamine polyphosphate
- Phosphate esters
- Melamine borate
- Zinc borate.

## 5.2 Information on alternatives from consultation

## 5.2.1 Information from consultation with industry

### **General Information**

During the course of the consultation for this project, a total of 10 completed questionnaires were received from industry stakeholders, while more than 60 others have responded (either to confirm their relevance or not to DecaBDE) without submitting a completed questionnaire. More specifically:

- 1 questionnaire was from an importer of DecaBDE, who is importing it for sale to a single downstream user
- 1 questionnaire was from a downstream user of DecaBDE for textile applications
- 2 questionnaires were from distributors, who supplied DecaBDE in a mixture to be used in plastic, textile and coating applications
- 3 questionnaires were from two former users of DecaBDE, plus one former non-EU manufacturer who now places an alternative substance on the EU market
- 3 questionnaires were submitted by suppliers of alternatives to DecaBDE, two of which supply the market with Inherently Flame Retardant Fibres (IFRF) and one with DecaBDE-free mixtures.

All of the submitted questionnaires, apart from the one from the importer, include references to alternative substances and technologies that have been evaluated by/are known to the stakeholders. In total, 12 different products have been mentioned in the questionnaires. These are shown in **Table 5-7**. Some information from consultation, where considered not confidential or could be used alongside information from literature, is presented in the remainder of Section 5. The remainder of this information collected is presented in a Confidential Annex to this document (Section **Error! Reference source not found.**) and is not made publicly available.

Tab	Table 5-7: Overview of the alternatives evaluated/referred to by industry stakeholders					
#	Name of alternative	CAS No	No of references	Applications		
1	Phosphoric acid, mixed esters with 1,1'-bisphenyl-4,4'-diol and phenol	1003300-73-9	1	Polymers		
2	Magnesium hydroxide	1309-42-8	1	Considered for special textiles		
3	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	1	Textiles		
4	Aluminium Trihydroxide (ATH)	21645-51-2	2	Polymers and textiles		
5	Diethylphosphinic acid, aluminium salt	225789-38-8	1	Textiles		
6	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	4090-51-1	1	Textiles		
7	2,2-Bis[4- [bis(phenoxy)phosphoryloxy] phenyl]propane (BDADP) / (1- methylethylidene)di-4,1- phenylenetetraphenyl diphosphate	5945-33-5; 181028-79-5	1	Polymers		
8	Diphosphoric acid, compd. with piperazine	66034-17-1/ Trade secret	1	Polymers		
9	Decabromodiphenyl ethane (EBP)	84852-53-9	4	Polymers, textiles, coatings		

Table 5-7: Overview of the alternatives evaluated/referred to by industry stakeholders							
#	Name of alternative	CAS No	No of references	Applications			
10	Mixture of phosphorus-based and melamine	Proprietary	1	Textiles			
11	Proprietary substance	Proprietary	1	Textiles			
12	Phosphate based FR	No data	2	Textiles for conventional and special uses			
13	Proprietary material	Proprietary	1	Textiles			
Sou	Source: Consultation						

### 5.2.2 Information from consultation with Member State Authorities

### **General Information**

Identification of alternatives was not the focus of the consultation with the Member State Competent Authorities. Nevertheless, a general question was included in the relevant questionnaire and a few Member States offered their views, along with background information.

The **German CA** had prepared a background paper on BFRs in 2008 which includes a brief comment on potential alternatives to DecaBDE and other substances (such as HBCD). The analysis is mainly qualitative, but it is commented that alternatives exist for the uses of DecaBDE in both plastics and textiles.

The **Danish EPA** has submitted a recent review (Danish EPA, 2013) which examines the most recent literature on BFRs and contains information about their uses and quantities in Denmark, their concentrations in the environment and their potential alternatives.

The **Norwegian CA** has also provided a list of brominated substances along with applications for which they are suitable.

In a 2009 report by **Keml (Sweden)**, it is also commented that for several of the applications of DecaBDE, potential alternatives do exist. The report presents a list of these, along with their toxicological properties and materials for which they are suitable. It is also mentioned, however, that the industry is more competent and better qualified to undertake the research and development of such alternatives<sup>43</sup>. Sweden also points out that incentives for substitution can be created through the promotion of public procurement criteria, which forbid the use of DecaBDE in e.g. furniture or textiles.

The **UK CA** only mentions EBP as a known alternative, stating that it is being marketed as a direct replacement for DecaBDE. No specific applications were mentioned. The substance was included in the 2012 CoRAP list and is currently being evaluated by the UK, as will be discussed later in Section 5.

Additional information on specific potential alternatives that were identified by MS authorities is presented in Annex 3 (Section 9.14).

Available online at (summary in English): <a href="http://www.kemi.se/Documents/Publikationer/Trycksaker/Rapporter/Rapport1">http://www.kemi.se/Documents/Publikationer/Trycksaker/Rapporter/Rapport1</a> 09 DekaBDE.pdf

#### **Plastics**

The **Danish EPA** review concluded that there are readily available and suitable alternatives to DecaBDE, based on their toxicological profiles and their availability, as expressed by their REACH registration. The three substances that can substitute DecaBDE in most (if not all) its applications are EBP, ethylene bis(tetrabromophthalimide) and tris(tribromophenoxy) triazine (CAS No. 25713-60-4). These substances appear to have similar or better toxicological profile to DecaBDE. Some polymeric FRs also appear to share the same range of applications with DecaBDE, such as Albemarle's proprietary GreenArmor (which, however, is not considered suitable for back-coating and for applications with thermosets and for wires and cables) (Danish EPA, 2013).

According to the **German CA**, for EEE, substitution with non-halogenated organophosphoric FR is possible, along with the substitution of ABS and HIPS with mixtures of them containing less flammable polymers, such as PC and PPE. These blends of PC/ABS, PS/PPE or PPE/HIPS have been marketed for a long time, either without FRs or with non-halogenated ones (resorcinol bis(diphenylphosphate) (RDP), bisphenol-A bis(diphenylphosphate) (BDP) and triphenyl phosphate (TPP)).

For low-voltage equipment another alternative could be to reduce the content of FR in these, as they usually had more than what was considered necessary for compliance. For smaller components made from polyester plastics (PBTE, PET) or polyamide (PA) suitable alternative FRs are magnesium hydroxide, micro-encapsulated red phosphor, melamines or organic phosphinates<sup>44</sup>.

#### **Textiles**

The review from the **Danish EPA** comments that although there is no single replacement for DecaBDE in textiles, a large number of non-halogen alternatives are available on the market. These alternatives include FR substances as well as inherently fire retardant fibres and blends, barrier linings, etc.

According to the **German CA**, use of glass fibres or FR plastics (e.g. polyaramides) can reduce the use of FRs in these (or prevent it completely). Using fibres with chemically bound FRs is another proposed alternative, e.g. polyester or cellulose fibres with chemically bound P-based FRs. There is no further information on the performance of these alternatives in the report from 2008, however. Important factors, as mentioned by the German CA, are the structure and density of a fabric or upholstery, which affect the fire resistance of the textile.

Intumescent systems are also mentioned as a possible alternative. They are also referenced in a recent report from the **Danish EPA** as one of the alternatives with the highest potential for substituting DecaBDE in textiles, along with those based on phosphorus (Danish EPA, 2013).

Available online at (in German): <a href="http://www.umweltbundesamt.de/publikationen/bromierte-flammschutzmittel-schutzengel-schlechten">http://www.umweltbundesamt.de/publikationen/bromierte-flammschutzmittel-schutzengel-schlechten</a>

# 5.3 Approach to the assessment of selected alternatives

## **5.3.1** Overview of approach

Literature presents a long list of substances that might be considered alternatives to DecaBDE. It is clearly impossible to assess all of them in detail. Firstly, the necessary information for a full analysis is not available for many of them. Secondly, information on the technical and economic feasibility of alternatives other than alternative FR substances is very scant, and providing a detailed analysis on them would be very difficult. Therefore, the focus has been on alternative FR substances and the general approach has been to develop a shortlist of alternative substances that could be looked at in more detail.

Different arguments may be made in relation to what would be the prime consideration of each user of DecaBDE in selecting a replacement for the substance: evidently, a replacement needs to be technically feasible at an acceptable cost. On the other hand, users of DecaBDE would also be concerned about the hazard profile of the alternatives, as they would not wish to choose a replacement, which may itself become the target of regulatory action later on.

Here, we take a conservative approach, in other words, we assume that users of DecaBDE will be primarily interested in using technically feasible alternatives that are of an acceptable cost and which are available on the market in sufficient quantities. Therefore, the sequence of screening the alternative substances will be as follows:

- Step 1 Identification of alternatives: collection of identities of alternatives in the open literature and identification of those alternatives confirmed as technically relevant by consultees.
- 2. Step 2 Screening of technical feasibility of alternatives: a two-pronged approach is followed: (a) alternatives that have been identified by consultees are automatically assumed to be technically feasible (in specified applications), and (b) the literature was assessed to establish how commonly the identified alternatives are mentioned as suitable replacements (in principle) for DecaBDE. The aim has been to eliminate substances that are perhaps more 'exotic' and therefore would not be among the most likely choices of industry stakeholders as far as the substitution of DecaBDE is concerned. The following sources have been considered:
  - Keml (2004, 2005, 2009)
  - Danish EPA (2006)
  - Washington State (2006)
  - JRC (2007)
  - US EPA (2014)
  - Illinois EPA (2007)
  - Troitzsch (2011)
  - UK HSE (2012)
  - Lowell Center for Sustainable Production, (2005)
  - EFRA (2012, 2012b)
  - PINFA (2013, 2010, 2010b, 2010c)
  - The ENFIRO project
  - Information from DecaBDE manufacturers (Albemarle (2013b) Chemtura (2013), ICL Industrial Products (2013b))
  - Member State authorities questionnaire responses for the purposes of this study.

- 3. Step 3 Screening of economic feasibility of alternatives: the rationale behind this step is to identify which of the alternatives are potentially far too costly in comparison to DecaBDE, and thus are less likely to become the preferred choice of industry stakeholders for a switch from DecaBDE. The information collected from consultation on the economics of alternatives is very limited, and so it has been complemented by information from the open literature.
- 4. **Step 4 Screening for hazards**: the rationale behind this step was to eliminate those substances which have been identified as having demonstrated hazards to the environment and human health, which would prevent the downstream users from considering them as suitable (long-term) replacements for DecaBDE. An example would be a substance that has already been included into the Annex XIV Authorisation List or a substance that has been identified as a Substance of Very High Concern (SVHC).
- 5. **Step 5 Market availability of alternatives**: the key criterion of market availability has been the availability of a REACH Registration for each substance. Priority is given to alternatives for which registration has been completed and the tonnage band is >10,000 t/y. Substances for which registration has been completed but the tonnage band is <10,000 t/y or confidential are also considered in principle available; on the other hand, substances without a registration are excluded as the per-registrant tonnage may be as low as 10 t/y. which would be unlikely to cover the needs of the bulk of current DecaBDE users. Nevertheless, it cannot be precluded that the availability of alternatives may not change (improve) in the future. This screening step is simply used to identify those alternatives that are readily available on the market and could serve a significant proportion of current DecaBDE users. There is insufficient additional information from literature on the availability of different substances, so this criterion should only be considered as indicative and merely aimed at ranking potential alternatives rather than identifying alternative FRs that can categorically not be used by industrial users.

#### **5.3.2** Shortlisted alternative substances

The screening of alternative FRs is described in detail in Annex 4 (Section 10) to this document. Based on the analysis presented in the Annex, the following list of shortlisted alternatives has been generated (see **Table 5-8**).

Tabl	Table 5-8: Shortlist of potential alternatives for DecaBDE for further consideration					
DecaBDE		CAS No	Structure	Primary use		
Bis-(pentabromophenyl) ether (DecaBDE)		1163-19-5	Br B	Polymers, textiles, coatings, adhesives		
No	Potential alternative substance	CAS No	Structure			
1	Triphenyl phosphate (TPP)	115-86-6		Polymers		

Tabl	Table 5-8: Shortlist of potential alternatives for DecaBDE for further consideration					
Deca	BDE	CAS No	Structure	Primary use		
	pentabromophenyl) ether aBDE)	1163-19-5	Br B	Polymers, textiles, coatings, adhesives		
No	Potential alternative substance	CAS No	Structure			
2	Magnesium hydroxide	1309-42-8	Mg(OH) <sub>2</sub>	Polymers, textiles, coatings/adhesives		
3	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8		Polymers, textiles		
4	Aluminium trihydroxide	21645-51-2; 8064-00-4	Al(OH) <sub>3</sub>	Polymers, textiles, coatings/adhesives		
5	Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	21850-44-2	Br Br Br Br Br Br Br	Polymers (textiles)		
6	Ethylene bis(tetrabromophthalimide)	32588-76-4	Br O O Br Br Br O O Br Br	Polymers, textiles, coatings/adhesives		
7	2,2'-Oxybis[5,5-dimethyl- 1,3,2-dioxaphosphorinane] 2,2'-disulphide	4090-51-1	H <sub>3</sub> C	Textiles		
8	Resorcinol bis(diphenylphosphate) (RDP)	57583-54-7; 125997-21-9		Polymers (textiles)		
9	Bisphenol-A bis(diphenyl phosphate) (BDP/BAPP)	5945-33-5; 181028-79-5	CH <sub>3</sub>	Polymers (textiles)		

Tab	Table 5-8: Shortlist of potential alternatives for DecaBDE for further consideration					
Dec	aBDE	CAS No	Structure	Primary use		
Bis-(pentabromophenyl) ether (DecaBDE)		1163-19-5	Br Br Br Br Br Br	Polymers, textiles, coatings, adhesives		
No	Potential alternative substance	CAS No	Structure			
10	Substituted amine phosphate mixture (P/N intumescent systems)	66034-17-1	HO OH HO P OH	Polymers (textiles, coatings/ adhesives)		
11	Red phosphorous	7723-14-0	*—————————————————————————————————————	Polymers, textiles, coatings/adhesives		
12	Ethane-1,2- bis(pentabromophenyl)	84852-53-9	Br Br Br Br Br Br	Polymers, textiles, coatings/adhesives		

# 5.3.3 Most likely alternative substances

Despite persistent efforts to communicate with industry on the issue of alternatives, only limited information has been obtained and the market shares of different alternatives have not been established. Therefore, developing a view as to which alternatives are most likely to replace DecaBDE cannot be formed with certainty. The discussion here is based on the information collected and a series of assumptions.

#### **Polymers**

The most prominent alternative for DecaBDE is EBP. This has been suggested by a company that has registered both DecaBDE and EBP under REACH and has described the substance as suitable for thermoplastics (HIPS, ABS, Polyolefins, TPU, Polyesters (PBTE)), polyamides/thermosets, textiles and coatings. Annex 3 presents several literature sources that support the argument for EBP being an attractive drop-in replacement. Some processing issues associated with the use of EBP as a replacement for DecaBDE have been reported, however, no further clarification was given other than that those can generally be overcome.

Information has been sought from non-EU administrations where the use of DecaBDE has been under regulatory pressure, namely the USA and Canada. The US EPA has noted, "Anecdotal information suggests [a switch from DecaBDE to EBP] is likely happening/will happen in the US" (US EPA, 2014b). Environment Canada has also confirmed a similar trend, "Canada has seen an

increased commercial interest for this substance as a direct drop-in replacement for DecaBDE (...) Based on a recent study on PBDEs in products (...), the primary substitute that is being used by manufacturers in Canada appears to be decabromodiphenyl ethane. Further, it seems that this compound is a cost-effective replacement for DecaBDE applications relevant to Canadian manufacturers" (Environment Canada, 2014).

Overall, it is fair to assume that EBP will be the primary replacement for DecaBDE. However, there is a large variety of polymer materials that are currently flame retardant with DecaBDE. Therefore, there are opportunities for using different alternative substances, depending on the substrate and the particular needs of products. Based on the frequency by which different alternatives appear in the literature (see **Table 10-1**) among the shortlisted alternatives, popular choices appear to be BDP/BAPP, RDP, ethylene bis(tetrabromophthalimide), MDH, TPP, ATH and red phosphorous.

For the purposes of calculating substitution costs (see below), significant information is missing:

- The change from DecaBDE to an alternative FR may not necessarily be a simple switch between additives. In order for the fire performance requirements to be met, changes in the polymer resin used may be needed, as explained at the beginning of Section 5. For instance, as the German CA has noted, for EEE, substitution with non-halogenated organophosphoric FR is possible, along with the substitution of ABS and HIPS with mixtures of them containing less flammable polymers, such as PC and PPE. These blends of PC/ABS, PS/PPE or PPE/HIPS are being marketed for a long time, either without FRs or with non-halogenated ones (RDP, BDP and TPP)
- A change in a polymer compound formulation may be much more extensive than a simple replacement of FR additives, particularly when the loading of the additive changes significantly. In such cases, other components of the formulation need to be added or removed for the formulation to balance. Limited information is available to the study team, despite extensive and persistent consultation efforts
- Finally, for some of the shortlisted alternative substances, information on their cost per tonne is not available. Even where some information is available, this may not be reliable. For example, the Alibaba.com website shows that TPP is ca. 20% less costly than DecaBDE, having a market price below €3,000 per tonne; however, HELCOM (2013) puts its price at €6,000 per tonne (still, the substance is described as "affordable").

On the other hand, an important element in this analysis is the effect of recent legislation. Due to the provisions of the RoHS Directive, the presence of DecaBDE in E&E, and in particular in styrenic applications, such as ABS and HIPS, has greatly reduced. Consultation suggests that the most prominent current use of DecaBDE in plastics is in polyolefins (PP/PE). This certainly affects the feasibility of different alternative FRs.

#### **Textiles**

Information availability for textiles allows us to be more straightforward in our approach. Several industry representatives have confirmed that they see EBP as the obvious choice, as it is technically compatible with the processes used in the industry, especially now that its price is comparable to that of DecaBDE. It is therefore more plausible to assume that EBP could replace the entire consumption of DecaBDE in textiles.

Backcoating seems to be the critical application of DecaBDE, so the focus of the consultation with the textile industry was on relevant companies. Due to the strict fire safety regulations in the UK, the majority of the answers that were received came from that country. It was established that the UK industry has largely moved away from DecaBDE and has been using EBP (roughly since 2012). A formulator, who supplies DecaBDE mixtures mainly for use in textiles, has also commented that marketing of products containing DecaBDE has become difficult in the EU due to the demands and requirements of downstream users (retailers of articles) who wish their products to be free of DecaBDE.

Two are the main reasons that have been given for the move away from DecaBDE:

- Inclusion of DecaBDE in the Candidate List, as a SVHC. This has caused many downstream users
  of textiles to request a different FR treatment, as they do not wish to market products
  containing a SVHC. Some standards, such as Oeko-Tex Standard 100 also ban DecaBDE<sup>45</sup>
- Price issues. It appears that the price of DecaBDE has risen in recent years and that of EBP has fallen, so it has become competitive. Reportedly, EBP was 50% more expensive in the past (see RPA, 2003); however, in recent years, its price has fallen while DecaBDE's has risen.

EBP is typically chosen for the similarity that it bears to DecaBDE in terms of bromine content and decomposition temperature. Consultees have indicated that the switch to EBP from DecaBDE is relatively easy and that it is used at essentially the same loading (the latter is confirmed in literature too). Conversely, alternatives based on phosphorous do not lend themselves to direct implementation.

Therefore, the assumption of full transition to EBP has substantial basis on reality, nevertheless, other alternatives may have a (minor) role to play as well (e.g. ATH, MDH, TDCPP, ethylene bis(tetrabromophthalimide), 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide (for viscose) and red phosphorous). The issues mentioned earlier on the lack of reliable information on the cost of alternatives apply here too.

Another important issue is whether each of the shortlisted alternatives would allow for the provisions of the relevant fire safety regulations to be met. Of particular importance are the UK Furniture and Furnishings (Fire) (Safety) Regulations 1988 (FFRs) which are the strictest in the EU. It is important that any replacement FR is able to meet the requirements of the UK FFRs. In consultation with textile industry experts, the following basic analysis of the FR effect of the relevant shortlisted alternative FRs can be provided (see **Table 5-9**). The table also indicates whether use in textiles is specifically mentioned in ECHA's database of registered substances.

similarly concerned and increasing numbers of enquiries from UK consumers (FIRA, undated).

4

It is of note that in November 2013, California announced a new furniture flammability test that will effectively remove FR chemicals from US furniture. The UK Department for Business, Innovation and Skills (BIS) believes this test offers poor fire-safety, but it nevertheless reflects growing concern amongst US consumers about the negative effects of FRs. The UK furniture industry report that they are receiving

elevance to textile treatment in EACH registration dossiers sed in "coatings, inks, paints and pofing" for PC 34 (Textile dyes, nishing and impregnating products; acluding bleaches and other rocessing aids) egistration dossier only refers to the nown use of the substance in foams and refers to service life of AC 5
pofing" for PC 34 (Textile dyes, nishing and impregnating products; acluding bleaches and other rocessing aids) egistration dossier only refers to the nown use of the substance in foams and refers to service life of AC 5
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abrics, textiles and apparel)
sed as "other chemical reagent" for C 34
nly use in polymers appears in the egistration data
nly use in polymers appears in the egistration data
ses as "treatment of textiles, use as eactive processing aide", "treatment of extiles etc, no inclusion onto the naterial" and "formulation of ipping/pouring/roller materials" for PC
n individual registration describes a mited use as "flame retardant in extile industry in closed systems" with ubsequent service life for AC 0 (Other: 06 - Fabrics, textiles and apparel: urtains, upholstery, carpeting/flooring, ugs (no intended release))
nly use in polymers appears in the egistration data
1

It has become known that the UK Department for Business, Innovation and Skills (BIS) has been undertaking a review of the FFRs, which have not been fully amended since their introduction in 1988. Part of this review is the revisiting of the use of FRs, particularly in light of concerns over the effects of BFRs on the environment, wildlife and human health. In recent years, BIS has explored ways in which FR levels in UK furniture might be reduced, without lowering fire safety levels and alternative test methods which could achieve this goal have been investigated.

The focus of this revision work is the FFRs' Schedule 5 Part 1 Match Resistance Test for visible covers, which is currently performed over non-combustion modified test foam (which does not appear in final furniture products for sale in the UK). This results in a substantial amount of FRs

introduced to covers with certain fibre compositions, e.g. polyester. Currently these types of thermoplastic materials are capable of passing the current Schedule 5 Part 1 test but require significant amounts of additional FR which may only serve to pass the test rather than actually provide an appropriate level of safety (the Schedule 5 Part 2 & 3 tests for stretch covers and invisible lining fabrics are, however, performed over combustion modified foams which requires the use of significantly less FRs in those covers). In light of this, the Schedule 5 Part 1 test is perhaps the only FFRs test which may offer significant scope for reducing FR use while also maintaining the required level of fire safety (FIRA, undated).

If the UK FFR requirements are reduced with a lowering of the required FR effects, some alternatives which are currently not considered technically attractive, could become more appealing as cost-effective alternatives to DecaBDE. It is suggested that a change along the above lines could result in a possible reduction in FR chemical usage for the match test by 30-50%. This change is subject to Ministerial clearance and public consultation, and BIS proposes to implement these changes in April 2015 (FIRA, undated).

#### EBP vs. other bromine alternatives

EBP is not the only 'drop-in' or near 'drop-in' replacement for DecaBDE. Ethylene bis(tetrabromophthalimide) and tetrabromobisphenol-A bis (2,3-dibromopropyl ether) are other BFRs which are promoted as suitable to replace DecaBDE (particularly the former). However, there is not a sufficient body of information or evidence on what changes would be required for these to act as a replacement for DecaBDE, although an assumption can be made that major reformulation would not be required (similar FR loading and similar ATO loading). In addition, information from the Alibaba.com website suggests that ethylene bis(tetrabromophthalimide) is more costly than both DecaBDE and EBP; therefore, it may be a less attractive alternative than EBP.

## 5.4 Estimates of substitution costs

### 5.4.1 Introduction to approaches taken for the cost estimates

For the reasons explained above, it is not possible to precisely estimate the costs associated with substituting DecaBDE for an alternative substance due to a lack of information. We have therefore developed a multitude of approaches to calculate substitution costs:

Polymers	Textiles
Approach A1: Complete transition from DecaBDE to EBP, as this can be assumed to be the least complicated and affordable 'drop-in' replacement for DecaBDE  Approach B1: Use of (past) data on market prices of polymers flame-retardant with or	Approach A2: complete transition from DecaBDE to EBP, as this can be assumed to be the least complicated and affordable 'drop-in' replacement for DecaBDE  Approach B2: not relevant to textiles
without DecaBDE for estimating production cost increases following the replacement of DecaBDE	
Approach C1: Use of information on the relative loading and price per kg for each alternative for estimating the cost of replacing DecaBDE by each of the polymer-related alternatives	Approach C2: Use of information on relative loading and price per kg for each alternative for estimating the cost of replacing DecaBDE by each of the textile-related alternatives

<u>Approach D1</u>: Use of information on the relative loading and price per kg for selected alternatives used in polyolefins (PP) for estimating the cost of replacing DecaBDE by a mixture of alternatives

Approach D2: not relevant to textiles

**Important notes**: the calculations of substitution cost shown below have been based on specific consumption and emission tonnages, which cannot be disclosed in full. Therefore, the tables below only provide approximate results with the full details shown in the Confidential Annex.

It is recognised that the switch from DecaBDE to an alternative FR may not simply require a reformulation of plastics and backcoating mixtures but may also demand process changes. It is possible that some of these process changes may be important both in terms of technical feasibility and economic feasibility. However, information from consultation has not been forthcoming and therefore this important element in the calculation of substitution costs has largely been excluded from the discussion that follows.

## **5.4.2** Substitution cost for polymer applications

### Approach A1: Replacement of DecaBDE by EBP

Information that has been collected from the Alibaba.com online marketplace indicates that EBP is ca. 18% more costly per tonne than DecaBDE. On the other hand, consultation responses suggest that EBP is of comparable price, 5% or 20% more costly than DecaBDE. For the purposes of these estimates, we make the following assumptions:

- The price of DecaBDE is ca. €4/kg. This is somewhat higher than what Alibaba.com suggests but is based on discussions with consultees in early 2014
- The price of EBP is between 5% and 20% higher than DecaBDE, i.e. €4.2-4.8/kg
- Additional costs associated with changes to production processes are assumed to be marginal (based on consultation testimonies) and are ignored.

The following table summarises the calculations of the substitution cost per kg of DecaBDE released for the entire tonnage of DecaBDE imported, used and disposed of in the EU, either as a substance or as finished plastic articles. This is estimated to be <€50 under the basic (low volume) scenario when the price of EBP is assumed to be only 5% higher than the price of DecaBDE. Details of the high volume scenario (where a higher price of EBP is assumed, 20% higher than that of DecaBDE) are given in the Confidential Annex (Section 12).

Table 5-10: Estimation of substitution cost for DecaBDE replacement in polymers – Approach A1 (EBP)							
Parameter	Low volume scenario	High volume scenario	Unit				
Tonnage of DecaBDE used in polymers made or imported into the EU	<5,000		t/y				
EBP:DecaBDE replacement ratio	1:1	1					
Tonnage of EBP to be used in polymers as DecaBDE replacement	<5,000	Averile le le de e	t/y				
Cost increase from replacement of FR (based on price	0.2	Available in the Confidential Annex	€/kg				
difference between EBP and DecaBDE, ATO cost remains same)	<1,000,000	only	€/y				
Current DecaBDE releases from polymer formulation, article manufacture and service life (see emissions data for DecaBDE in polymers in <b>Table 4-19</b> )	<20,000		kg/y				
Cost of substitution per kg DecaBDE released	<50		€/kg				

Approach B1: Replacement of DecaBDE by a range of alternatives – Based on cost of FR resin

The calculations adopted under this approach have been drawn from the 2006 Danish EPA report, as shown in **Table 5-11**. Although this information is now ca. 10 years old, more recent information of similar detail is not available. It should be noted that those consultees from the polymers industry largely declined the opportunity to provide quantified information for the purposes of this analysis.

Table 5-11: Cost comparison of alternatives to DecaBDE-based formulations – Danish EPA (2006)						
Comparison	Polymer/compound	European price range(€/kg)				
	Standard HIPS	0.95 – 1.25				
	HIPS + DecaBDE	1.50 - 1.80				
HIPS compounds	HIPS + other BFR:					
Till 3 compounds	- UL 94 V-0	1.90 – 2.10				
	- UL 94 V-1	1.70 – 1.90				
	HIPS/PPE + halogen-free FR	2.30 – 2.90				
Comparison	Polymer/compound	Resin costs(€/kg)				
	FR HIPS + DecaBDE	1.6 – 1.8				
Various V-0 systems	FR ABS + TBBPA or brominated epoxy oligomer	1.9 – 2.5				
for enclosures on the American market in	FR ABS/PC + Halogenated FR	2.5 – 3.0				
2004	FR PC + Halogenated FR	3.0 – 3.6				
	FR HIPS/PPO + Halogen-free FR	3.4				
Source: Danish EPA (200	6)					

Median values have been taken from **Table 5-11** and it has been assumed that the market prices still apply.

Table 5-12: Assumptions on market value of different FR resins – Approach B1								
Resin types	Cost factor/source	Assumed price	Assumptions					
FR HIPS + DecaBDE	Median of 1.6 – 1.8	€1.7/kg	12% loading					
FR HIPS + EBP	1.05-1.2x DecaBDE price	€1.72-1.8/kg	Price increase per kg of FR: €200- 800/kg 12% loading, same ATO					
FR HIPS + e.g. ethylene bis(tetrabromophthalimide)	1.4x DecaBDE price (Alibaba.com)	€1.9/kg	Price increase per kg of FR: 40% or €1,600/kg 12% loading, same ATO					
FR ABS/PC + halogenated FR	Median of 2.5 – 3.0	€2.75/kg	We will not use this category in our calculations as the only halogenated FR that has been shortlisted is TDCPP which is not used in polymers					
FR HIPS/PPO + halogen-free FR (e.g. RDP, BDP/BAPP, TPP)	Upper end of 2.30 – 2.90	€2.9/kg						

The tonnage of DecaBDE-based resin can be estimated based on a nominal DecaBDE loading of 12%.

Importantly, the market prices incorporate production cost and a profit margin. In the absence of information from industry,, it has been assumed that resin manufacturers operate with a flat 10% profit margin, for both DecaBDE-based and DecaBDE-free resins.

The following table shows the substitution cost of DecaBDE, expressed as € per kg DecaBDE release avoided, when the substance is wholly replaced by each of the FR options shown above. The calculations are based on the following equations (see column headed "Parameter"):

 $C = A \times B$ 

 $\mathbf{D} = \mathbf{C} \times 1.7 \times 1000 \times 0.9$ 

**E** (low scenario for EBP) =  $(1.72 - 1.7) \times 1000 \times \mathbf{C} \times 0.9$ 

 $\mathbf{E}_{\text{(high scenario for EBP)}} = (1.8 - 1.7) \times 1000 \times \mathbf{C} \times 0.9$ 

Table 5-13: Estimation of substitution cost for DecaBDE replacement in polymers – Approach B (resin cost)								
Parameter	Parameter	Low volume scenario	High volume scenario	Unit				
Tonnage of DecaBDE used in polymers made or imported into the EU	Α	<5,000		t/y				
DecaBDE loading in resin (average)	В	12	Available in the	%				
Estimated DecaBDE-based resin tonnage manufactured or imported into the EU	С	<40,000	Confidential Annex only	t/y				
Estimated production cost of DecaBDE-based resin (market price: €1.7/kg, profit margin: 10%)	D	<50 million	Ailliex Olliy	€/y				

	Parameter Parameter			ble 5-13: Estimation of substitution cost for DecaBDE replacement in polymers rameter Parameter Low volume			High volume	Unit
EBP	Estimated <b>production cost increase</b> of EBP-based resin (market price: €1.72-1.8/kg, profit margin: 10%)		scenario <1 million	scenario	€/y			
BFRs	Estimated <b>production cost increase</b> of BFR-based resin (market price: €1.9/kg, profit margin: 10%)	E	<10 million		€/y			
HFFRs	Estimated <b>production cost increase</b> of HFFR-based resin (market price: €2.9/kg, profit margin: 10%)		<50 million		€/y			
Current DecaBDE releases from polymer formulation, article manufacture and service life (see emissions data for DecaBDE in polymers in <b>Table 4-19</b> )			<20,000		kg/y			
	Cost of substitution	per kg DecaBl	DE released					
		<40	See Confidential Annex	€/kg				
BFRs (e.g. ethylene bis(tetrabromophthalimide, Tetrabromobisphenol-A bis (2,3-dibromopropyl ether))		<4	100	€/kg				
	HFFRs (e.g., RDP, BDP/BAPP, TPP, RP)			100	€/kg			

On the other hand, it would not be realistic to assume that any of the identified alternatives (particularly alternatives other than EBP) would be capable of replacing the entire consumption of DecaBDE. Moreover, we are unable to determine the potential uptake of replacements for DecaBDE. We therefore consider it appropriate to develop a mixed scenario with assumptions on the split of the market as follows:

- 50% of the DecaBDE-based resin would be replaced by EBP-based resin
- 10% of the DecaBDE-based resin would be replaced by other BFR-based resin
- 40% of the DecaBDE-based resin would be replaced by resin blends flame-retardant with halogen-free FRs.

The above figures are based on informed guesses on the understanding that:

- EBP would still dominate the alternatives market
- BFRs other than EBP would find limited use (given that EBP would be the 'number one' choice among BFRs)
- The remainder of the DecaBDE tonnage would be replaced by a range of HFFRs.

Other combinations of percentages may also be assumed. However, as long as no specific percentage is 'too high' (for example, if 80% of the DecaBDE-based resin would be replaced by resin blends flame-retardant with HFFRs), the overall substitution cost would not greatly differ to what is shown in the following table.

As above, the tonnage of DecaBDE-based resin can be estimated based on a nominal DecaBDE loading of 12%. For both DecaBDE-based and DecaBDE-free resins, it is assumed that the market prices include a 10% profit margin and the remainder reflects production costs.

Parame	eter	Low volume scenario	High volume scenario	Unit
Tonnag EU	e of DecaBDE used in polymers made or imported into the	<5,000		t/y
DecaBD	DE loading in resin	12	1	%
	red DecaBDE-based resin tonnage manufactured or ed into the EU	<40,000		t/y
	ed production cost of DecaBDE-based resin t price: €1.7/kg, profit margin: 10%)	<50 million		€/y
EBP	Estimated EBP-based resin tonnage used as replacement for DecaBDE (50% of total)	<20,000		t/y
	Estimated <b>production cost increase</b> of EBP-based resin (market price: €1.72-1.8/kg, profit margin: 10%)	<1 million	Available in	€/y
BFRs	Estimated BFR-based resin tonnage used as replacement for DecaBDE (10% of total)	<5,000	the Confidential	t/y
	Estimated <b>production cost increase</b> of BFR-based resin (market price: €1.9/kg, profit margin: 10%)	<1 million	Annex only	€/y
HFFRs	Estimated HFFR-based resin tonnage used as replacement for DecaBDE (40% of total)	<15,000		t/y
	Estimated <b>production cost increase</b> of HFFR-based resin (market price: €2.9/kg, profit margin: 10%)	<15 million		€/y
Estima	ed overall production cost increase	<20 million		€/y
manufa	DecaBDE releases from polymer formulation, article acture and service life (see emissions data for DecaBDE in rs in Table 4-19)	<20,000		kg/y
<u> </u>	substitution per kg DecaBDE released	<1,000	1	€/kg

### Approach C1: Cost estimates based on alternatives' loadings and prices per kilogram

Loadings and prices for alternative substances

This third approach takes into account the relative loadings of each of the shortlisted alternative substances and their assumed market prices per kg. The relevant information is summarised in **Table 5-15** and is presented in more detail in Section 5.5 for each of the shortlisted alternatives.

It is acknowledged that there are several types of polymer resins that could be used in the manufacture of FR polymers. It would not be possible to delve into the details of each polymer; therefore, the table focuses on one or two important polymers for each of the alternatives. In addition, it must be noted that for the assumed prices, the following approach has been taken:

- Price differences between DecaBDE and each alternative, expressed as %, were taken from the Alibaba.com site, unless better information was derived from the consultation (see Section 10.2.2)
- The above price differences have been applied to the price of DecaBDE of €4/kg (obtain from consultation)
- The loadings of ATO synergist are taken from consultation (the information summarised in Section 5.5 for each shortlisted alternative FR).

Shortlisted alternative	Relevant polymer	Min. loading	Max. loading	Assumed min. price	Assumed max. price	Assume load			
Triphonyl phosphato	PC/ABS	8%	14%	€6/kg		SC //		00	0/
Triphenyl phosphate	PPE/HIPS	13%	20%			U	0%		
Magnesium hydroxide	PA	45%	50%	€1,	/kg	09	%		
Tris(1,3-dichloro-2-propyl) phosphate	N/A – Not relevant to polymers								
Aluminium trihydroxide	PP	50%	60%	€0.5	5/kg	09	%		
Tetrabromobisphenol-A bis	HIPS	5	%	62.4	1 /1.0	59	%		
(2,3-dibromopropyl ether)	PP	8%	10%	€2.4/kg		2.7%	3.3%		
Ethylene	HIPS	1:	2%	€5.6/kg		4%			
bis(tetrabromophthalimide)	THES	12	2 70						
2,2'-Oxybis[5,5-dimethyl-									
1,3,2-dioxaphosphorinane]		N	/A – Not re	elevant to pol	ymers				
2,2'-disulphide									
Resorcinol	PC/ABS	8%	11%	£3 I	5/kg	09	0/_		
bis(diphenylphosphate)	PPE/HIPS	16%	20%	€3	D/ Ng	Ů.	′0		
Bisphenol-A bis(diphenyl	PC/ABS	10%	14%	€2/kg	€4/kg	09	0/.		
phosphate)	PPE/HIPS	10%	20%	€Z/Kg	€4/ Kg	0.	′0		
Substituted amine									
phosphate mixture	Only confidential information is available; see Confidential Annex								
Red phosphorous	PA	5%	8% €3.2/kg		09	%			
Ethane-1,2-	HIPS or ABS	1:	12% €4.2/kg €4.8/kg		49	 %			

### Market price of polymer resins

The next element in the calculations is the identification of the cost of the resin that needs to be flame retardant. It has not been possible to obtain reliable information for all possible materials; therefore, we have focused on those that appear to be most relevant to DecaBDE and the shortlisted alternatives. Information on market prices (over the last 6 months) has been obtained from the following sources:

- An April 2014 article on the online European Plastics News portal
- The polymer database of the Plasticker Material Exchange, which appears to focus mostly on reclaimed material (the focus of our searches was on material that was described as "virgin")
- A number of short market research reports by the market analysts Tecnon Orbichem. These are available online but cannot be reproduced without permission. Therefore, whilst they have been seen, their contents are not presented here.

The information that has been obtained from these sources is presented in **Table 5-16**.

Table 5-16: Cost of selected polymer resins – Literature review of 29 April 2014								
0.0 - 4	Grade	Data	Price in €/kg			Comme		
Material		Date	Min.	Max.	Average	Source		
	Homo injection	Mar 2014	1.46	1.50	1.48	European Plastics News*		
PP	Homo injection	Apr 2014	1.10	1.20	1.13	Plasticker Material Exchange**		
	Western Europe, homo GP	Oct 2013	Not reproduced here; see original source			Tecnon Orbichem***		
HIPS	Injection	Mar 2014	1.97	1.97 2.01 1.99		European Plastics News*		
	Various virgin grades	Apr 2014	1.20	2.92	1.71	Plasticker Material Exchange**		
ABS	Western Europe, GP injection, natural	Oct 2013	Not reproduced here; see original source			Tecnon Orbichem†		
PC/ABS	Various virgin grades	Apr 2014	1.00	2.85	1.88	Plasticker Material Exchange**		
	Various virgin grades	Apr 2014	1.80	4.15	2.36	Plasticker Material Exchange**		
PC	Western Europe grades	Oct 2013	Not reproduced here; see original source		•	Tecnon Orbichem††		
PPE/PS	Various virgin grades	Apr 2014	3.74	4.10	3.92	Plasticker Material Exchange**		
	Various virgin grades	Apr 2014	0.85	1.25	1.05	Plasticker Material Exchange**		
PA	PA6	Oct 2013	Not reproduced here; see original source		-	Tecnon Orbichem†††		

<sup>\*</sup> Available at: <a href="http://www.europeanplasticsnews.com/subscriber/newscat2.html?cat=14&channel=400&id=4289">http://www.europeanplasticsnews.com/subscriber/newscat2.html?cat=14&channel=400&id=4289</a> (accessed on 29 April 2014)

The review of the aforementioned sources was collated with the compilation of a list of resin prices per kg that were used in the substitution cost estimates. The list is shown in **Table 5-17**.

Table 5-17: Final price figures for polymer resins for use in cost estimates					
Material	Price used	Notes			
PP	€1.5/kg				
HIPS	€2.0/kg				
ABS	€2.0/kg				
PC/ABS	€2.2/kg	Given the prices of ABS and PC, the price for ABS/PC blends shown at Plasticker Material Exchange is not considered reliable and an assumed price of €2.2/kg will be used in the calculations			
PC	€2.4/kg				
PPE/PS	€4.1/kg	This price is estimated from the information available at the Plasticker Material Exchange and the €105 premium of HIPS over PS suggested by the European Plastics News website. This is only a rough approximation			
PA	€2/kg	The price for PA shown at Plasticker Material Exchange is not considered reliable			

<sup>\*\*</sup> Available at: <a href="http://plasticker.de/recybase/listaog">http://plasticker.de/recybase/listaog</a> en.php?aog=A (accessed on 29 April 2014)

<sup>\*\*\*</sup> Available at: <a href="http://www.tecnon.co.uk/userfiles/CNF%20Samples/ppr\_13\_11.pdf">http://www.tecnon.co.uk/userfiles/CNF%20Samples/ppr\_13\_11.pdf</a> (accessed on 29 April 2014)

<sup>†</sup> Available at: http://www.orbichem.com/userfiles/CNF%20Samples/abs 13 11.pdf (accessed on 29 April 2014)

<sup>††</sup> Available at: http://www.orbichem.com/userfiles/CNF%20Samples/pca 13 11.pdf (accessed on 29 April 2014)

<sup>†††</sup> Available at: http://www.orbichem.com/userfiles/CNF%20Samples/par 13 11.pdf (accessed on 30 April 2014)

#### Reformulation considerations

Different FRs require different loading in the polymer matrix as shown above. Therefore, their use as replacements for DecaBDE/ATO would require reformulation. In addition, it is not always clear what the current composition of DecaBDE formulations are, beyond the presence of the resin, of DecaBDE and ATO. For example,

- A PC/ABS formulation may only contain FR (Supresta, undated) or a small quantity of antioxidant (0.3 per hundred resin) (Choi, et al., 2000)
- An ABS formulation may contain a small quantity of filler TiO<sub>2</sub> (1-3 per hundred resin), thermal stabiliser (0.8-1.3 per hundred resin), lubricant (0.5-1 per hundred resin) and antioxidant (0.2-0.5 per hundred resin) (Dow, 2005)
- An EVA formulation may contain anti-ageing system (5.4 per hundred resin), processing aids, coupling and plasticiser (11.5 per hundred resin), curing system (7.4 per hundred resin) (PINFA, 2010b)
- Polypropylene and polyethylene may be filled with talc (example concentration 14%-15%) (Papazoglou, 2004)
- Polyamide, PBTE and PET formulations may be filled with glass fibre (example concentration 30%) (Papazoglou, 2004).

Although, these examples demonstrate the presence of other components, knowledge of the % concentration of the FR without knowledge of its presence expressed as "per hundred resin" does not allow us to gauge the relative concentration of polymer:FR. For the purposes of our cost estimates, the following assumptions on the composition of DecaBDE-based polymers will be made.

Table 5-18: Assumed simplified compositions of selected V-0 graded polymers containing DecaBDE (% by weight)								
Material	Polymer	DecaBDE	АТО	Fillers and other additives				
PP/PE	50%	21%	7%	22% (14% filler)				
HIPS	84%	12%	4%	Nil				
ABS	80%	14%	4%	2%				
PA	51%	14%	5%	30% (glass fibre)				

**Important note**: The above figures are based on consultation and the information presented earlier in this report on different formulations. These are only approximations used for the purpose of our calculations and cannot be assumed to represent the most appropriate or common formulations of DecaBDE-containing polymers. It must also be noted that there are polymers which are relevant to DecaBDE but are not used here as an example (e.g. PBTE/PET, engineering thermoplastics, etc.)

For the purposes of our calculations, it is assumed that, if a FR replacement for DecaBDE/ATO is used in loadings lower than the combined loading of DecaBDE/ATO, the composition of the polymer will need to be balanced. Polymer compounders may consider (a) increasing the percentage of the resin or (b) adding a cheaper filler to the formulation.

Some information on fillers and other key additives has been collected from online sources. information from the USA suggest that the highest demand as a filler for polymer resins is for ground calcium carbonate followed by  $TiO_2$  and ATH. Talc, kaolin, mica, wollastonite, silica, barites, and organoclays have a much smaller share of the market (Xanthos, 2010).

As regards the price of some key filler materials, the following have been obtained from literature:

- Calcium carbonate: in 2012, ground calcium carbonate from the UK was priced at US\$75-103 per tonne or ca. €0.06-0.08/kg. Precipitated calcium carbonate had a price of US\$500 per tonne or ca. €0.4/kg (Roskill, 2012)
- TiO<sub>2</sub>: October 2013 prices in countries such as the UK, Germany, France and Spain were ca. US\$3.5/kg or ca. €2.5/kg (Litcoat, 2013)
- Glass fibre: a recent (2013) report by the JRC describes the average global price of glass fibres at €1.8/kg (JRC, 2013b)
- ATH: ATH is another substance that is often used as filler, as shown above, its price is at ca. €0.5/kg.

It is acknowledged that there is a large variety of components that might be added to plastic formulations. In our calculations, we shall use a flat price of €0.4/kg for all additives other than the polymer resin and the FR. This is a simplification in the face of the lack of detailed information.

### Estimates of substitution cost

The estimates of the substitution cost under Approach C1 are provided below. Key assumptions include:

- For estimating the changes in the formulations after the replacement of DecaBDE/ATO, we assume that the original ratio of resin:filler will remain the same, and thus the new resin and filler percentages have been adjusted accordingly
- For brominated alternatives, ATO would still be used at specified concentrations at cost of €6/kg
- In order to show cost ranges, low concentrations of alternative FRs in **Table 5-15** are combined with low prices per kg in the same table, where information is available. High concentrations are combined with high prices per kg (for example, for bisphenol-A bis(diphenyl phosphate) the loading of 10% in PC/ABS is used alongside the low price of €2/kg and the higher loading of 14% is combined with the high price of €4/kg)
- As we do not have information on the market importance of the polymer applications of DecaBDE, we assume that for each alternative and under each scenario, the entire consumption (low tonnage) of DecaBDE is replaced by said alternative.

Table 5-19: Substitution cost for each alternative FR in polymer applications – Approach C1								
Alternative FR	New polymer	Total cost difference (rounded)	Cost per kg DecaBDE emitted (low scenario - rounded)					
Triphenyl phosphate	PC/ABS	€1-7 million	<€100 to <€500/kg					
Triphenyi phosphate	PPO/HIPS	€55-60 million	€3,600 to €4,000/kg					
Magnesium hydroxide	PA	-€19-20 million	-€1,250 to -€1,300/kg					
Aluminium trihydroxide	PP	-€20-22 million	-€1,350-1,450/kg					
Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	PPO/HIPS	€50 million	€3,200/kg					
	PP	-€10-12 million	-€700 to -€800/kg					
Ethylene bis(tetrabromophthalimide)	HIPS	€8 million	<€500/kg					
Resorcinol bis(diphenylphosphate)	PC/ABS	-€2-4 million	-€150 to -€250/kg					
	PPO/HIPS	€45-46 million	€3,000/kg					
Bisphenol-A bis(diphenyl	PC/ABS	-€7 million to <€1 million	- <€500/kg to <€10/kg					
phosphate)	PPO/HIPS	€42-48 million	€2,800 to €3,200/kg					
Red phosphorous	PA	-€11-13 million	-€700 to -€850/kg					
Ethane-1,2- bis(pentabromophenyl)	HIPS	<€1 to 3 million	<€50 to <€200/kg					

Using the aforementioned prices per tonne for DecaBDE (€4/kg), the alternative FRs (**Table 5-15**), the polymer resins (**Table 5-17**), ATO (€6/kg) and fillers (€0.4/kg), the following summary results can be obtained (NB. figures have been rounded).

The general conclusions are:

- The substitution costs significantly vary by alternative FR but also vary by polymer resin
- The change that makes the greatest difference is the switch from HIPS to PPO/HIPS, due to the higher relative price of the latter.

The total cost figures are should only be considered as indicative because DecaBDE is used in a range of plastic types, not in a single type. It is not possible to provide a more accurate estimate of the overall substitution cost using the above set of information, as it is not clear how the use of DecaBDE is broken down by polymer resin, which alternative FRs would replace it and how much DecaBDE is contained within each polymer resin. It is noted that there are several other resins in which DecaBDE is used (e.g. PET/PBTE) which have not been used in these examples.

Alternative FR	Scenario	Resin used		Original composition (100 parts)					New composition (100 parts)			
		With DecaBDE	With alt. FR	Polymer resin	DecaBDE	АТО	Fillers etc.	Polymer : filler ratio	Polymer resin	FR	АТО	Filler
Triphenyl phosphate	Low %	ABS	PC/ABS	80%	14%	4%	2%	40	90%	8%	0%	2%
	High %	ABS	PC/ABS	80%	14%	4%	2%	40	84%	14%	0%	2%
	Low %	HIPS	PPO/HIPS	84%	12%	4%	0%	N/A	87%	13%	0%	0%
	High %	HIPS	PPO/HIPS	84%	12%	4%	0%	N/A	80%	20%	0%	0%
Magnesium hydroxide	Low %	PA	PA	51%	14%	5%	30%	1.7	35%	45%	0%	20%
	High %	PA	PA	51%	14%	5%	30%	1.7	31%	50%	0%	19%
Aluminium trihydroxide	Low %	PP	PP	50%	21%	7%	22%	2.3	35%	50%	0%	15%
	High %	PP	PP	50%	21%	7%	22%	2.3	28%	60%	0%	12%
Tetrabromobisphenol- A bis (2,3- dibromopropyl ether)		HIPS	PPO/HIPS	84%	12%	4%	0%	N/A	90%	5%	5%	0%
	Low %	PP	PP	50%	21%	7%	22%	2.3	62%	8%	3%	27%
	High %	PP	PP	50%	21%	7%	22%	2.3	60%	14%	3%	26%
Ethylene bis(tetrabromo- phthalimide)		HIPS	HIPS	84%	12%	4%	0%	N/A	82%	14%	4%	0%
Resorcinol bis(diphenyl phosphate)	Low %	ABS	PC/ABS	80%	14%	4%	2%	40	90%	8%	0%	2%
	High %	ABS	PC/ABS	80%	14%	4%	2%	40	87%	11%	0%	2%
	Low %	HIPS	PPO/HIPS	84%	12%	4%	0%	N/A	84%	16%	0%	0%
	High %	HIPS	PPO/HIPS	84%	12%	4%	0%	N/A	80%	20%	0%	0%
Bisphenol-A bis(diphenyl phosphate)	Low %	ABS	PC/ABS	80%	14%	4%	2%	40	88%	10%	0%	2%
	High %	ABS	PC/ABS	80%	14%	4%	2%	40	84%	14%	0%	2%
	Low %	HIPS	PPO/HIPS	84%	12%	4%	0%	N/A	90%	10%	0%	0%
	High %	HIPS	PPO/HIPS	84%	12%	4%	0%	N/A	80%	20%	0%	0%

		Resin used			h and without DecaBDE/ATO – Approach C1 (loadings & prid Original composition (100 parts)				New composition (100 parts)			
Alternative FR	Scenario	With DecaBDE	With alt. FR	Polymer resin	DecaBDE	АТО	Fillers etc.	Polymer : filler ratio	Polymer resin	FR	АТО	Filler
	Low %	PA	PA	51%	14%	5%	30%	1.7	60%	5%	0%	35%
Red phosphorous	High %	PA	PA	51%	14%	5%	30%	1.7	58%	8%	0%	34%
Ethane-1,2- bis(pentabromo- phenyl)	Low price	HIPS	HIPS	84%	12%	4%	0%	N/A	84%	12%	4%	0%
	High price	HIPS	HIPS	84%	12%	4%	0%	N/A	84%	12%	4%	0%

## Approach D1: Cost estimates based on alternatives' loadings and prices per kilogram for a mixture of alternatives used in polyolefins

The above estimates are generic and disregard a very important parameter that has affected the use of DecaBDE in recent years. As noted earlier, due to the provisions of the RoHS Directive, the presence of DecaBDE in E&E, and in particular in ABS and HIPS applications, has greatly reduced. In other words, the replacement of DecaBDE by substances such as TPP, RDP and BDP/BAPP (with a concomitant switch to polymeric blends) has already occurred and would not result from a new restriction on the substance. Consultation suggests that the most prominent current use of DecaBDE in plastics is in polyolefins (PP/PE).

We have, therefore, developed a new scenario where it is assumed that the entire consumption of DecaBDE is in polypropylene (PP). A review of the relevant applications for the shortlisted alternatives (see Section 5.5) would suggest that those with confirmed use in PP applications include:

- Aluminium trihydroxide
- Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)
- Ethylene bis(tetrabromophthalimide)
- Substituted amine phosphate mixture
- Ethane-1,2-bis(pentabromophenyl)

While magnesium hydroxide and triphenyl phosphate might also be considered, the use of the former is typically focused on PA applications and the latter is considered relevant only by virtue of being a member of the wider group "phosphate esters".

We do not hold sufficient information on the substituted amine phosphate mixture, therefore we cannot feasibly include this alternative into our calculations. Among the remaining four alternatives (which notably comprise a mineral FR and three BFRs), we make an educated guess on the breakdown of the replacement of DecaBDE-based PP:

- 50% of DecaBDE-treated PP will be replaced by EBP-treated PP
- 13% of DecaBDE-treated PP will be replaced by aluminium trihydroxide-treated PP
- 13% of DecaBDE-treated PP will be replaced by tetrabromobisphenol-A bis (2,3-dibromopropyl ether)-treated PP
- 13% of DecaBDE-treated PP will be replaced by ethylene bis(tetrabromophthalimide)-treated PP.

Using the loading and price per kg data presented above, we may develop the following table on the consumption of resin, FR, ATO synergist and plastic filler.

		Share of	(	Compositi	on of FR	PP polyr	ner
Low volume scenario		DecaBDE polymer market	Resin	FR	АТО	Filler	Resin: filler ratio
Current	DecaBDE	100%	50%	21%	7%	22%	2.3
Future mix of FRs	Aluminium trihydroxide	13%	31%	55%	0%	14%	2.3
	Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	13%	61%	9%	3%	27%	2.3
	Ethylene bis(tetrabromophthalimi de)	13%	50%	21%	7%	22%	2.3
	Ethane-1,2- bis(pentabromophenyl)	50%	50%	21%	7%	22%	2.3

Using the price information presented above, it can be calculated for the low volume scenario that the total substitution cost would be a **saving** of ca. €4 million per year or a cost per kg DecaBDE emission avoided of - <€300. For the overall substitution cost to increase and become a real cost rather a saving, the shares of EBP and ethylene bis(tetrabromophthalimide) would need to increase, as their use leads to additional costs.

#### Comparison of validity of approaches to estimating substitution costs

The four different approaches give results that are considerably different. This can be explained by the different assumptions as to the extent to which non-EBP alternatives may replace DecaBDE. A comparison outlining the validity of the four sets of calculations is provided in the table below.

This analysis should be seen as a snapshot of the assumed current situation. Of course, it must be remembered that the tonnages of DecaBDE that will be used and released in the future are expected to decline and that the prices of alternatives are likely to fluctuate.

	Approach A1	Approach B1	Approach C1	Approach D1
Realism  Pros: due to the more straightforward replacement of DecaBDE by EBP, the calculation of costs is relatively reliable		Pros: reasonable results if assumed that a blend of FRs will be used to replace DecaBDE, as it reflects the wide variaty of alternative solutions available on the market	<b>Pros</b> : takes a closer look at how formulations may change due to the use of different resins, FR loadings and other additiives	<b>Pros</b> : it reflects the current situation on the DecaBDE market, where use in E&E has diminished
	Cons: non-EBP alternatives are available and are already used	Cons: unrealistic to assume that DecaBDE would be wholly replaced by a single type of alternatives.  HFRs not considered as an option due to their general absence from the shortlist	Cons: unrealistic to assume that DecaBDE would be wholly replaced by a single alternative. Creating a combined scenario would require significant details which are not currently available	Cons: due to data limitations, it focuses on PP articles only and only a small number of potential alternative FRs
Accuracy of cost increases/ decreases per	Pros: more accurate, as price per tonne data for EBP and DecaBDE have been obtained from consultation	<b>Pros</b> : cost of FR polymer is used and this porbably includes other production costs	<b>Pros</b> : the approach aims to take into account some key reformulation parameters	<b>Pros</b> : the approach aims to take into account some key reformulation parameters
tonne	Cons: calculations do not take into consideration the (apparently limited) costs associated to changes to production processes	Cons: approach is based on price data from the 2000s	Cons: approach based on several assumptions and simplifications. It does not consider changes in production costs other than raw materials	Cons: approach based on several assumptions and simplifications. It does not consider changes in production costs other than raw materials
Accuracy of calculation of overall costs	<b>Pros</b> : more accurate, due to the simplicity of calculations	Pros: N/A	<b>Pros</b> : approach allows the calculation per alternative and for different resins, thus taking into account resin-specific parameters	<b>Pros</b> : approach allows the calculation per alternative and for different resins, thus taking into account FR-specific parameters

	Approach A1	Approach B1	Approach C1	Approach D1	
	Cons: approach underestimates the overall costs as it assumes that the cheapest alternative FR is used	Cons: less accurate, due to simplified assumptions made on the take-up of different categories of alternatives, and on profit margins/production costs. Result is greatly dependent on assumptions made	Cons: approach overestimates costs when costly alternatives are used in expensive resins such as PPO/HIPS	Cons: approach probably underestimates costs. Result is greatly dependent on assumptions made	
Assessment of calculated overall costs	Substitution cost is estimated at <€1million/y or <€50/kg of DecaBDE released. This is relatively low	Substitution cost could be as high as <€50 million/y or <€2,500/kg of DecaBDE released for the most costly FRs; when a blend of alternative FRs is assumed, the estimated overall production cost increase is <€15 million or <€1,000/kg of DecaBDE released	Substitution cost could be as high €60 million/y or less than €4,000/kg of DecaBDE released for the most costly FRs/polymer resins. Certain alternative FRs would – theoretically – lead to cost savings if they replaced DecaBDE in polymer applications in full	Overall, a cost saving of ca. €4 million can be calculated or -<€300 per kg of DecaBDE released	
	All approaches have their advantages and disadvantages. The one with fewer unknown parameters is Approach A1 which also implicitly takes into account the replacement of DecaBDE in E&E equipment (e.g. by RDP/BDP/TPPP and changes in the polymer resin). Approach C1 is probably the farthest from reality, while approach D1 may also give unrealistic results, depending on the assumptions made				

### 5.4.3 Substitution cost for textile applications

#### Approach A2: Replacement of DecaBDE by EBP

The assumptions made on the price of EBP have been described earlier. The following table summarises the calculations of the substitution cost per kg of DecaBDE released. This is estimated to be <€50/kg.

This cost estimate may well be an underestimate of the total cost, if non-EBP alternatives are considered. For example, 2,2'-oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide is significantly more costly than DecaBDE and its use in viscose fibres in combination with IFFRs (aramids, etc.) results in textile articles which may significantly more costly than DecaBDE-treated textiles. More generally, several bromine-free FRs may face serious difficulties in achieving the required fire safety standards in man-made fibres (as opposed to cotton), as they typically require high loadings and suffer from poorer durability. The fact that non-EBP alternatives currently find some use, suggests that certain users are prepared to pay a higher cost, nevertheless, the extent of use for non-EBP alternatives is expected to be limited, based on consultation findings.

Table 5-23: Estimation of substitution cost for DecaBDE replacement Approach A2 (EBP)	nt in textile finis	hing in the EU –		
Parameter	Low volume scenario	High volume scenario	Unit	
Tonnage of DecaBDE used in textiles finished or imported into the EU	<5,000	A ilalala ira da	t/y	
EBP:DecaBDE replacement ratio	1:1	Available in the Confidential		
Tonnage of EBP to be used in textiles as DecaBDE replacement	<5,000		t/y	
Cost increase from replacement of FR (based on price difference	0.2	0.2 Annex only		
between EBP and DecaBDE, ATO cost remains same)	<1 million		€/y	
Current DecaBDE releases from compounding, article coating and article service life (see emissions data for DecaBDE in textiles in <b>Table 4-19</b> )	<20,000	Available in the Confidential	kg/y	
Cost of substitution per kg DecaBDE released	<50	Annex only	€/kg	

Approach C2: Cost estimates based on alternatives' loadings and prices per kilogram

For textiles, in the face of available information, an approach simpler than for polymers is followed. We consider the relative loading of suitable alternative substances and the price per kg. The following table summarises the information that is used in the calculations. 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide is not included in the calculations as it finds very specific uses (in viscose) which are not representative of the full range of current DecaBDE uses.

Shortlisted alternative	Min. loading	Max. loading	Assumed min. price	Assumed max price	
Magnesium hydroxide	5× De	caBDE	€1,	/kg	
Tris(1,3-dichloro-2-propyl) phosphate	1.2× D	1.2× DecaBDE		2/kg	
Aluminium trihydroxide	3× De	caBDE	€0.5	5/kg	
Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)		sed in textiles; ion available	€2.4/kg		
Ethylene bis(tetrabromophthalimide)	1× DecaBDE (assumption based on information on polymer applications)		€5.6	€5.6/kg	
2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	0.9× D	ecaBDE	Considerably higher price than DecaBDE; discussed in the Confidential Annex		
Resorcinol bis(diphenylphosphate)	=	sed in textiles; ion available	€3.5/kg		
Bisphenol-A bis(diphenyl phosphate)		sed in textiles; ion available	€2/kg	€4/kg	
Substituted amine phosphate mixture (P/N intumescent systems)	uted amine phosphate (P/N intumescent N/A – Not relev		evant to textiles		
Red phosphorous	No information available; generally, limited applicability to textiles		€3.2	2/kg	
Ethane-1,2- bis(pentabromophenyl)	1× De	caBDE	€4.2/kg	€4.8/kg	

Using the information available on the tonnage of DecaBDE imported for use in textiles or in textiles articles and the estimated emissions of DecaBDE throughout the lifecycle of the relevant textiles, the following estimated substitution costs can be calculated on the assumption that each alternative would fully and individually replace DecaBDE. For EBP, the lower price per kg has been used.

	Current site DecaBDE scen		After De replace		Total	Cost per kg
Alternative FR	Quantity of DecaBDE used (t/y)	Quantity of ATO used (t/y)	Quantity of alternative FR used (t/y)	Quantity of ATO used (t/y)	substitution cost (€/y)	DecaBDE emitted (€/kg)
Magnesium hydroxide	<5,000	<1,500	<25,000	0	- <5 million	- <250
Tris(1,3-dichloro-2- propyl) phosphate	<5,000	<1,500	<6,000	0	- <10 million	-<500
Aluminium trihydroxide	<5,000	<1,500	<15,000	0	- <20 million	-<1,100
Ethylene bis(tetrabromo- phthalimide)	<5,000	<1,500	<5,000	<1,500	<10 million	<400
EBP	<5,000	<1,500	<5,000	<1,500	<1 million	<50

The results in **Table 5-25** show that the substitution costs vary by alternative FR and for some alternatives would lead to overall savings. Nevertheless, this presents an inaccurate picture of a future without DecaBDE in textiles. It is certain that mineral FRs of phosphates would not be able to replace the entire current consumption of DecaBDE; therefore, we consider it appropriate to develop a mixed scenario, and the assumptions on the split of the market are taken as follows:

- 50% of the DecaBDE consumption would be replaced by EBP
- 13% of the DecaBDE consumption would be replaced by each of the other relevant alternative FRs in our shortlist.

The above percentages are based on informed guesses on the understanding that:

- EBP would still dominate the alternatives market
- BFRs other than EBP would find limited use (given that EBP would be the number one choice among BFRs)
- No other of the non-EBP alternatives in the shortlist would command a particularly large portion of DecaBDE consumption.

The results of the mixed scenario are shown in **Table 5-26**.

Table 5-26: Estimation of substitution cost for DecaBDE replacement in textile finishing in the EU – Approach C2 (loadings and prices – Mixed scenario)					
Alternative FR	Share of DecaBDE	After DecaBDI Quantity of alternative	Quantity of ATO used	Substitution cost (€/y)	Substitution cost per kg DecaBDE
	consumption	FR used (t/y)	(t/y)	6652 (6/ 4/	released (€/kg)
Magnesium hydroxide	13%	<3,000	0	-<0.5 million	-<250
Tris(1,3-dichloro-2- propyl) phosphate	13%	<1,000	0	- <1 million	-<500
Aluminium trihydroxide	13%	<2,000	0	-2 million	-<1,100
Ethylene bis(tetrabromo-phthalimide)	13%	<5,000	<500	<1 million	<400
Ethane-1,2- bis(pentabromophenyl)	<1,000	<0.5 million	<50		
Overall substitution cost (€/y)					million
Su	-<1	.50			
* Estimates for the "high scenario" are provided in the Confidential Annex					

The table suggests that cost savings would arise from the use of this mixture of alternatives. Different assumptions would result in costs rather than savings, i.e. if the combined shares of the BFRs would exceed 80% of current DecaBDE consumption. It must also be remembered that not all alternative FRs are equally effective as DecaBDE replacements on different textile materials and this will play a significant role in the choice of alternatives as replacements for DecaBDE.

#### Comparison of validity of approaches to estimating substitution costs

The two different approaches give results that are considerably different; this is explained by the different assumptions on the extent to which non-EBP alternatives may replace DecaBDE. A comparison of the realism and accuracy of the two sets of calculations is provided in the next table.

Table 5-27: Cor applications	nparison of two approaches to the calculation	of substitution costs for DecaBDE in textile
	Approach A2	Approach C2
Realism	Pros: due to the more straightforward replacement of DecaBDE by EBP, the calculation of costs is relatively reliable. EBP appears to be the preferred alternative FR among those industry stakeholders that have made a contribution to the consultation exercise	<b>Pros</b> : it reflects the wide variaty of alternative solutions available on the market and the significantly variable loadings and prices
	Cons: non-EBP alternatives are available and are already used	Cons: the replacement of the entire tonnage of DecaBDE by non-EBP alternatives is an unrealistic proposition.  The breakdown of DecBDE replacement in the 'mixed scenario' is based on educated guesses
Accuracy of cost increases/	<b>Pros</b> : more accurate, as price per tonne data for EBP and DecaBDE have been obtained from consultation	<b>Pros</b> : the approach aims to take into account some key reformulation parameters
decreases per tonne	Cons: calculations do not take into consideration the (apparently limited) costs associated to changes to production processes	<b>Cons</b> : approach based on several assumptions and simplifications. It does not consider changes in production costs other than raw materials
Accuracy of calculation of overall costs	<b>Pros</b> : more accurate, due to the simplicity of calculations	<b>Pros</b> : approach allows the calculation per alternative, thus taking into account FR-specific-parameters
	Cons: approach underestimates the overall costs as it assumes that the cheapest alternative FR is used	Cons: approach underestimates costs when less costly alternatives are used to replace DecaBDE.  Appraoch fails to take into account the FR efficiency of different alternatives which may limit their practical updtake.  The assumptions made for the 'mixed scenario' are based on educated guesses
Assessment of calculated overall costs	Substitution cost is estimated at <1million/y or <€50/kg of DecaBDE released. This is relatively low	Substitution cost could be negative (i.e. cost savings), even if a blend of FRs is used with EBP accounting for 50% of the replaced DecaBDE volume
	be assumed that the overall cost would be	BDE would probably be replaced by EBP, it can close to the <€1 million/y or <€50 per kg of ated under Approach A2

## 5.5 Detailed assessment of shortlisted alternatives

## 5.5.1 Alternative 1: Triphenyl phosphate (TPP) (CAS No. 115-86-6)

#### Technical feasibility issues

Relevant applications

There are several literature sources describing the applicability of TPP as a FR. A summary is provided below. Entries in italics refer to "phosphate esters" in general, rather than specifically to TPP.

Table 5-28: Applications f	or Triphenyl phosphate (TPI	P) (CAS No. 115-86-6)	
Application	Material - substrate	Notes	Source
Profiles- Trim	ABS, PC blends, Polycarbonate	Attributed to "phosphate esters"	PINFA (2013)
Castings, Coatings, RIM parts	Polyurethane (PU)	Attributed to "phosphate esters"	PINFA (2013)
Flooring	Phenolic resins	Attributed to "phosphate esters"	PINFA (2010b)
Ceiling Sidewalls Panels Structural parts	Phenolic resins	Attributed to "phosphate esters"	PINFA (2010b)
Automotive parts (dashboard instruments, etc.)	ABS, PC/ABS		PINFA (2010b)
Sealants (flame-retardant and/or fire-resistant)	PUR, acrylics, epoxy, elastomers, PVC	Attributed to "phosphate esters"	PINFA (2010b)
Cables Electrical cables PV cables Control cables Lift cables Fire alarm cables	Polyolefins Elastomers Thermoplastic Elastomers (TPE)	Attributed to "phosphate esters". Flame inhibition and charring properties	PINFA (2010b) PINFA (2013)
Films: Tarpaulins	Flexible PVC	Attributed to "phosphate esters"	PINFA (2013)
Sheets: Roofing, Glazing, Lighting	Polycarbonate and blends	Referred to as "Phosphate esters"	PINFA (2013)
Thin films: roofing underlay	TPU	Attributed to "phosphate esters"	PINFA (2013)
E&E – UL94 V-0	PC, PC/ABS, PPE/HIPS		Troitzsch (2011)
Printed circuit boards, Thei polymers Thermosets and epoxy resi Photographic film			Environment Agency (2009b)

Table 5-28: Applications for Triphenyl phosphate (TPP) (CAS No. 115-86-6)					
Application	Material - substrate	Notes	Source		
Not specified	HIPS/PPO, PC/ABS		JRC (2007)		
E&E Enclosures V-0	PC/ABS, PPE/HIPS, phenolic		Danish EPA (2006)		
Not specified	PC/ABS, HIPS/PPO, epoxy resins, phenolic resins		UK HSE (2012)		
Electronics	HIPS/PPO, PC/ABS		US EPA (2014)		
Hydraulic fluids, PVC, elect video display units cables, engineering thermoplastics resins, phenolic resins	casting resins, glues,		van der Veen & de Boer (2012)		

Using TPP as a replacement for DecaBDE in polymers would require manufacturers to switch to different resins, e.g. from HIPS to HIPS/PPO plastic (Department of Ecology State of Washington, 2008). It is also mentioned in literature that TPP is a constituent of products (made of HIPS/PPO and PC/ABS) containing RDP at approximately <5-6% (Washington State, 2006).

No information was made available from consultation on the applications and use of TPP.

#### **Economic feasibility issues**

#### Loading

Information on the loading of the substance in its applications has been identified in certain sources, as summarised below.

Table 5-29: Loa	Table 5-29: Loadings for TPP (CAS No. 115-86-6)					
Loading (bw)	Material	Notes	Source			
8-12%	PC/ABS	UL94 V-0 grade	Danish EPA (2006)			
14%	PC/ABS	UL94 V-0 grade	PINFA (2010)			
30%	HIPS/PPO		Department of Ecology State of Washington (2008)			
11%	4:1 PC/ABS	UL94 V-0 grade	Papazoglou (2004)			
9%	8:1 PC/ABS	UL94 V-0 grade				
13%	HIPS/PPO	UL94 V-0 grade				

#### Price issues

Information on the price of TPP per kg is not available from consultation. Some information from literature is available. HELCOM (2013) suggests that the price of TPP is €6/kg, which would make it ca. 50% more costly than DecaBDE (at present). Nevertheless, the cost of ATO needs to be taken into consideration when DecaBDE is used. Typically, DecaBDE is used at a loading of 10-15% in polymers with an additional 4-5% ATO. It would therefore be assumed that for every kg of DecaBDE, 1/3 of a kg ATO is needed. According to the Metal Pages website 46, the price of ATO min 99.5% FOB China is ca. US\$8.7/kg or €6.3/kg. So 1 kg of DecaBDE would be accompanied by ca. 0.33 kg ATO at an estimated additional cost of ca. €2. Thus, the cost of DecaBDE+ATO per kg of FR would be ca. €6,

<sup>&</sup>lt;sup>46</sup> Available here: <a href="http://www.metal-pages.com/metalprices/antimony/">http://www.metal-pages.com/metalprices/antimony/</a> (accessed on 10 March 2014).

similar to that of TPP. Nevertheless, the loading of TPP could be higher than DecaBDE making the total cost of TPP input higher than that of DecaBDE/ATO formulations. Nevertheless, HELCOM asserts that producers would face minimal or no affordability issue if TPP was to be used in HIPS/PPO or PC/ABS resins (HELCOM, 2013).

By way of comparison, information from the Alibaba.com online marketplace would suggest that TPP might have a price ca. 20% lower than that of DecaBDE (see **Table 10-3**). This price difference is not considered a reliable indicator of the price of TPP.

Substitution cost calculations

The following table summarises the relevant information for TPP, based on the analysis presented in Section 5.4.

Table 5-30: Substitution cost calculations for TPP (CAS No. 115-86-6)							
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes			
Polymers	A1	Not relevant	Not relevant				
	B1	HFFR full: <50 million HFFR mix: <15 million	<2,100	TPP assumed to be a 'member' of the HFFR group			
	C1	PC/ABS: 17 million PPO/HIPS: 55-60 million	PC/ABS: <100 to <500 PPO/HIPS: 3,600-4,000				
	D1	Not relevant	Not relevant				
Textiles	A2	Not relevant	Not relevant				
	C2	Not relevant	Not relevant				

#### Hazard profile

REACH Registration and C&L data

**Important note**: The substance is included in the CoRAP and will undergo evaluation by the UK authorities. This substance evaluation process is expected to generate additional information on the hazard profile of the substance. Information from literature is presented here without prejudice to the outcome of the substance evaluation process and without claiming that the information shown is complete.

**Table 5-31** summarises the hazard profile TPP based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-31: REACH	Registration data TPP (CAS	No. 115-86-6)	
Category	Parameter	TPP	Notes
Physical state		Solid	Registration dossier
Classification for	Acute hazards to the	Aquatic Acute 1 - H400	Self-notified (C&L
environmental	aquatic environment		inventory)
hazards	Long-term hazards to	Aquatic Chronic 1 - H410	Self-notified *C&L
	the aquatic		inventory)
	environment		Registration dossier
			indicates Aqua Chronic
			2 – H411
Classification for	Carcinogenicity	N/A	
human health	Mutagenicity	N/A	
hazards	Reproductive toxicity	N/A	
	Acute toxicity	N/A	
	Irritation	N/A	
	Sensitisation	N/A	
	Specific target organ	N/A	
	toxicity		
PBT assessment	Persistence	Not P	
	Bioaccumulation	Not B	
	Toxicity	Not T	NOEC is 0.037 mg/L,
			which is > 0.01 mg/L
	Conclusion	Not a PBT	
Key	Partition coefficient	4.63 (20 °C)	
physicochemical	Water solubility	1.9 mg/L (20 °C)	
properties	Vapour pressure	0.00000835 hPa (25 °C)	
Ecotoxicological	PNEC aqua (freshwater)	0.0037 mg/L	
information	PNEC aqua (marine	0.00037 mg/L	
	water)		
	PNEC aqua (intermittent	0.0025 mg/L	
	releases)		
	PNEC STP	5 mg/L	
	PNEC sediment	0.2397 mg/kg sediment dw	
	(freshwater)		
	PNEC sediment (marine	0.2397 mg/kg sediment dw	
	water)		
	PNEC soil	0.0385 mg/kg soil dw	
	PNEC oral predators	0.833 mg/kg food	

#### Past PBT hazard assessments

The following table summarises information on the assessment of the PBT properties of TPP. The substance does not meet the PBT criteria but its aquatic toxicity is noted, as explained above.

Table 5-32: PBT properties of TPP	(CAS No. 115-86-6)		
Persistence	Bioaccumulation	Toxicity	Source
P criterion is not met	B criterion is not fulfilled (reported BCFs <1,750)	Moderate to high acute aquatic toxicity but studies in rats have shown low acute and sub-chronic toxicity	(Keml, 2009)
Readily biodegradable, which is considered equivalent to a half-life of less than 40 days in freshwater.  P criterion not met	BCF value of 420 selected from the available data. B criterion not met	Lowest NOEC value from the available tests was 0.037 mg/L; an estimated NOEC for invertebrates was also available, 0.032 mg/L. The substance was not classified for mammalian effects.  T criterion not met	(Environment Agency, 2009b)
T1/2 =12 hours atmospheric; T1/2 hydrolysis < 5 days - 366 days (pH 9 – pH 3); criterion is > 60 days	BCF = 113 – 1,743; criterion is > 1,000; LogKow < 4.77	Low oral rat 3,500-20,000 mg/kg; However, aquatic toxicity is high, not mutagenic Ames test; low reprotoxicity, low teratogenic toxicity, low neurotoxicity	(JRC, 2007)
TPP is inherently biodegradable and has been found to biodegrade extensively under both aerobic and anaerobic conditions in various test systems. Half- lives in water/sediment simulation tests range from 3-12 days in river water/sediment and pond sediment, whereas half-lives ranging from 50-60 days are obtained in pond hydrosoil. No data have been found on ready biodegradability. Based on the available data, TPP is not considered to meet the P or vP criteria (half-life > 40 days and > 60 days in freshwater, respectively and half-life > 120 days and > 180 days in freshwater sediment, respectively)	TPP does not meet the B criterion as the experimentally determined BCF values (range 84-364) are < 2,000	It is questionable whether TPP meets the T criterion, as the validity of the chronic NOEC values reported (range 0.087-0.23 mg/L) are uncertain. The acute L(E)C <sub>so</sub> values are typically < 1 mg/L but higher than 0.1 mg/L, which is the screening level assignment of potentially toxic substances	
t ½ in water=<5-366 days (pH dependent), persistent at low pH	BCF=18-2590, not bioaccumulative	Highly toxic	(Illinois EPA, 2007)

On the other hand, a review of PBT properties of TPP was undertaken within the ENFIRO project. The Danish EPA discusses this and reports: "TPP has been studied extensively and it is clearly persistent, bioaccumulative, and toxic (PBT)" (Danish EPA, 2013). A table summarising the relevant findings is given below and the PBT status of TPP does not appear to be a clear-cut case.

Table 5-33: Overview of PBT properties for selected halogen-free flame retardants in the ENFIRO Project (as reported by the Danish EPA)

		Bioaccu-	vPvB?	Toxicity			
Compound	Persistence	mulation		Ecotoxicity	In Vivo toxicity	In vitro toxicity	
TPP	Low to high	Low to high	(Yes)	Low to high	Low	Low to high	
RDP	Low to high	Low to high	No	Low to high	Low (to moderate)	(Low)	
BDP	Low to high	(Low to high)	(No)	Low to high	(Low)	(Low)	
ATH	_	(Low)	(no)	Low to high	(Low)	(Low)	
Mg(OH) <sub>2</sub>	_	n.d.	n.d.	n.d.	(Low)	n.d.	

Source: (Waaijers, et al., 2013)

Note by the authors of the paper: "Please note that this table gives an overview of the data found in literature and it is not an assessment". (Bracketed) = based on two or less studies, n.d. = no data

Overall, based on its intrinsic properties, TPP is not considered a PBT substance.

#### Other hazard assessments

In 2007, the Illinois Environmental Protection Agency characterised TPP as a potentially problematic alternative for DecaBDE. There was 'high' concern over its acute and chronic aquatic toxicity (very wide range of fish lethality levels, algal inhibition  $EC_{50}=0.26-2.0$  mg/L; Daphnia  $LC_{50}=1.0-1.2$  mg/L; fish LC<sub>50</sub>=0.36-290 mg/L; chronic Daphnia NOEC=0.1 mg/L(estimated); fish NOEC for survival and growth=0.0014 mg/L), 'low' concern for other effects based on existing data and professional judgement, but also key data deficiencies on cancer and two-generation reproductive/developmental studies (Illinois EPA, 2007).

In 2009, the Environment Agency for England and Wales published an environmental risk evaluation for TPP. It was found that TPP could enter the environment from its production and use, and from the use of articles made from materials containing it. Based on the available information, potential risks were identified for all of the life cycle steps for one or more of the protection goals. The overall conclusions are summarised in **Table 5-34** in a simplified form.

Table 5-34: Conclusions of environmental risk evaluation for Triphenyl phosphate TPP (CAS No. 115-86-6) by the Environment Agency for England and Wales (2009)									
Lifecycle stage	Surface water	Sediment	WWTP	Air	Soil	Aquatic food chain	Terrestrial food chain	Marine water	Marine sediment
Production		✓							
Printed circuit boards	✓	✓			✓			✓	✓
Thermoplastics/styrenics	✓	✓			✓		✓	✓	✓
Thermosets/epoxy resins	✓	✓			✓			✓	✓
Photographic film	✓	✓			✓			✓	✓
Regional									
Source: Environment Agency (2009b)									

An assessment of environmental and human health risks for a number of FRs was recently undertaken by Arcadis & EBRC (Arcadis & EBRC, 2011) under contract to the European Commission. This work has used information from the Environment Agency 2009 evaluation of the substance and concluded that the PEC/PNEC rations were below one.

With regard to human health risk assessment, three sub-scenarios were identified for which a risk characterisation has been performed: indoor air (monitoring data), service life of furniture and airborne particulates (monitoring data). A first tier dermal exposure assessment to TPP using the ECETOC TRA Consumer tool showed that the service life of furniture was associated with an RCR above one. During a second industry consultation period it was explained by industry that the concentration of the FR in the final matrix (artificial leather) used for the dermal exposure assessment refers to a mixture of FRs, whereas TPP is only present to a small extent in this mixture. Taking the new figure given by industry a reduction in the dermal exposure estimate led to a RCR < 1. No risk was identified for the inhalation route using measured exposure data (Arcadis & EBRC, 2011).

Most recently, the US EPA finalised its assessment of alternatives to DecaBDE<sup>47</sup>. A summary of their findings for TPP is presented below. It must be noted that some parameters may be assessed in a different way to the EU (for example, PBT properties). The table provides a summary of findings for those parameters that have been marked of "moderate" concern. On the other hand, parameters of "high" or "very high" concern are discussed in more detail after the table.

<sup>&</sup>lt;sup>47</sup> The US EPA was enquired as to whether this output by the Agency includes the most recent scientific information on the alternatives for DecaBDE. The US EPA confirmed that most of the work was done in 2011. Later on, additional studies were included if they were brought to the Agency's attention either formally during public comments or informally. Therefore, some information published in 2013 has also been incorporated into the analysis presented in the final output (US EPA, 2014c).

Table	Table 5-35: US EPA Assessment of TPP (CAS No. 115-86-6)													
	Human Health Effects							Aquatic Toxicity**		Environme ntal Fate				
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
L	М	L	L	ш	ш	Н	L	No data	L	VL	VH	VH	L	M
Carcin	Carcinogenicity  OncoLogic modelling indicates a marginal to low potential for carcinogenicity. No long-term carcinogenicity assays were found					ong-								
Bioaco	cumula	tion	There is to 364)	s moder	ate pote	ential for	bioaccu	ımulatio	n base	d on ex	perime	ental BC	F value	s (68

Source: US EPA (2014)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

The following parameters have been identified as being of "High" or "Very High" concern (US EPA, 2014):

- Repeated dose: evaluation based on weight of evidence including reduced body weight in male rats administered TPP in the diet for 28 days. The NOAEL of 23.5 mg/kg-day and the LOAEL of 161.4 mg/kg-day span across the "high" and "moderate" hazard designation ranges (the US Department for the Environment criteria are for 90-day repeated dose studies; criteria values are tripled for chemicals evaluated in 28-day studies making the High hazard range < 30 mg/kg-day and the "moderate" hazard range between 30 and 300 mg/kg-day)
- Acute aquatic toxicity: evaluation based on experimental fish 96-hour LC<sub>50</sub> values of 0.4 and 0.85 mg/L
- **Chronic aquatic toxicity**: evaluation based on an experimental fish 30-day LOEC = 0.037 mg/L. No chronic experimental data were available for daphnia or algae.

TPP is also on the CoRAP List for the year 2015 to be assessed by the UK. Its inclusion into the lists was due to the following concerns:

- Human health: potential endocrine disruptor
- Exposure: wide dispersive use, consumer use, aggregated tonnage.

#### Other hazard information

Meeker & Stapleton reported that TPP levels in house dust were associated with decreased sperm concentration in men (n=50) recruited from an infertility clinic. Altered prolactin levels were also associated with increased levels of TPP in dust (Meeker & Stapleton, 2010). TPP has also been listed

among other chemicals that are believed to be neurotoxic to humans (Grandjean & Landrigan, 2006). The recent update of that list by the same researchers still includes TPP in a similar list of chemicals known to be human neurotoxicants (Grandjean & Landrigan, 2014).

In *in vitro* studies, TPP was shown to increase the activities of two human nuclear receptors, the constitutive androstane receptor (CAR) and the pregnane X receptor (PXR) by > 5-fold and > 2-fold, respectively (Honkakoski, et al., 2004). These receptors regulate the expression of important drug metabolizing enzymes (e.g. cytochrome P450 isozymes). It has been shown that CAR is switched off in vitro by two testosterone metabolites (summarised in Li & Wang (2010)). PXR is involved in the expression of cytochrome P450 isozyme CYP3A4 and certain sulfotransferase isozymes. Activation of PXR might affect androgen levels by inducing CYP3A4 and sulfotransferase isozymes which hydroxylate and conjugate testosterone (Zhang, et al., 2010). PXR may also play a role in cholesterol metabolism and lipid homeostasis (Zhou, et al., 2009) (Krowech, 2012).

Honkakoski et al. (2004) reported that TPP decreased human glucocorticoid receptor activity by 20% and decreased human androgen receptor activity by 40-50%. In another study, TPP had moderate binding affinity for the androgen receptor (Fang, et al., 2003).

#### Available monitoring data

The US EPA indicates that TPP has been detected, among other compartments, in fish tissues and in the blubber of bottlenose dolphins collected from the Gulf of Mexico (US EPA, 2014). TPP was also detected in human milk, adipose tissue and human plasma (US EPA, 2014). A TPP metabolite, diphenyl phosphate was identified in urine (USA: 9 samples, median: 1.8  $\mu$ g/L, range: 0.569-63.8  $\mu$ g/L; Germany: 19 samples, median: 1.3  $\mu$ g/L, 95<sup>th</sup> percentile: 28.6  $\mu$ g/L). TPP itself was found in breast milk in Sweden (pooled samples) with a median concentration of 8.5 ng/g lipid (Krowech, 2012).

Another recent review (2012) of monitoring data for TPP was presented by van der Veen & de Boer. In biota, TPP was present in concentrations ranging between <0.05  $\mu$ g/kg (blue mussel, Norway) and 810  $\mu$ g/kg (carp, Sweden).

#### Conclusion on Alternative 1

The following table summarises the conclusions from the above information on the feasibility and suitability of TPP as a replacement for DecaBDE.

Table 5-36: Conclusions on suitability and feasibility of TPP (CAS No. 115-86-6)					
Category	Conclusion				
Suitability	Environmental hazards: TPP is not a PBT substance based on its intrinsic properties, as it does not meet the PBT criteria. However, the degradation products have not been taken into account in the PBT assessment. TPP shows aquatic toxicity TPP with self-notified classification for aquatic toxicity (H400/H410) and associated low PNEC values for water and sediment  Human health hazards: TPP poses moderate hazards to human health, including concerns over neurotoxicity and endocrine disruption. The substances is on the CoRAP List (2015 by the UK)				
Technical feasibility	TPP can feasibly be used in polymer applications only. Typical applications include: HIPS/PPO, PC/ABS, phenolic resins and epoxy resins				
Economic feasibility	Available information would suggest that TPP could have a higher price than DecaBDE but the price difference could balance out if the cost of ATO is taken into account. The loading of the substance could be significantly higher than DecaBDE. Nevertheless,				

Table 5-36: Conclusions on suitability and feasibility of TPP (CAS No. 115-86-6)					
Category	Conclusion				
	literature describes TPP as affordable.				
	Substitution cost estimates in polymers vary and for TPP in PC/ABS or PPO/HIPS, costs				
	may range between €17 and 60 million per year or €100-4,000/kg emissions avoided				
Overall conclusion	TPP can be technically feasible alternative for certain applications of DecaBDE but it is				
	likely to be more costly to use. Its use would be accompanied by hazards to the				
	aquatic environment and potentially to human health				

## 5.5.2 Alternative 2: Magnesium hydroxide (MDH) (CAS No. 1309-42-8)

## Technical feasibility issues

Relevant applications

There are several literature sources describing the applicability of magnesium hydroxide (MDH) as a FR. A summary is provided below.

Table 5-37: Applications for magnesium hydroxide (MDH) (CAS No. 1309-42-8)					
Application	Material - substrate	Source			
Not specified	PP/PE, PS, PVC, ABS, UPR, PUR	Keml (2005)			
Not specified	PP/PE, PS, PVC, ABS, PC, UPR, PUR, Rubber	Keml (2009)			
	Textiles				
Profiles- window, doors, trim	Rigid PVC	PINFA (2013)			
Pipes	HDPE, PP	PINFA (2013)			
Cable trays, skirting boards	PP	PINFA (2013)			
Facade decoration	Aluminium Composite Panels (ACP) – inner layer made of PE, PE/EVA, Ethylene-co-polymers	PINFA (2013)			
Flooring (incl. linoleum)	PE/PP, Elastomers	PINFA (2010b) PINFA (2013)			
Electrical cables Low voltage Medium voltage PV cables Emergency lighting Control cables Fire alarm cables Information cables LAN cables Telephone cables Rigid sheets: Aluminium	LDPE, EVA, Polyolefins, Elastomers, silicone rubbers (SiR)  Polyolefins (mostly HDPE, PP)	PINFA (2010b) PINFA (2013)			
Rigid sheets: Aluminium Composites Panels, building scaffolds (walk ways)	Polyoletins (mostly HDPE, PP)	PINFA (2013)			
Water-proofing membranes	Tar bitumen, EPDM, TPO, HDPE	PINFA (2010)			
E&E – UL94V0	Polypropylene (PP)	Troitzsch (2011)			
Not specified	PA, PP, PE	JRC (2007)			
E&E V-0 connectors and wires	PA (connectors), PP (wires), Thermoplastic polyester and elastomers, PVC, EPDM, PE/EVA	Danish EPA (2006)			

Table 5-37: Applications for magnesium hydroxide (MDH) (CAS No. 1309-42-8)						
Application	lication Material - substrate					
Not specified	EVA copolymers, thermoplastic elastomers, PE, PP, PA, PE/EVA, flexible PVC, EPDM, TPU, acrylic resins, silicone	UK HSE (2012)				
Wire and Cables, Electrical conne HDPE, PP, Soft PVC, PA	ICL Industrial Products (2013b)					
Wire and cable	PP, PE, EVA, Elastomers	US EPA (2014)				
Public buildings	PP, PE, EVA, Elastomers	1				
Construction materials	PP, PE, EVA, Elastomers	1				
Automotive	PP, PE, EVA, Elastomers					
Aviation PP, PE, EVA, Elastomers						
Shipping pallets	PP, PE					
Waterborne emulsions and coatings	PP					

MDH and ATH (discussed later) act, in general, in the same way, but MDH thermally decomposes at slightly higher temperatures around 325 °C. Combinations of ATH and MDH function as efficient smoke suppressants in PVC (SFT, 2009). A potential use of MDH in technical textiles has been discussed by consultees; in it, the role of MDH has been described as problematic, as discussed in the Confidential Annex. Its high loading (see below) demonstrates its lower efficiency compared to DecaBDE.

#### **Economic feasibility issues**

#### Loading

Limited information is available. In a document on halogen-free FRs for E&E applications, MDH is reported to require high filler levels of about 45 to 50% to reach UL 94 V-0. Because of its limited temperature stability, it is mainly used in low glass fibre PA-6 (PINFA, 2010).

Consultation has suggested a 5-times higher loading compared to DecaBDE in special textiles with FR performance still lagging behind that of DecaBDE/ATO formulations.

#### Price issues

Information from consultation is not available. On the other hand, information from the Alibaba.com online marketplace would suggest that MDH might be significantly cheaper in terms of price per kg than DecaBDE by ca. 75% (see **Table 10-3**). The substance does not require the presence of ATO, thus it might be considered even less costly per kg compared to DecaBDE/ATO mixtures. Nevertheless, its very significant comparative loading counterbalances, to an extent, this cost saving.

#### Substitution cost calculations

The following table summarises the relevant information for MDH, based on the analysis presented in Section 5.4.

Table 5-38: Substitution cost calculations for MDH (CAS No. 1309-42-8)							
Application area	Approach Substitution cost		Cost per kg DecaBDE emission avoided (€/kg)	Notes			
Polymers	A1	Not relevant	Not relevant				
	B1	Not relevant	Not relevant				
	C1	PA: -19-20 million	PA: -1,250 to -1,300				
	D1	Not relevant	Not relevant				
Textiles	A2	Not relevant	Not relevant				
	C2	Full: -<5 million	-<250				
		Mix: -<0.5 million	-~250				

## Hazard profile

REACH Registration and C&L data

The table that follows summarises the hazard profile of MDH based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-39: REACH	Registration data for MDH (CAS	No. 1309-42-8)	
Category	Parameter	MDH	Notes
Physical state		Solid	
Classification for	Acute hazards to the aquatic	N/A	Self-notified (C&L
environmental	environment		Inventory)
hazards	Long-term hazards to the	N/A	Self-notified (C&L
	aquatic environment		Inventory)
Classification for	Carcinogenicity	N/A	Self-notified (C&L
human health			Inventory)
hazards	Mutagenicity	N/A	Self-notified (C&L
			Inventory)
	Reproductive toxicity	N/A	Self-notified (C&L
			Inventory)
	Acute toxicity	N/A	Self-notified (C&L
			Inventory)
	Irritation	N/A	Self-notified (C&L
			Inventory)
	Sensitisation	N/A	Self-notified (C&L
			Inventory)
	Specific target organ toxicity		
PBT assessment	Persistence	Persistent	Inorganic substance
	Bioaccumulation	Not relevant	Inorganic substance
	Toxicity	Not T	Registration dossier: two
			studies on the long-term
			toxicity of read-across
			substance magnesium
			chloride to aquatic
			invertebrates, with LC <sub>50</sub>
			values of 360 mg/L and
			570 mg/L, respectively
	Conclusion	Not a PBT	
Key	Partition coefficient	Not relevant	
physicochemical	Water solubility	1.78 mg/L, 20.3 °C, pH 8.3	Registration dossier
properties	Vapour pressure	Not relevant	
Ecotoxicological	PNEC aqua (freshwater)	0.1 mg/L	AF: 1000

Table 5-39: REA	Table 5-39: REACH Registration data for MDH (CAS No. 1309-42-8)				
Category	Parameter	MDH	Notes		
information	PNEC aqua (marine water)	0.01 mg/L	AF 10000		
	PNEC aqua (intermittent releases)	1 mg/L	AF: 100		
	PNEC STP	1 mg/L	AF: 100		
	PNEC sediment (freshwater)	0.08188 mg/kg sediment dw	Partition coefficient		
	PNEC sediment (marine water)	0.008188 mg/kg sediment dw	Partition coefficient		
	PNEC soil	0.01912 mg/kg soil dw	Partition coefficient		
	PNEC oral predators	66.67 mg/kg food	AF: 300		

#### Past PBT hazard assessments

A PBT assessment is not relevant to MDH due to its inorganic nature.

#### Other hazard assessments

In 2007, the Illinois Environmental Protection Agency characterised MDH as a potentially unproblematic alternative for DecaBDE. No cancer or reproductive/developmental data were found, but risks were believed to likely be low<sup>48</sup>, based on professional judgement. There was 'low' concern for other effects based on existing data and professional judgement (human exposure data from food, medicinal, and cosmetic uses); key data deficiencies included cancer, reproductive/developmental, and chronic aquatic toxicity studies (Illinois EPA, 2007).

The 2011 review by Arcadis & EBRC for the European Commission did not reveal any concerns for human health or environmental exposure from the use of MDH in consumer products. For human health, one sub-scenario was identified for which a risk characterisation has been performed, service life of textiles for carpets or furniture (Arcadis & EBRC, 2011).

The summary of the US EPA's recent assessment of the substance is provided below. The table provides a summary of findings for those parameters that have been marked of "moderate" concern. On the other hand, parameters of "high" concern are discussed in more detail after the table.

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 $<sup>^{48}</sup>$  This is for information only, as conclusions on risks may not be extrapolated to the EU.

Table	5-40: l	JS EPA	Assessm	ent of N	1DH (CA	S No. 13	09-42-8	)						
	Human Health Effects							uatic icity <sup>**</sup>	Environtal I					
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
L	L	L	L	L	L	L	L	No data	M	L	L	L	н	L
Eye ir	Based on irritation and damage to the corneal epithelium in rabbits that cleared within 2-3 days					thin								

Source: US EPA (2014)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

The US EPA confirms the limited concerns surrounding the substance. The "High" concern regarding persistence purely reflects the inorganic nature of the compound. MDH is not expected to biodegrade, oxidise in air, or undergo hydrolysis under environmental conditions. As a naturally occurring compound, it may participate in natural cycles and form complexes in environmental waters (US EPA, 2014).

#### **Conclusion on Alternative 2**

The following table summarises the conclusions from the above information on the feasibility and suitability of MDH as a replacement for DecaBDE.

Table 5-41: Conclusi	Table 5-41: Conclusions on suitability and feasibility of MDH (CAS No. 1309-42-8)			
Category	Conclusion			
Suitability	Environmental hazards: as an inorganic substance, MDH cannot be classified a PBT Human health hazards: MDH has raises little concern overall			
Technical feasibility	MDH can be used in almost the full range of applications that are relevant to DecaBDE but it cannot be assumed that it would perform as efficiently as DecaBDE/ATO formulations			
Economic feasibility	MDH requires very high loadings compared to DecaBDE but it is likely to have a price per kg significantly lower than DecaBDE. It does not require the use of ATO.  Calculations of the substitution cost for the use of MDH in polymers and textiles suggests that the use of the substance would lead to cost savings			
Overall conclusion	MDH is likely to be an affordable and benign alternative to DecaBDE for a wide range of applications. However, it is expected to be technically suitable for less demanding applications due to its lower FR efficiency and its limited temperature stability			

## 5.5.3 Alternative 3: Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) (CAS No. 13674-87-8)

#### Technical feasibility issues

Relevant applications

There are few literature sources describing the applicability of tris(1,3-dichloro-2-propyl) phosphate (TDCPP) as a FR. A summary is provided below.

Table 5-42: Applications for tris(1,3-dichloro-2-propyl) phosphate (TDCPP) (CAS No. 13674-87-8)					
Application	Material - substrate	Notes	Source		
Not specified	Flexible PU foam, epoxy resin and phenolics, unsaturated polyesters	Excellent processing, good thermal and hydrolytic stability, low fogging	ICL Industrial Products (2013b)		
Automotive industry and furniture	An additive FR in resins, latexes and foams, textiles		van der Veen & de Boer (2012)		

US sources indicate that TDCPP has been the main FR used in automotive foam cushioning for many years and is frequently used in upholstered furniture foam. TDCPP has been referred to as one of the primary FRs replacing PentaBDEs in polyurethane foam (NRDC, 2010). In the 1970s, TDCPP was briefly used in children's sleepwear after tris(2,3-dibromopropyl)phosphate (TRIS) was banned. The use of TDCPP in sleepwear in the USA was withdrawn in 1977 (OEHHA, 2011).

Although banned from children's pyjamas in 1977, TDCPP continues to be in widespread use in baby nursery items, strollers, nursing pillows, and other children's products at concentrations of up to 5% (by weight), as well as other foam-padded furniture, such as couches, chairs, and sofa beds (NRDC, 2010). Recent research in the USA suggests that TDCPP could be detected in baby product foam used in car seats, changing table pads, sleeping wedges, portable mattresses, baby walkers, high chairs, rocking chairs, baby carriers, nursing pillows and infant bath slings at a concentration of 0.05-124 mg/g foam (Stapleton, 2011). TDCPP is used in the same kind of products as TCPP, but because of the higher price of TDCPP, it is only used in applications where a more effective FR is required (van der Veen & de Boer, 2012).

Consultation suggests that the substance is promoted by some formulators as alternative to DecaBDE-based formulations for textile backcoating. However, it is not suitable for all fabrics.

#### **Economic feasibility**

#### Loading

Consultation with actors in the textiles industry suggests that TDCPP may need to be used at a loading ca. 5% higher than DecaBDE. On the other hand, foam samples from the USA sampled between 2003 and 2009 were analysed and the most frequently detected FR, found in 15 samples, was TDCPP with a concentration of 1-5% (w/w) (van der Veen & de Boer, 2012).

#### Price issues

Consultation suggests that TDCPP may be 20% less costly per kg than DecaBDE for textile applications. On the other hand, information from the Alibaba.com online marketplace would suggest that TDCPP might be significantly lower price per kg than DecaBDE, by ca. 75% (see **Table 10-3**); this value is unlikely to be a reliable indicator. The substance does not require the presence of ATO.

#### Substitution cost calculations

The following table summarises the relevant information for TDCPP, based on the analysis presented in Section 5.4.

Table 5-43: S	Table 5-43: Substitution cost calculations for (TDCPP) (CAS No. 13674-87-8)					
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes		
Polymers	A1	Not relevant	Not relevant			
	B1	Not relevant	Not relevant			
	C1	Not relevant	Not relevant			
	D1	Not relevant	Not relevant			
Textiles	A2	Not relevant	Not relevant			
	C2	Full: -<10 million Mix: -<1 million	-<500			

#### Hazard profile

#### REACH Registration and C&L data

The table that follows summarises the hazard profile of TCDPP based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-44: REACH	Registration data for TDCPP (CAS	No. 13674-87-8)	
Category	Parameter	TDCPP	Notes
Physical state		Liquid	
Classification for environmental	Acute hazards to the aquatic environment	N/A	
hazards	Long-term hazards to the aquatic environment	Aquatic Chronic 2 - H411	
Classification for	Carcinogenicity	Carc. 2 - H351	
human health	Mutagenicity	N/A	
hazards	Reproductive toxicity	N/A	
	Acute toxicity	Acute Tox. 4 - H302	Self-notified (C&L Inventory)
	Irritation	N/A	
	Sensitisation	N/A	
	Specific target organ toxicity	N/A	
PBT assessment	Persistence	P, not vP	
	Bioaccumulation	Not B	BCF ≤ 2,000 L/kg
	Toxicity	Not T	
	Conclusion	Not a PBT	
Key	Partition coefficient	3.69	
physicochemical	Water solubility	18.1 mg/L (20 °C)	

Table 5-44: REACH I	Table 5-44: REACH Registration data for TDCPP (CAS No. 13674-87-8)				
Category	Parameter	TDCPP	Notes		
properties	Vapour pressure	0.0000056 Pa (25 °C)			
Ecotoxicological	PNEC aqua (freshwater)	0.01 mg/L	AF: 50		
information	PNEC aqua (marine water)	0.001 mg/L	AF: 500		
	PNEC aqua (intermittent	0.011 mg/L	AF: 100		
	releases)				
	PNEC STP	100 mg/L	AF: 100		
	PNEC sediment (freshwater)	0.83 mg/kg sediment dw	AF: 10		
	PNEC sediment (marine water)	0.166 mg/kg sediment	AF: 50		
		dw			
	PNEC soil	0.33 mg/kg soil dw	AF: 10		
	PNEC oral predators	3.3 mg/kg food	AF: 30		

### Past PBT hazard assessments

The following table summarises information on the assessment of the PBT properties of TDCPP. The substance does not meet the PBT criteria but its aquatic toxicity is noted.

Table 5-45: PBT properties	s of TDCPP (CAS No. 13674-8	37-8)	
Persistence	Bioaccumulation	Toxicity	Source
Persistent	The criterion is not fulfilled (reported BCF values <120)	Classified as carcinogenic (Cat 2); recent EU risk assessment (under the ESR) suggests that it should be classified as category 2) and toxic for reproduction (category 2)	(Keml, 2009)
The available screening studies show that TDCPP is not readily biodegradable so the screening criterion for persistence is met.  Summary of PBT assessment, TDCP can be considered to be potentially persistent (P) or potentially very persistent (vP) based on its ultimate mineralisation. The available information on bioaccumulation shows that TDCP does not meet the B or vB criterion. The T criterion is not met	TDCPP has a measured fish BCF of 31-59 in the only acceptable result of three studies and hence does not meet the B criterion	The lowest aquatic NOEC for TDCPP is 0.5 mg/L from a 21-day Daphnia study. Regarding human health effects, TDCPP is classified as Carcinogenic Category 3 R40 (Limited evidence of a carcinogenic effect). This classification is based on the results of a 2-year carcinogenicity study. Based on the current evidence, combined with the aquatic toxicity results, there is no definite concern for chronic toxicity and hence the T criterion is not met	(ECB, 2008)

#### Other hazard assessments

The substance has also been subject to a risk assessment under the Existing Substances Regulation (ECB, 2008). Unacceptable risks were identified for:

- The reasonable worst case dermal exposure during the manufacture of the substance (worker scenario 1), manufacture of flexible PUR foam – slabstock (worker scenario 2a) and manufacture of flexible PUR foam – moulded (worker scenario 2b) in relation to repeated dose toxicity and carcinogenicity
- A conclusion (i) "on hold" applied to effects on female fertility for both regional and local exposures.

The 2011 Arcadis & EBRC assessment for the European Commission looked into three sub-scenarios, PUR foam in furniture and consumer exposure by inhalation, dermal exposure and oral exposure (hand to mouth contact, child). No risks to human health from consumer products were identified (Arcadis & EBRC, 2011).

The US Consumer Product Safety Commission concluded in 2006 that TDCPP is a probable human carcinogen based on sufficient evidence in animals. TDCPP is structurally similar to TRIS and tris(2-chloroethyl)phosphate, which are both listed as causing cancer under Proposition 65 (OEHHA, 2011)<sup>49</sup>.

#### Other hazard information

A 2011 review of the hazard profile of TDCPP has noted that the substance's *in vitro* neurotoxicity is similar to that of chlorpyrifos (Dishaw et al., 2011)<sup>50</sup>. TDCPP was described as potent a neurotoxicant as the pesticide chlorpyrifos in rat neuronal cells *in vitro* and TDCPP exposure in zebrafish embryos affects survival and induces developmental abnormalities, similar to chlorpyrifos (Stapleton, 2011).

#### Available monitoring data

A recent (2012) review of monitoring data for TDCPP was presented by van der Veen & de Boer. As far as biota is concerned, TDCPP was found in concentrations between <0.025  $\mu$ g/kg (beach crab, Norway) and 140  $\mu$ g/kg (perch, Sweden) (van der Veen & de Boer, 2012).

Associations have been made between TDCPP in house dust and a decrease in free Thyroxine (T4) and an increase in prolactin (Meeker and Stapleton, 2010)<sup>51</sup> (Stapleton, 2011).

In April 2013, it was reported that seven US states were to introduce restrictions on the use of TDCPP and other FRs. Legislation of relevance to TDCPP included (CTT, 2013).

<sup>&</sup>lt;sup>50</sup> Full reference not provided.

Full reference not provided.

#### **Conclusion on Alternative 3**

The following table summarises the conclusions from the above information on the feasibility and suitability of TDCPP as a replacement for DecaBDE.

Table 5-46: Conclusi	ions on suitability and feasibility of TDCPP (CAS No. 13674-87-8)
Category	Conclusion
Suitability	Environmental hazards: TDCPP displays persistence and aquatic chronic toxicity and its registration dossier bears a classification of Aquatic Chronic 2 (H411). TDCPP has PNEC values which are considerably low. TDCPP is not a PBT substance Human health hazards: TDCPP is classified as Carc Cat 2 in its REACH registration and is accompanied by (low) acute toxicity (Acute Tox. 4 (H302), self-classification in the C&L inventory). Recent research raises concerns with regard to the neurotoxicity properties of the substance. Under the ESR, potential female fertility effects were identified
Technical feasibility	TDCPP can be used in foam applications which are generally of limited significance to DecaBDE as well as in textile backcoating. Its applicability does not span all fabrics of relevance to DecaBDE
Economic feasibility	TDCPP requires marginally higher loadings compared to DecaBDE but it is likely to have a price per kg lower than DecaBDE. It does not require the use of ATO.  Calculations of the substitution cost for the use of TDCPP in textiles suggests that the use of the substance could lead to cost savings
Overall conclusion	TDCPP does not have a favourable hazard profile and can only be used in a limited range of relevant applications for textiles

# 5.5.4 Alternative 4: Aluminium trihydroxide (ATH) (CAS No. 21645-51-2; 8064-00-4)

#### Technical feasibility issues

Relevant applications

ATH has been used as a FR and smoke suppressant since the 1960's and it is available in a variety of particle sizes as commercial products.

There are several literature sources describing the applicability of ATH as a FR. A summary is provided below.

Table 5-47: Applications fo	Table 5-47: Applications for aluminium trihydroxide (ATH) (CAS No. 21645-51-2; 8064-00-4)				
Application	Material - substrate	Notes	Source		
Upholstery, blinds, blackout curtains, automotive textiles	Not specified	In-expensive filler, relatively insoluble. Little real FR effect, potentially poor fabric handle	RPA (2003)		
Not specified	PE/PP, PS, PVC, ABS, UPR, Epoxy, PU		Keml (2005)		
Not specified	PE/PP, PS, PVC, ABS, PC, UPR, Epoxy, PU, Textiles		Keml (2009)		
Cables and wires	PVC, Silicone rubber, EPDM, EVA, LDPE		EFRA (2011)		

Application	Material - substrate	Notes	Source
• •	iviateriai - substrate	Notes	
Semi-durable textile finishes	Cotton, polyester		EFRA (2012)
Solid thermoplastics	EVA copolymer, PP, PE,		PINFA (2010c)
Solid thermoplastics	1		PINFA (2010c)
Гоо <i>н</i> оо	Thermoplastic elastomers		PINFA (2010b)
Foams	PE foam, PVC/nitrile foam,		
<del>-</del>	Rubber (elastomer)		_
Thermosets	Epoxy, Phenolic, Unsaturated		
	Polyester, Vinyl esters, Acrylic		1
Wires & cables	Silicone, PVC flexible, EPDM,		
	PE/EVA, PP (boehmite)		
Textiles	Textile backcoating		
Coatings/Adhesives	Hot melts, Paints		
Transportation flooring	PVC, PE/PP, Epoxy, Elastomers		PINFA (2010b)
Transportation ceiling,	Unsaturated Polyesters (UP),		1
sidewalls, panels,	Vinyl ester (VE), Acrylate resin,		
structural parts	Polyurethane (PU)		
Dashboard instruments,	RIM, UPR		1
instrument panels,			
instrument cluster			
housing, etc.			
Transportation coatings	2K-PU, epoxy, acrylates		1
Sealants (flame-retardant	PUR, acrylics, epoxy,		-
and/or fire-resistant)	elastomers, PVC		
Transportation textiles	ciastomers, rvc	Back-coating or	1
rransportation textiles		added to polymer	
		melt	
Films: Tarpaulins	Flexible PVC	cic	PINFA (2013)
Sheets	Unsaturated polyester		
			-
Rigid sheets: Aluminium	Polyolefins (mostly HDPE, PP)		
Composites Panels,			
building scaffolds (walk			
ways)	DVC line le		-
Flooring	PVC, linoleum		1
Profiles- window, doors,	Rigid PVC		
trim Pines	3		-
Pipes	HDPE, PP		4
Cable trays, skirting boards	PP		
Facade decoration	Aluminium Composite Panels		
	(ACP) – inner layer made of PE,		
	PE/EVA, Ethylene-co-polymers		
Water-proofing	Tar bitumen, EPDM, TPO, PVC,		PINFA (2010)
membranes	EVA, PU, EPR, UPR, Acrylates		
E&E – UL94 V-0	Epoxy resins (EP), Unsaturated		Troitzsch (2011)
	polyester resins (UP)		' '
Electronics	Thermosets		US EPA (2014)
Wire & cable	PP, EVA, elastomers		1
WITE & CADIC	ii, EVA, Clastofficis		

Application	Material - substrate	Notes	Source
Public buildings	PP, EVA, elastomers,		
	thermosets		
Construction materials	PP, EVA, elastomers,		
	thermosets		
Automotive	PP, EVA, elastomers,		
	thermosets		
Aviation	PP, EVA, elastomers,		
	thermosets		
Textiles	Emulsions		
Waterborne emulsions	Thermosets		
and coatings			
Not specified	EVA copolymers, PE,		UK HSE (2012)
	thermoplastic elastomers, rigid		
	and flexible PVC,		
	rubbers/elastomers, hot melts,		
	epoxy resins, phenolic resins,		
	unsaturated polyester, vinyl		
	esters, acrylic resins, silicone,		
	EPDM, TPU, PE/EVA		
Printed circuit boards,	Epoxy resins		Anonymous (undated)
electronic components			
encapsulations,			
technical laminates,			
electrical encapsulating &			
casting			
Wire and cable	EVA		
Thermoplastics	PE/Copolymers		Albemarle (2013)
•	Elastomers		, ,
	PVC		
Foams	Polyolefin foams, PVC/Nitrile		
	foams, Elastomer foams		
Wire and cable	Silicone, EPDM, PE/EVA, XL		
	PE/EVA, TPU, PVC		
Thermosets	Epoxy, phenolic, UPR, vinyl		
	esters, SMC/BMC, PU/CASE,		
	Latex		

The table suggests that ATH finds a wide range of applications; however, its performance generally does not match that of DecaBDE/ATO formulations. For instance, consultees have identified possibilities for use of ATH in some polymer and technical textile applications for which, however, its performance would be inadequate (additional details are presented in the Confidential Annex).

#### **Economic feasibility**

#### Loading

ATH needs to be used at loadings significantly higher than DecaBDE. Consultation has suggested loadings 5 times higher than DecaBDE in polymer applications and 3 times higher in textile

applications. The substance is described as a "cheap filler" (RPA, 2003) which cannot meet the performance of DecaBDE/ATO formulations.

ATH loading levels can be reduced with a correct choice of particle size, surface modification and proper dispersion in the matrix material. A Norwegian report refers to recently developed coated filler products (e.g. ZHS-coated ATH) which offer the possibility of equivalent or better flame retardancy and smoke suppression at significantly reduced incorporation levels (SFT, 2009).

#### Price issues

Robust information on the cost of ATH is not available. Limited information from consultation would suggest that ATH has a price per kg that is marginally higher than DecaBDE. On the other hand, information from the Alibaba.com online marketplace would suggest that ATH might have a price tag which is only a small fraction of DecaBDE's (see **Table 10-3**). The substance does not require the use of ATO.

#### Substitution cost calculations

The following table summarises the relevant information for ATH, based on the analysis presented in Section 5.4.

Table 5-48: Substitution cost calculations for ATH (CAS No. 21645-51-2; 8064-00-4)						
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes		
Polymers	A1	Not relevant	Not relevant			
	B1	Not relevant	Not relevant			
	C1	PP: -20-22 million	PP: -1,350-1,450			
	D1	Not estimated per	Not estimated per			
		alternative substance	alternative substance			
Textiles	A2	Not relevant	Not relevant			
	C2	Full: -<20 million Mix: -<2 million	-<1,100			

#### Hazard profile

#### REACH Registration and C&L data

The table that follows summarises the hazard profile of ATH based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-49: REACH Registration data for ATH (CAS No. 21645-51-2; 8064-00-4)						
Category	Parameter	ATH	Notes			
Physical state		Solid				
Classification for environmental	Acute hazards to the aquatic environment	N/A				
hazards	Long-term hazards to the aquatic environment	N/A				
Classification for	Carcinogenicity	N/A				
human health	Mutagenicity	N/A				
hazards	Reproductive toxicity	N/A				
	Acute toxicity	N/A				
	Irritation	N/A				

Table 5-49: REACH Registration data for ATH (CAS No. 21645-51-2; 8064-00-4)					
Category	Parameter	ATH	Notes		
	Sensitisation	N/A			
	Specific target organ toxicity	N/A			
PBT assessment	Persistence	Persistent (inorganic)	Inorganic substance		
	Bioaccumulation	Not applicable	Inorganic substance		
	Toxicity	Not T			
	Conclusion	Not a PBT			
Key	Partition coefficient	Not applicable	Inorganic substance		
physicochemical	Water solubility	≤ 0.09 mg/L (20 °C)			
properties	Vapour pressure	Not applicable			
Ecotoxicological	PNEC aqua (freshwater)	74.9 μg/L	AF: 1		
information	PNEC aqua (marine water)	Aquatic toxicity unlikely			
	PNEC aqua (intermittent	Aquatic toxicity unlikely			
	releases)				
	PNEC STP	20 mg/L	AF: 10		
	PNEC sediment (freshwater)	No or insufficient data			
		available at present			
	PNEC sediment (marine	No or insufficient data			
	water)	available at present			
	PNEC soil	No or insufficient data			
		available at present			
	PNEC oral predators	No or insufficient data			
		available at present			

#### Past PBT hazard assessments

A PBT assessment is not relevant to ATH as it is an inorganic substance. Its acute toxicity is also low.

#### Other hazard assessments

In 2007, the Illinois Environmental Protection Agency characterised ATH as a potentially unproblematic alternative for DecaBDE. No cancer data were found, but risks were believed to likely be low based on professional judgement<sup>52</sup>; "low" concern was identified for other effects based on existing data and professional judgement (human exposure data from antidiarrheal and antacid uses); key data deficiencies included cancer, neurological effects, and chronic aquatic toxicity studies; acute aquatic toxicity was likely only at very low pH (Daphnia  $LC_{50}$ =2.6-3.5 mg/L) (Illinois EPA, 2007).

The 2011 review by Arcadis & EBRC for the European Commission did not identify any risks to human health from airborne particles. The only scenario considered - inhalation exposure to aluminium hydroxide vapour - was considered not relevant due to the ionic nature of the substance. Dermal exposure was not assessed, due to the negligible dermal absorption of aluminium and no systemic/local effects are expected for aluminium cations following exposure to skin; the dermal route was thus considered not to be a relevant exposure pathway. No assessment of environmental risks was undertaken (Arcadis & EBRC, 2011).

The summary of the US EPA's assessment is provided below. The table provides a summary of findings for those parameters that have been marked of "moderate" concern. On the other hand, parameters of "high" concern are discussed in more detail after the table.

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<sup>&</sup>lt;sup>52</sup> This cannot be readily extrapolated to the EU.

Table	Table 5-50: US EPA Assessment of ATH (CAS No. 21645-51-2; 8064-00-4)													
Human Health Effects								Aquatic Toxicity**			Environme ntal Fate			
							TOA	City	IItai	ucc				
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
L	L	L	L	L	M	м	L	No data	VL	VL	М	М	н	L
Neurological			in a labyrinth maze test in a 90-day oral study in rats at 35 mg Al/kg/day as aluminium hydroxide with citric acid. Impaired learning in a labyrinth maze test was also reported in rats orally exposed to 300 mg Al/kg/day ATH; there is uncertainty in the threshold of response, the possibility that effects occur at doses <100 mg/kg/day (in the Moderate - High hazard designation range) cannot be ruled out  ATH is estimated to have potential for immunotoxicity based on professional judgment and comparison to analogous aluminum compounds. ATH is of low hazard for repeated dose effects based on an experimental study indicating no adverse effects in rats											
Repeated dose  following oral doses up to 14,470 ppm (302 mg/kg-day). In addition, a low prepeated dose effect is estimated based on professional judgment and column analogous aluminium compounds						poten	tial for							
Acute	aq. to	cicity						zard for				-	-	
Chronic aq. toxicity		on potential for dissolved aluminum species to cause adverse effects in aquatic species, as described in the EPA New Chemical Categories document, which includes inorganic salts of aluminum (professional judgement, <a href="http://www.epa.gov/oppt/newchems/pubs/npcchemicalcategories.pdf">http://www.epa.gov/oppt/newchems/pubs/npcchemicalcategories.pdf</a> ). Additional studies for acute toxicity to daphnia and algae are ongoing; the results of these studies may affect the acute aquatic hazard designation												
Source: US EPA (2014)														

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

The table confirms that there is generally limited reason for concern. The US EPA gives the persistence criterion a high score but this is due to the substance's inorganic nature, which means that ATH is not expected to biodegrade or oxidise under typical environmental conditions.

#### Other hazard information

A 2009 paper discussed "significant behavioural and neuropathological outcomes with aluminum hydroxide and some additionally significant outcomes due to a combination of adjuvants" (Shaw & Petrik, 2009). The authors suggest that the demonstrated neurotoxicity of ATH and its relative ubiquity as an adjuvant suggest that greater scrutiny by the scientific community is warranted, however they also note that their results were achieved under minimal conditions and the likelihood exists that a synergistic effect between adjuvants and other variables such as stress, multiple vaccinations, and exposure to other toxins likely occurs. In addition, a genetic background in context to aluminium exposure may play a crucial role (Shaw & Petrik, 2009). Issues of neurotoxicity have been discussed elsewhere too (Fenwick, et al., 2005).

#### **Conclusion on Alternative 4**

The following table summarises the conclusions from the above information on the feasibility and suitability of ATH as a replacement for DecaBDE.

Table 5-51: Conclusi	Table 5-51: Conclusions on suitability and feasibility of ATH (CAS No. 21645-51-2; 8064-00-4)				
Category	Conclusion				
Suitability	Environmental hazards: ATH does not give rise to any concern and, as an inorganic				
	substance, it is not a PBT				
	Human health hazards: ATH raises little concern overall, although recent research has				
	highlighted behavioural and neuropathological outcomes with ATH				
Technical feasibility	ATH can be used in a wide range of applications that are relevant to DecaBDE but it does				
	not necessarily perform as efficiently or effectively as DecaBDE/ATO formulations				
Economic	ATH requires very high loadings compared to DecaBDE but it is likely to have a price per				
feasibility	kg significantly lower than DecaBDE. It does not require the use of ATO.				
	Calculations of the substitution cost for the use of ATH in polymers and textiles suggests				
	that the use of the substance could lead to cost savings				
Overall conclusion	ATH is a benign alternative to DecaBDE for a wide range of applications, which				
	requires high loadings in order to achieve acceptable performance. It is expected to				
	be technically suitable for less demanding applications				

## 5.5.5 Alternative 5: Tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)

#### Technical feasibility issues

Relevant applications

There are several literature sources describing the applicability of tetrabromobisphenol-A bis (2,3-dibromopropyl ether) as a FR. A summary is provided below.

Table 5-52: Applications for tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)					
Application	Material - substrate	Notes	Source		
Fabricated plastic sheets for electrical cabinets, textiles, paints, and hot melts, pipes, water barriers, kitchen hoods, household, and in	PP, HDPE, LDPE, HIPS Textiles		NIEHS (NIEHS, 2002)		
TV, hifi-audio, and electronics					
Not specified	HIPS, PP, PE, Crystalline PS		Keml (2009)		
E&E UL94 V-0	PP		Troitzsch (2011)		

Table 5-52: Applications for tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)						
Application	Material - substrate	Notes	Source			
Not specified	PP		JRC (2007)			
Not specified	HIPS, PP	This chemical is marketed for use in HIPS, but is mainly used in other polymers including polypropylene	Washington State (2006)			
Enclosures	HIPS (UL94 V-0)	A supplier claims that it is	Danish EPA (2006)			
Wires	PP (UL94 V-0)	very effective in PP and in  HIPS at low dosage. Along				
Not specified	PE, crystal PS	with the melting characteristics of SAYTEX HP-800A flame retardant, this results in minimal impact on mechanical properties of the resin; good thermal stability				
E&E equipment, textiles, construction materials	PP, PE, PS, HIPS		Arcadis & EBRC (2011)			
Not specified	HIPS, PP, PE, PS, TPU		UK HSE (2012)			
Not specified	PP, HIPS, ABS	Good FR efficiency and thermal stability	ICL Industrial Products (2013b)			
Electronics	PP, Elastomers		US EPA (2014)			
Public buildings	PP, Elastomers					
Construction materials	PP, Elastomers					
Automotive	PP, Elastomers					

The table indicates that tetrabromobisphenol-A bis (2,3-dibromopropyl ether) can find applications mainly in polymers and less so in textiles.

#### **Economic feasibility**

#### Loading

Some information is available from the Danish EPA. To achieve a V-0 fire rating in HIPS, a low loading of 5% is referred to in combination with a "styrenic based resin", and 5% antimony trioxide. By comparison, DecaBDE requires a 12-13% loading and 4-5% antimony trioxide synergist (Danish EPA, 2006).

Additional detail is available from the Existing Substances Regulation Risk Assessment Report (RAR) for TBBPA. In polypropylene, the substance may be used at a loading of 8-10% to meet the UL94 V-0 rating. The minimum amount necessary to meet the UL94 V-2 rating and Glow Wire rating is 1.5% of the FR with 0.5% ATO and 1% of the FR with 0.33% ATO respectively. Additionally, 12% of the FR with 4% ATO and 14.5% of the FR with 5.2% ATO are used in formulations to meet the UL94 V-0 rating in PP homopolymers and in block copolymers respectively. It is also reported that the UL94 V-2 rating is met using formulations containing 3% of the FR with 1% ATO and 4.5% of the FR with 1.5% ATO in polypropylene homopolymers and in block copolymers, respectively (EU, 2006).

Relevant information from consultation is not available.

#### Price issues

Information is generally not available. Data from the Alibaba.com online marketplace would suggest that tetrabromobisphenol-A bis (2,3-dibromopropyl ether) may have a price per kg which is ca. 50% of DecaBDE's price (see **Table 10-3**), but the reliability of this estimate is uncertain. The substance is assumed to require the use of ATO at similar levels to DecaBDE, as discussed above.

#### Substitution cost calculations

The following table summarises the relevant information for tetrabromobisphenol-A bis (2,3-dibromopropyl ether), based on the analysis presented in Section 5.4.

Table 5-53: Substitution cost calculations for tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)							
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes			
Polymers	A1	Not relevant	Not relevant				
	B1	BFR full: <10 million BFR mix: <1 million	<400	Assumed to be a 'member' of the BFR group			
	C1	PPO/HIPS: 50 million PP: -10-12 million	PPO/HIPS: <3,200 PP: -700-800				
	D1	Not estimated per alternative substance	Not estimated per alternative substance				
Textiles	A2	Not relevant	Not relevant				
	C2	Not relevant	Not relevant				

#### Hazard profile

#### REACH Registration and C&L data

The table that follows summarises the hazard profile of tetrabromobisphenol-A bis (2,3-dibromopropyl ether) based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-54: REACH Registration data for tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)					
Category	Parameter	Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)  Notes			
Physical state		Solid			
Classification for environmental	Acute hazards to the aquatic environment	N/A			
hazards	Long-term hazards to the aquatic environment	N/A			
	Carcinogenicity	N/A			
	Mutagenicity	N/A			
Classification for	Reproductive toxicity	N/A			
human health	Acute toxicity	N/A			
hazards	Irritation	N/A			
	Sensitisation	N/A			
	Specific target organ toxicity	N/A			

Table 5-54: REACH 21850-44-2)	Table 5-54: REACH Registration data for tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)				
Category	Parameter	Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	Notes		
	Persistence	vP	Hydrolysis half-life > 1 year and is not readily biodegradable		
DRT assessment	Bioaccumulation	Not B	Bioaccumulation in fish study estimates the highest BCF value of 130		
PBT assessment	Toxicity	Not T	EC50 for aquatics organisms (Fish, daphnia and algae) is higher than 100 mg/L.  NOEC for earthworm is 512 mg/kg soil dw		
	Conclusion	Not a PBT			
Key	Partition coefficient	> 7.2			
physicochemical	Water solubility	0.144 μg/L (20 °C)			
properties	Vapour pressure	> 0.027 < 0.031 Pa (20 °C)			
	PNEC aqua (freshwater)	No hazard identified			
	PNEC aqua (marine water)	No hazard identified			
	PNEC aqua (intermittent releases)	No hazard identified			
Ecotovicological	PNEC STP	No hazard identified			
Ecotoxicological information	PNEC sediment (freshwater)	927 mg/kg sediment dw	Extrapolation method: partition coefficient		
	PNEC sediment (marine water)	92.7 mg/kg sediment dw	Extrapolation method: partition coefficient		
	PNEC soil	No hazard identified			
	PNEC oral predators	55.3 mg/kg food	AF: 300		

#### Past PBT hazard assessments

The following table summarises information on the assessment of the PBT properties of tetrabromobisphenol-A bis (2,3-dibromopropyl ether). The substance does not meet the PBT criteria but some concern on carcinogenicity has been raised.

Table 5-55: PBT properties of tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)				
Persistence	Bioaccumulation	Toxicity	Source	
No data	No data	Suspected of being carcinogenic. Very limited data on the environmental and health properties	Keml (2009)	
Insufficient data; low degradability	LogKow = 11.52 (estimated, KowWin)	Low acute toxicity (LD <sub>50</sub> = 20g/kg, oral); relatively low sub-chronic toxicity NOAEL = 200 mg/kg; mutagenic Concerns by the US National Toxicology Program (NTP) over its carcinogenic potential <sup>53</sup>	JRC (2007)	

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Tetrabromobisphenol A bis(2,3-dibromopropyl ether) was nominated for toxicological characterisation by the US National Institute of Environmental Health Sciences (NIEHS) based on studies of 2,3-dibromo-1-propanol (DBP) and the DBP-based flame retardant tris(2,3-dibromopropyl)phosphate (TBP) that showed clear evidence of carcinogenicity in all sex-species combinations in two-year dermal and feed studies, respectively, conducted by the US National Toxicology Program (NTP). Out of 32 compounds identified with

In comparison to tetrabromobisphenol-A (TBBPA), a substance that has raised concern in the past, the environmental fate of derivatives of TBBPA has been much less studied. The ESR RAR for TBBPA considered that some of the simple ether derivatives of TBBPA, including the bis(2,3-dibromopropyl ether, appear, at least theoretically, to have some potential to form TBBPA in the environment through a (bio)degradation process, but the significance of this is unknown. The persistence of tetrabromobisphenol-A bis (2,3-dibromopropyl ether) in a sediment mesocosm has recently been investigated by De Jourdan et al. (2013). This study found that the median dissipation time for tetrabromobisphenol-A bis (2,3-dibromopropyl ether) was around 32 days in the particulate phase and 102 days in the sediment phase. TBBPA was detectable in some of the samples as a degradation product (information taken from Danish EPA, 2013).

Bergman et al. (2012) give estimated LogKow values and Koc values for several derivatives of TBBPA. The derivatives all have relatively high LogKow and Koc values, indicating that they will partition preferentially onto sediment and soil in the environment. For tetrabromobisphenol-A bis (2,3-dibromopropyl ether) the values were 8.51 and  $1.01 \times 10^6$  respectively (as cited in Danish EPA, 2013).

The US EPA agrees that it is not evident that TBBPA will be released from tetrabromobisphenol-A bis (2,3-dibromopropyl) ether and the conditions necessary for such degradation are not known. If TBBPA is released through the degradation, the associated hazard profile would be influenced by any toxicity associated with TBBPA (US EPA, 2014).

#### **Concerns about TBBPA**

The ESR RAR for TBBPA found that the substance meets only the persistence criteria for the PBT assessment (it is considered to be P or vP) based on the EC Technical Guidance Document/REACH criteria (ECB, 2008). Although the measured BCF value is around 60% of the threshold value, it was considered to be a maximum value as it may include a contribution from metabolites. The substance potentially meets the T criterion on the basis of a fish study that gave inconclusive results. Overall, TBBPA was not considered to meet the REACH PBT criteria (OSPAR, 2011). However, the EU RAR also considers a study in estuarine sediments that has indicated that TBBPA has the potential to degrade through debromination under anaerobic conditions to form bisphenol-A, which is relatively stable under anaerobic conditions. Potential adverse effects of bisphenol-A on aquatic molluscs at low concentrations remain uncertain despite extensive scientific investigations but the substance is a potential endocrine disrupter. Another potential metabolite/degradation product (tetrabromobisphenol-A bis(methyl ether)) may be formed by O-methylation of tetrabromobisphenol-A, and this substance can be considered to meet the ESR/REACH screening criteria for a vPvB substance (OSPAR, 2011).

On the other hand, TBBPA does meet all the OSPAR PBT criteria which are different to those under REACH<sup>54</sup>, although it should be acknowledged that the B decision is borderline (OSPAR, 2011).

#### Other hazard assessments

In the 2011 review of Arcadis & EBRC for the European Commission, three sub-scenarios were identified for which a human health risk characterisation was performed: saturated vapour concentration (inhalation), service life of textiles used for carpets (dermal) and service life of textiles

the DBP substructure, only TBBPA-DBPE was found in November 2002 to be in production and use (NIEHS, 2002).

P: Half-life ≥50 days, B: LogKow ≥4 or BCF ≥500 L/kg, T: Acute L(E)C<sub>50</sub> ≤1 mg/L or long-term NOEC ≤0.1 mg/L or CMR or chronic mammalian toxicity.

used for carpets (inhalation). First tier exposure assessments were performed using the ECETOC TRA Consumer tool with some simple refinements like the saturated vapour concentration for a more plausible inhalation exposure assessment. This tentative risk assessment using conservative exposure estimations showed a risk with respect to the dermal exposure to textiles used for carpets. However, this application was questioned as being relevant for the domestic environment. No risk was identified for the inhalation of vapour or airborne particulates (Arcadis & EBRC, 2011).

With regard to the recent US EPA assessment, the following table summarises the results of the recent assessment of the substance by the US EPA. The table provides a summary of findings for those parameters that have been marked of "moderate" concern. On the other hand, parameters of "high" or "very high" concern are discussed in more detail after the table.

Table 44-2)	Table 5-56: US EPA Assessment of tetrabromobisphenol-A bis (2,3-dibromopropyl ether) (CAS No. 21850-44-2)													
	Human Health Effects				_	Aquatic Toxicity**		Environme ntal Fate						
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Reproductive Developmental Neurological Skin Sensitization Respiratory Sensitization Eye Irritation Chronic Persistence Bioaccumulation							Bioaccumulation			
L	М	M	М	М	L	М	L	No data	L	Г	L	L	VH	Н
Carcir	ogenic	ity	for alky	lation a	nd profe	essional j	judgeme							
Genot	TBBPA bis (2,3-dibromopropyl) ether was mutagenic to <i>Salmonella typhimurium</i> in one assay, while it was negative in other assays in <i>S. Typhimurium</i> and <i>E. coli</i> . This substance was also negative for mutagenicity in mouse lymphoma cells. TBBPA bis (2,3-dibromopropyl) ether is also estimated to have potential for genotoxicity based on the potential for alkylation. TBBPA bis (2,3-dibromopropyl) ether did not cause chromosomal aberrations or sister chromatid exchanges in Chinese hamster ovary (CHO) cells (in vitro), was negative in an in vivo micronucleus assay in mice and did not produce unscheduled DNA synthesis in rats													
Repro	<b>Estimated</b> to have potential for reproductive effects based on the potential for alkylation and professional judgement					ylation								
Devel	Estimated to have potential for developmental effects based on the potential for alkylation and professional judgement					ial for								
Repea	There is potential for liver toxicity because TBBPA bis (2,3-dibromopropyl) ether is a highly brominated compound and potential for immunotoxicity associated with polyhalogenated aromatic hydrocarbon structure. Located data were insufficient													

Source: US EPA (2014)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

The assessment of the US EPA for those parameters that have been identified as being of "High" or "Very High" concern was as follows (US EPA, 2014):

- **Persistence**: high persistence of tetrabromobisphenol-A bis (2,3-dibromopropyl) ether is expected as a result of located biodegradation studies and the absence of other expected likely removal processes under environmental conditions. In the course of a 28-day Japanese Ministry of International Trade and Industry (MITI) test, only 1% of tetrabromobisphenol-A bis (2,3-dibromopropyl) ether was degraded. Tetrabromobisphenol-A bis (2,3-dibromopropyl) ether will exist primarily in the particulate phase in the atmosphere and is not expected to undergo removal by gas phase oxidation reactions. It is also not anticipated to undergo removal by hydrolysis
- **Bioaccumulation**: based on an estimated bioaccumulation factor of 12,000 and its detection in Great Lakes Herring gull eggs, potential for bioaccumulation is high.

### Other hazard information

With regard to CMR properties, carcinogenicity, as well as reproductive and developmental effects might be of concern based on the potential for alkylation and professional judgement. They substance was mutagenic to *Salmonella typhimurium* in one assay, while it was negative in other assays in *S. Typhimurium* and *E. coli*. This substance was also negative for mutagenicity in mouse lymphoma cells. It is also estimated to have potential for genotoxicity based on the potential for alkylation. Tetrabromobisphenol-A bis (2,3-dibromopropyl) ether did not cause chromosomal aberrations or sister chromatid exchanges in Chinese hamster ovary (CHO) cells (*in vitro*), was negative in an in vivo micronucleus assay in mice and did not produce unscheduled DNA synthesis in rats (US EPA, 2014).

#### Available monitoring data

According to the US EPA, tetrabromobisphenol-A bis (2,3-dibromopropyl) ether has been detected in Great Lakes Herring gull eggs (US EPA, 2014).

#### Conclusion on Alternative 5

The following table summarises the conclusions from the above information on the feasibility and suitability of tetrabromobisphenol-A bis (2,3-dibromopropyl) ether as a replacement for DecaBDE.

Table 5-57: Conclusions on suitability and feasibility of tetrabromobisphenol-A bis (2,3-dibromopropyl) ether (CAS No. 21850-44-2)			
Category	Conclusion		
Suitability	Environmental hazards: tetrabromobisphenol-A bis (2,3-dibromopropyl) ether may raise concerns about its persistence and bioaccumulation but it is not a recognised PBT. Its breakdown products have also been under the spotlight but current knowledge is limited. In theory, the substance may have some potential to form TBBPA in the environment through a (bio)degradation process but the significance of this is unknown Human health hazards: concerns have been raised about its potential carcinogenic properties but no conclusive results appear to be available in the literature		
Technical feasibility	Tetrabromobisphenol-A bis (2,3-dibromopropyl) ether can be used in HIPS, PP, PE,		
	crystalline PS and less so in textiles		

Table 5-57: Conclusions on suitability and feasibility of tetrabromobisphenol-A bis (2,3-dibromopropyl) ether (CAS No. 21850-44-2)			
Category	Conclusion		
Economic feasibility	Tetrabromobisphenol-A bis (2,3-dibromopropyl) ether may require similar loadings to DecaBDE and requires the use of ATO. Its price is suggested in the electronic literature as lower than DecaBDE but this assertion is not supported by consultation findings. Substitution cost estimates in polymers vary and in PPO/HIPS and PP, costs may range between -€10 million and 50 million per year or -€800 to <3,200/kg emissions avoided		
Overall conclusion	Tetrabromobisphenol-A bis (2,3-dibromopropyl) ether raises some concerns over its environmental fate and potential CMR properties and can be used in a modest range of relevant applications with a substitution cost that would appear to depend on the type of product (polymer)		

# 5.5.6 Alternative 6: Ethylene bis(tetrabromophthalimide) (CAS No. 32588-76-4)

# Technical feasibility issues

Relevant applications

There are several literature sources describing the applicability of ethylene bis(tetrabromophthalimide) as a FR. A summary is provided below.

Table 5-58: Applications f	Table 5-58: Applications for ethylene bis(tetrabromophthalimide) (CAS No. 32588-76-4)					
Application	Material - substrate	Notes	Source			
E&E UL94 V-0	PE, PP, HIPS, ABS, PET, PBTE, PC, PC/ABS, PPE/HIPS, epoxy, UPR, thermoplastic styrene- block copolymers (TPE- S), thermoplastic polyurethanes (TPU)		Troitzsch (2011)			
Wires and cables – VW 1	Thermoplastic polyester elastomers (TPE-E)					
Not specified	HIPS, ABS, PBTE, PP, PE, PC/ABS, HIPS/PPO		JRC (2007)			
Not specified	HIPS, ABS, PC/ABS, HIPS/PPO		Washington State (2006)			
Enclosures	HIPS, ABS, PC/ABS, PPE/HIPS	Compared to DecaBDE, it may display better	Danish EPA (2006)			
Connectors	PA, PET/PBTE	bloom resistance,				
Wires	PP, PP	thermal stability and UV stability. Claimed to be a popular choice for resins used in office automation equipment, such as photocopiers and printers where UV stability is an important performance criterion				

Application	Material - substrate	Notes	Source
Not specified	ABS, HIPS, PBTE/PET, PC,		UK HSE (2012)
	PP, PE, PC/ABS,		
	HIPS/PPO, thermoplastic		
	elastomers, silicone,		
	PVC, EPDM, TPU,		
	PE/EVA, thermosets		
	(epoxy and phenolic		
	resins, unsaturated		
<del>-</del> 1 1 .:	polyesters)		All (2010)
Thermoplastics	ABS, HIPS, Polyester, PC,		Albemarle (2013)
	PP, PE, SAN, PC/ABS, HIPS/PPO, Elastomers,		
	PVC		
Foams	Polyolefin, PVC/Nitrile,		
i oams	Elastomers		
Wire & cable	Silicone, EDPM, PP,		
	PE/EVA, TPU, PVC		
Thermosets	Epoxy, phenolic, UPR,		
	VE, SMC/BMC, PU, Latex		
Electronics	PP, PE, HIPS,		US EPA (2014)
	Thermoplastics		
Wire & cable	CPE, PP, PE		
Public buildings	PP, PE		
Construction materials	PP, PE, Elastomers		
Automotive	PP, PE		
Shipping pallets	PP, PE		
Not specified	HIPS, PE, PP,		Consultation with
	thermoplastic		Norway
	polyesters, PA, EPDM,		(NIEHS, 1999)
	rubbers, PC, ethylene co-		
	polymers, ionomer		
	resins, textiles		

Ethylene bis(tetrabromophthalimide) is one of the substances with the widest range of applications as a DecaBDE replacement and can be used both in polymers and textiles.

# **Economic feasibility**

# Loading

The Danish EPA suggests that ethylene bis(tetrabromophthalimide) can be used at the same loading as DecaBDE, i.e. 12-13% with 4-5% ATO in order to achieve a V-0 fire rating in HIPS (Danish EPA, 2006).

#### Price issues

Information from the Alibaba.com online marketplace would suggest that ethylene bis(tetrabromophthalimide) might have a price per kg that is higher than DecaBDE's by ca. 40% (see **Table 10-3**). It is assumed to require the presence of ATO at loadings similar to that for DecaBDE.

#### Substitution cost calculations

The following table summarises the relevant information for ethylene bis(tetrabromophthalimide), based on the analysis presented in Section 5.4.

Table 5-59: S	Table 5-59: Substitution cost calculations for ethylene bis(tetrabromophthalimide) (CAS No. 32588-76-4)					
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes		
Polymers	A1	Not relevant	Not relevant			
	B1	BFR full: <10 million BFR mix: <1 million	<400	Assumed to be a 'member' of the BFR group		
	C1	HIPS: 8 million	HIPS: <500			
	D1	Not estimated per alternative substance	Not estimated per alternative substance			
Textiles	A2	Not relevant	Not relevant			
	C2	Full: <10 million Mix: <1 million	<400			

# Hazard profile

# REACH Registration and C&L data

The table that follows summarise the hazard profile of ethylene bis(tetrabromophthalimide) based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-60: REACH Registration data for ethylene bis(tetrabromophthalimide) (CAS No. 32588-76-4)					
Category	Parameter	Ethylene bis(tetrabromophthalimide)	Notes		
Physical state		Solid			
Classification for	Acute hazards to the aquatic environment	N/A			
environmental hazards	Long-term hazards to the aquatic environment	N/A			
	Carcinogenicity	N/A			
	Mutagenicity	N/A			
Classification for	Reproductive toxicity	N/A			
Classification for human health	Acute toxicity	N/A			
hazards	Irritation	N/A			
	Sensitisation	N/A			
	Specific target organ toxicity	N/A			

Table 5-60: REACH	Registration data for ethyl	lene bis(tetrabromophthalimide)	(CAS No. 32588-76-4)
Category	Parameter	Ethylene bis(tetrabromophthalimide)	Notes
	Persistence	vP	It is expected to partition predominantly to soil, where it is expected to be very persistent (vP)
PBT assessment	Bioaccumulation	Not B	Based on low octanol solubility and the size of the molecule and its molecular weight
	Toxicity	Not T	
	Conclusion	Not a PBT	
Key	Partition coefficient	Test not feasible	
physicochemical	Water solubility	< 1 mg/L	
properties	Vapour pressure	0.000227 Pa (20 °C)	
	PNEC aqua (freshwater)	No data: aquatic toxicity unlikely	
	PNEC aqua (marine	No data: aquatic toxicity	
	water)	unlikely	
	PNEC aqua	No data: aquatic toxicity	
	(intermittent releases)	unlikely	
Ecotoxicological	PNEC STP	No data: aquatic toxicity unlikely	
information	PNEC sediment	No data available: testing	
	(freshwater)	technically not feasible	
	PNEC sediment (marine	No data available: testing	
	water)	technically not feasible	
	DNEC coil	No data available: testing	
	PNEC soil	technically not feasible	
	PNEC oral predators	No potential for bioaccumulation	

# Past PBT hazard assessments

The following table summarises information on the assessment of the PBT properties of ethylene bis(tetrabromophthalimide). The substance does not appear to meet all PBT criteria, although it is very persistent.

Table 5-61: PBT properties of ethylene bis(tetrabromophthalimide) (CAS No. 32588-76-4)					
Persistence	Bioaccumulation	Toxicity	Source		
Highly persistent	Criterion not met	Limited data available, but one study shows low acute aquatic toxicity. A full assessment of the environmental and health characteristics is not possible	(Keml, 2009)		
Not readily biodegradable based on the results of a single test. Considered to meet	Based on the estimated LogKow value (9.80), it meets the screening criterion for consideration as bioaccumulative (B) and very bioaccumulative (vB) (LogKow >	The only available study of the aquatic toxicity of the substance indicates that acute toxic effects occur at levels much higher than the	Danish EPA in JRC (2007)		

Table 5-61: PBT properties of ethylene bis(tetrabromophthalimide) (CAS No. 32588-76-4)					
Persistence	Bioaccumulation	Toxicity	Source		
the very persistent (vP) criterion	4.5). Little uptake of the substance has been seen in fish exposed via water (BCF < 3.3). Based on the single bioaccumulation study available, the bioaccumulation criterion is not fulfilled. In support of the results from the bioaccumulation study, the high molecular weight (951.5 g/mol) indicates that it is unlikely to bioaccumulate significantly regardless of the LogKow value due to possible steric hindrance of passage of gill membranes or cell membranes of respiratory organs	estimated water solubility. Long-term NOEC values are not found in the literature. More ecotoxicology data are required for assessment of the toxicity (T) criterion			

#### Other hazard assessments

The 2011 assessment by Arcadis & EBRC for the European Commission did not identify any risks to human health from the use of the substance in consumer products (Arcadis & EBRC, 2011).

The substance was considered in a recent review by the European Food Safety Authority (EFSA, 2012) and the LogKow and Koc were reported to be 6.63 and 96,500 L/kg, respectively, which indicate that the substance will adsorb strongly to sediment and soil. The BCF in fish was reported to be low (<33 L/kg), but the EFSA report considered the potential for accumulation in mammals to be high, based on modelling. The overall environmental persistence (Pov) was estimated to be >500 days, again based on modelling (cited in Danish EPA, 2013).

In its recent assessment of alternatives to DecaBDE, the US EPA provided some information on the substance. This is summarised below. The table provides a summary of findings for those parameters that have been marked of "moderate" concern. On the other hand, parameters of "high" or "very high" concern are discussed in more detail after the table.

No.		Human Health Effects							Aquatic E		Environment al Fate				
L M L L M L L No data VL VL L L VH  Carcinogenicity  Estimated based on lack of experimental carcinogenicity data for this compound or a suitable analog; carcinogenicity cannot be ruled out  Ethylene bis(tetrabromophthalimide) did not cause developmental effects in rat rabbits following gestational exposure at oral doses as high as 1,000 mg/kg bw-However, there is a lack of developmental neurotoxicity data for this compound concern for developmental neurotoxicity has been identified for DecaBDE, an analog shares a key structural feature with ethylene bis(tetrabromophthalimide). Ethy bis(tetrabromophthalimide) also possesses structural features that are not present DecaBDE and, as a result, the confidence in this assignment is low. Given the absence developmental neurotoxicity data, potential concerns cannot be ruled out, and	Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Suitable analog; carcinogenicity cannot be ruled out  Ethylene bis(tetrabromophthalimide) did not cause developmental effects in rat rabbits following gestational exposure at oral doses as high as 1,000 mg/kg bw-However, there is a lack of developmental neurotoxicity data for this compound concern for developmental neurotoxicity has been identified for DecaBDE, an analog shares a key structural feature with ethylene bis(tetrabromophthalimide). Ethy bis(tetrabromophthalimide) also possesses structural features that are not preser DecaBDE and, as a result, the confidence in this assignment is low. Given the absence developmental neurotoxicity data, potential concerns cannot be ruled out, and	L	М	L	L	М	L	L	L		VL	VL	L	L	VH	н
US EPA															

The assessment of the US EPA for those parameters that have been identified as being of "High" or "Very High" concern was as follows (US EPA, 2014):

judgement

italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional

- Persistence: the very high persistence for ethylene bis(tetrabromophthalimide) is based on limited experimental data and quantitative structure activity relationship (QSAR) estimates. No degradation was observed in activated sludge during a MITI test, indicating it is not biodegradable under the stringent test conditions. Findings from biodegradation models provided similar results and indicate that it will be recalcitrant under aerobic conditions. Anaerobic degradation under methanogenic conditions is not considered probable. The atmospheric half-life of ethylene bis-tetrabromophthalimide is estimated to be 3.3 hours, although it is expected to exist primarily in the particulate phase in air. Resistance to most environmental fate processes indicates that ethylene bis-tetrabromophthalimide is expected to be persistent in the environment
- **Bioaccumulation**: the potential for bioaccumulation of ethylene bis(tetrabromophthalimide) is high based on the estimated bioaccumulation factor. The BAF estimate is consistent with that anticipated for high molecular weight chemicals with a high degree of bromination.

According to a recent report by the European Food Safety Agency (EFSA), the substance is a TEBP-Anh and ethylenediamine product, fully brominated on the aromatic rings. It can be expected to undergo reductive debromination in the environment (EFSA, 2012). Tetrabromophthalic acid is a possible degradation product<sup>55</sup>.

#### Available monitoring data

No information has been retrieved.

#### Conclusion on Alternative 6

The following table summarises the conclusions from the above information on the feasibility and suitability of ethylene bis(tetrabromophthalimide) as a replacement for DecaBDE.

Table 5-63: Conclusions on suitability and feasibility of ethylene bis(tetrabromophthalimide) (CAS No. 32588-76-4)				
Category	Conclusion			
Suitability	Environmental hazards: ethylene bis(tetrabromophthalimide) is very persistent and its bioaccumulation raises concerns but the substance does not appear to meet the criteria for a PBT. On the other hand, the issue of debromination in the environment has been raised in the literature  Human health hazards: no particular concern is raised on the basis of REACH registration information, but the US EPA has raised concerns over carcinogenicity and developmental toxicity due to the lack of data			
Technical feasibility	Ethylene bis(tetrabromophthalimide) can be used in a wide range of applications that are relevant to DecaBDE at similar loadings to DecaBDE and in the presence of ATO			
Economic feasibility	Ethylene bis(tetrabromophthalimide) requires similar loadings to DecaBDE but it is likely to have a price per tonne considerably higher than DecaBDE. It also requires the use of ATO.  Substitution cost estimates in HIPS polymer show a costs of €8 million/y or <€500/kg emission avoided. For textiles, depending on the assumptions made, substitution costs ranges between <€10 million and >€1 million or <€400/kg emissions avoided			
Overall conclusion	Ethylene bis(tetrabromophthalimide) is an alternative which compatibility with a wide range of applications, which does not appear to meet all PBT criteria, but has a price considerably higher than that of DecaBDE			

# 5.5.7 Alternative 7: 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide (CAS No. 4090-51-1)

#### Technical feasibility issues

Relevant applications

Information from the relevant industry association that represents manufacturers of phosphorous and nitrogen-based FRs (PINFA) confirms that the substance may only find uses as a FR in viscose textiles (PINFA, 2010c). This certainly limits the scope of the substance to act as a widespread replacement for DecaBDE. Information from consultation confirms its role as a FR additive in this context. It is probably used mainly in clothing, so its share in DecaBDE-related products is expected to be very low.

As indicated here: <a href="http://pubs.acs.org/doi/suppl/10.1021/es903383a/suppl file/es903383a si 001.pdf">http://pubs.acs.org/doi/suppl/10.1021/es903383a/suppl file/es903383a si 001.pdf</a> (accessed on 5 February 2014).

A supplier of viscose fibres that are flame-retardant with the substance has provided information during consultation and this is presented in the Confidential Annex. In summary, the supplier has claimed that the technical characteristics of its fibre are equivalent of better than DecaBDE-backcoated textiles, while offering better aesthetics and lifetime.

### **Economic feasibility**

#### Loading

A recent patent describes the use of the substance in making FR viscose fibres. It is used at a concentration of no lower than 15% by weight of dry yarn and is accompanied by 5% by weight TBBPA (Tozzi-Spadon, et al., 2011). The information obtained from consultation suggests a lower loading, ca. 10%, which is lower than that for DecaBDE/ATO.

#### Price issues

The price per kg of 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide has been described as several times higher than that of DecaBDE. As far as the final article (textile) is concerned, its manufacture becomes considerably more costly than that of DecaBDE-backcoated articles. This cost difference has more to do with the use of more costly raw materials (because of the more costly fibres that need to be used) rather than with increased operating costs (additional detail is provided in the Confidential Annex).

#### Substitution cost calculations

The substance has not been included in the substitution costs calculations in Section 5.4.

#### Hazard profile

#### REACH Registration and C&L data

The table that follows summarises the hazard profile of 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-64: REACH Registration data for 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide (CAS No. 4090-51-1)						
Category	Parameter	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	Notes			
Physical state		Solid				
Classification for environmental	Acute hazards to the aquatic environment	N/A				
hazards	Long-term hazards to the aquatic environment	N/A				
Classification for	Carcinogenicity	N/A				
human health	Mutagenicity	N/A				
hazards	Reproductive toxicity	N/A				
	Acute toxicity	N/A				
	Irritation	N/A	_			
	Sensitisation	N/A				

		Oxybis[5,5-dimethyl-1,3,2-	-dioxaphosphorinane] 2,2'-disulphide
(CAS No. 4090-51-1 Category	Parameter	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	Notes
	Specific target organ toxicity	N/A	
PBT assessment	Persistence	P or vP	First PBT assessment classifies the substance as P, the second as vP. First assessment uses screening criteria (not readily biodegradable; hydrolysis under environmental conditions assumed to be slow). Second uses both Annex XIII and screening criteria; Annex XIII Criteria: half-lives and rate constants determined at pH 9 at 20 and 30 °C were 166 and 195 days, respectively PBT Screening criteria: not readily biodegradable; hydrolysis under environmental conditions assumed to be slow
	Bioaccumulation	Not B	LogKow of the submission substance was experimentally determined as 2.48
	Toxicity	Not T	No EC <sub>10</sub> or EC <sub>50</sub> could be determined. Reliable aquatic toxicity tests (all reliability category 1) are available for freshwater algae ( <i>Scenedesmus subspicatus</i> ), freshwater invertebrates (Daphnia magna, acute), freshwater fish (zebra fish, acute) and sewage treatment plant microorganisms (activated sludge respiration inhibition test, 3 hours). In all these tests, nominal limit concentrations far above the actual water solubility of the submission substance were used (77 or 1000 mg/L). However, no signs of toxicity were observed in any of these tests. Thus, the submission substance was demonstrated to be non-toxic to freshwater organisms at water saturation level
	Conclusion	Not a PBT	
Key physicochemical	Partition coefficient Water solubility	2.48 1.4 mg/L (20 °C)	
properties	Vapour pressure	0.0000034 Pa (25 °C)	
Ecotoxicological	PNEC aqua (freshwater)	No hazard identified	

Category	Parameter	2,2'-Oxybis[5,5- dimethyl-1,3,2- dioxaphosphorinane] 2,2'-disulphide	Notes
information	PNEC aqua (marine water)	No hazard identified	
	PNEC aqua (intermittent releases)	No hazard identified	
	PNEC STP	No hazard identified	
	PNEC sediment (freshwater)	No hazard identified	
	PNEC sediment (marine water)	No hazard identified	
	PNEC soil	No hazard identified	
	PNEC oral predators	No potential to cause	
		toxic effects if	
		accumulated (in	
		higher organisms) via	
		the food chain	

No other information has been retrieved.

# **Conclusion on Alternative 7**

The following table summarises the conclusions from the above information on the feasibility and suitability of 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide as a replacement for DecaBDE.

Table 5-65: Conclusions on suitability and feasibility of 2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane]					
2,2'-disulphide (CAS	2,2'-disulphide (CAS No. 4090-51-1)				
Category	Conclusion				
Suitability	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide is very persistent (based on Annex XIII and screening criteria), however, it does not meet all PBT criteria and its human health hazard profile does not appear to raise concerns				
Technical feasibility	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide appears to be suitable for replacing DecaBDE in textile applications when used as a FR for a specific fibre type (viscose)				
Economic feasibility	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide requires lower loadings than DecaBDE but it has a higher price than DecaBDE and requires the use of more expensive raw material fibres, but does not require the use of ATO. The cost of production and the market price of the textile articles becomes considerably higher				
Overall conclusion	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide shows high persistence in the environment but no other notable hazard concern. It can find limited application as a DecaBDE replacement and is considerably costlier				

# 5.5.8 Alternative 8: Resorcinol bis(diphenylphosphate) (RDP) (CAS No. 57583-54-7; 125997-21-9)

# Technical feasibility issues

Relevant applications

Commercial RDP is a mixture of chemicals (State of Hawaii Department of Health, 2008):

- 65-80% phosphoric acid, 1,3-phenylene tetraphenyl ester (CAS No. 57583-54-7)
- 15-30% phosphoric acid, bis[3-[(diphen-oxyphosphinyl)oxylphenyl] phenyl ester (CAS No. 98165-92-5), and
- <5% triphenyl phosphate (TPP).</li>

According to the US EPA, the material used by industry for FR applications is most likely the polymeric material with CAS No. 125997-21-9, although the CAS No. for the discrete organic where n=1, 57583-54-7 (Phosphoric acid, P,P'-1,3-phenylene P,P,P',P'-tetraphenyl ester), has been used interchangeably with 125997-21-9 in the publicly available literature (US EPA, 2014).

There are several literature sources describing the applicability of RDP as a FR. A summary is provided in **Table 5-66**.

Table 5-66: Applications for	Table 5-66: Applications for resorcinol bis(diphenylphosphate) (RDP) (CAS No. 57583-54-7; 125997-21-9)					
Application	Material - substrate	Notes	Source			
Enclosures	PC/ABS, PPE/HIPS	Superior flammability performance and lower volatility than is obtainable with conventional triaryl phosphates	Danish EPA (2006)			
Transportation: Dashboard instruments, instrument panels, instrument cluster housing, and other parts	ABS, PC/ABS		PINFA (2010b)			
Automotive foams	Not specified		PINFA (2010b)			
Automotive E&E components	HIPS/PPO, PC/ABS (4:1)		PINFA (2010b)			
E&E – UL94V0	PC, PC/ABS, PPE/HIPS, TPU		Troitzsch (2011)			
Not specified	PC/ABS, Epoxy resins, Phenolic resins		ICL Industrial Products (2013)			
Not specified	Textiles					
Electronics	PC/ABS, PPE/HIPS		US EPA (2014)			

RDP is an aryl phosphate which is used as a substitute for halogenated FRs as well as for TPP because it has a lower volatility, a higher thermal stability, and a higher P-content in comparison to TPP. This would not be of influence on the FR efficiency if RDP were only working in the solid phase of burning materials. The primary mechanism of RDP is the solid phase mechanism, but in addition, a (weaker)

gas phase mechanism is also assumed. The active substance content lies between 10 and 11% of phosphorus weight, depending on the product. RDP is used as a substitute for TCPP as it is less volatile, and therefore less likely to be released into the environment (van der Veen & de Boer, 2012).

RDP cannot be used in HIPS as a drop-in replacement for DecaBDE. In order to use RDP, the manufacturer must use a different plastic to achieve the same fire rating. Other plastic blends using RDP, such as HIPS/PPO or PC/ABS, have been identified as viable alternatives to DecaBDE/HIPS TV enclosures. RDP is used instead of other phosphate FRs like TPP, because the amount of phosphate in RDP is higher and therefore would lead to the higher total phosphorus loading (Department of Ecology State of Washington, 2008).

#### **Economic feasibility issues**

#### Loading

Several literature sources refer to the loadings of RDP, as shown in **Table 5-67**.

Table 5-67	Table 5-67: Loadings for resorcinol bis(diphenylphosphate) (RDP) (CAS No. 57583-54-7; 125997-21-9)				
Loading	Material	FR grade	Source		
10%	PC/ABS	V-0	Danish EPA (2006)		
9%	PC/ABS	V-0	Department of Ecology State of Washington (2008)		
17-20%	PPE/PS		Takamura et al., (2013)		
9%	PC/ABS	V-0	PINFA (2010)		
8-9.5%	PC/ABS (PC: 60-80%, ABS: 10-30%)	V-0	Supresta (undated)		
11%	4:1 PC/ABS	V-0	Papazoglou (2004)		
9%	8:1 PC/ABS	V-0			
16%	PPE/HIPS	V-0			
8-13%	Blend of poly(2,6-dimethylphenylene ether), polyphenylethylene-poly(ethylene/butylene)-polyphenylethylene block copolymer and a styrene-(ethylene/propylene-styrene)-styrene copolymer		Kosaka (2006)		

#### Price issues

Information from HELCOM (2013) suggests that the price of RDP is below €3.5/kg. The cost to producers has been described as "affordable". No other source of relevant information is available.

#### Substitution cost calculations

The following table summarises the relevant information for RDP, based on the analysis presented in Section 5.4.

Table 5-68: S	Table 5-68: Substitution cost calculations for RDP (CAS No. 57583-54-7; 125997-21-9)						
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes			
Polymers	A1	Not relevant	Not relevant				
	B1	HFFR full: <50 million HFFR mix: <15 million	<2,100	RDP assumed to be a 'member' of the HFFR group			
	C1	PC/ABS: -2 to -4 million PPO/HIPS: 45-46 million	PC/ABS: -150 to -250 PPO/HIPS: 3,000				
	D1	Not relevant	Not relevant				
Textiles	A2	Not relevant	Not relevant				
	C2	Not relevant	Not relevant				

# Hazard profile

REACH Registration and C&L data

The table that follows summarises the hazard profile of RDP based on information from the ECHA Dissemination Portal and the C&L Inventory.

Category	Registration data for RDP (CAS I	RDP	Notes
	Parameter		Notes
Physical state		Liquid	
Classification for	Acute hazards to the aquatic	N/A	
environmental	environment		
hazards	Long-term hazards to the	N/A	
	aquatic environment	,	
Classification for	Carcinogenicity	N/A	
human health	Mutagenicity	N/A	
hazards	Reproductive toxicity	N/A	
	Acute toxicity	N/A	
	Irritation	N/A	
	Sensitisation	N/A	
	Specific target organ toxicity	N/A	
PBT assessment	Persistence	Not P	Readily biodegradable in a slightly modified closed bottle test (61% degradation in 28 days)
	Bioaccumulation	Not B	BCF: 969 L/kg
	Toxicity	Not T	The lowest toxicity value was a NOEC of 0.021 mg/l in a 21-day Daphnia magna reproduction test
	Conclusion	Not a PBT	
Key	Partition coefficient	4.93	
physicochemical	Water solubility	1.05 mg/L (20 °C)	
properties	Vapour pressure	0.00259 Pa (20 °C)	
Ecotoxicological	PNEC aqua (freshwater)	0.42 μg/L	AF: 50
information	PNEC aqua (marine water)	0.042 μg/L	AF: 500
	PNEC aqua (intermittent releases)	0.74 μg/L	AF: 100
	PNEC STP	12.16 mg/L	AF: 10

Table 5-69: REACH Registration data for RDP (CAS No. 57583-54-7; 125997-21-9)					
Category	Parameter	RDP	Notes		
	PNEC sediment (freshwater)	0.52 mg/kg sediment dw	Extrapolation method: partition coefficient		
	PNEC sediment (marine water)	0.05 mg/kg sediment dw	Extrapolation method: partition coefficient		
	PNEC soil		Extrapolation method: partition coefficient		
	PNEC oral predators	2.53 mg/kg food	AF: 300		

# Past PBT hazard assessments

The following table summarises information on the assessment of the PBT properties of RDP. The substance does not meet the PBT/vPvB criteria.

Table 5-70: PBT properties of RDP (	CAS No. 57583-54-7; 125	5997-21-9)	
Persistence	Bioaccumulation	Toxicity	Source
RDP is considered inherently biodegradable but it is not possible to determine whether the specific criteria are met. The substance undergoes hydrolysis in water with a half-life at 10 °C shorter than the criteria. However, this is for primary degradation, and the results indicate that the reaction may reach equilibrium after one or two half-lives. This is not considered sufficient evidence that the substance does not meet the criteria. Hence, the substance is considered to meet the first stage screening criteria for P and vP	A fish BCF of 969 L/kg has been estimated. Hence, the substance does not meet the B criterion	The lowest measured NOEC value is 0.021 mg/L and the lowest estimated NOEC is 0.014 mg/L. The substance does not meet the T criterion	(Environment Agency, 2009c)
P criterion not met	Uncertain. BCF (based on estimated LogKow) = 3000, BCF (based on measured LogKow) = 316.	Moderate acute aquatic toxicity. Studies in rats and rabbits indicate low acute toxicity.  A full assessment of the environmental and health effects is not possible due to limited data	(Keml, 2009)
In water (at 20 °C; pH 7) = 7-17 days (EFRA). In water, 11 days at 20 °C at pH 4; 17 days at 20 °C at pH 7; 21 days at 20 °C at pH 9	LogKow (estimated) = 7.41; BCF (estimated) = 3000 (EPA PBT Profiler). BCF = 316 (calculated) based on measured LogKow = 3.9-4.8	Low for lab animals, medium aquatic toxicity. Negative mutagenicity studies; no carcinogenicity	JRC (2007)

The ENFIRO assessment of RDP has concluded that the substance has low to high ecotoxicity and persistence, see also **Table 5-33**.

#### Other hazard assessments

The German Federal Environmental Agency (Umweltbundesamt) published a study in 2001 in which RDP was one of 13 FRs assessed. The study was not able to make a recommendation on the substance due to lack of data<sup>56</sup>.

The Environment Agency for England and Wales undertook an evaluation of environmental risks for RDP in 2009. The conclusions are presented in the following table. Based on the available information, potential risks were identified for all of the life cycle with the exception of production for one or more compartments (Environment Agency, 2009c).

Table 5-71: Summary of potential environmental risks identified for RDP by the Environment Agency for England and Wales (2009c)										
Lifecycle stage	Surface water	Sediment	WWTP	Air	Soil	Aquatic food chain	Terrestrial food chain	Marine water	Marine sediment	
Production										
Pigment dispersions		✓			✓			<b>✓</b>	✓	
PVC		✓			✓				✓	
Paints and coatings		✓			✓				✓	
Thermoplastics/ styrenics	<b>✓</b>	✓			✓			<b>√</b>	✓	
Polyurethane		✓			✓			✓	✓	
Regional										
Source: Environment Agency (2009c)										

The Arcadis & EBRC assessment for the European Commission of human health risks from the use of consumer products that contain RDP looked into the service life of E&E equipment and did not identify any unacceptable risks (Arcadis & EBRC, 2011).

In its recent assessment of alternatives to DecaBDE, the US EPA provided some information on the substance. This is summarised below. The table provides a summary of findings for those parameters that have been marked of "moderate" concern. On the other hand, parameters of "high" or "very high" concern are discussed in more detail after the table.

Available at <a href="http://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/1988.pdf">http://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/1988.pdf</a> (accessed on 7 February 2014).

Table	Table 5-72: US EPA Assessment of RDP (CAS No. 57583-54-7; 125997-21-9)													
	Human Health Effects								Aqı Toxi	uatic icity**	Envir ntal I	onme Fate		
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
L	М	L	L	M	M	M	L	No data	L	VL	VH	VH	M	н
Carcin	nogenic	ity				certain profess		al for ca	arcinog	enicity	based	l on an	alogy t	to aryl
Devel	opmen	tal	rats. A dose of following/kg	Adverse 500 mg ng oral a bw-day	effects g/kg bw- administ	included day. No ration o	d delaye adverse of resorc	in a two d vagina e develo inol bis- 0.5 mg/L	al open pment diphen	ing an al effec yl pho	d prep cts wer sphate	outial se re obser at dose	paratio ved in i	n at a rabbits o 1000
Neuro	ological		(NOAEI	. = 0.1 m	ng/L); cri	iteria va	lues are	tripled f	or chei	micals	evalua	ted in 2	8-day s	tudies;
Repea	ated do	se	Expering rats following fo	nental d lowing a sign for or mists udy eval exposure s also po	ata for r a 4-wee the End based of uations e-related of mg/kg	esorcino k inhala vironme n 90-da making d gross for liver	ol bis-dip tion exp nt criter y repeat the Mo or micr toxicity	henylph cosure to ia thres ed dose oderate oscopic based of alog (hig	osphat o 0.5 r hold fo studies hazard pathol n a con	e repong/L action a lower a lo	rted al erosol w haza ria valu from as ider al anal	veolar h (NOAEL and designess are to 0.06 –0 ntified intigention	istiocyt = 0.1 gnation tripled to mg/ n any	is 0.2 for 28- L. No organ. effects
Persis	tence		Modera experin the cor inherer degrad after 5 oligomo nm, an The atr to be 6 particu phenol No. 108	nental bennental bennerciantly bloomation - to the total therefus (n=1) and the total	sistence siodegradal polymodegrada he Close and n=2 fore, are sio and 4.1 ase in a b. 108-99 hrough	dation seric mixed Bottle biodegre (2) do no e not expire (n=2) h ir. Enzy (5-2), dip	studies to kture. In leg the good to radation to contain to contai	or reso hat indi The com guideline After 28 occurr n chrome o be sus bis(diph chough t r basic nosphate osphory	cate the mercial set of [8] days, ed. I ophore sceptible hey are hydroly e (CAS	ne poted mixt Directive 37% be Resorci s that a le to de cosphane expectors is leader 1830.	ential fure wave 84/iodegrainol babsorb irect pate) oligeted to ading t 8-85-7/	or biodors determined the second of the seco	egradatemined C, C.6 occurrently nylphoselength s by suare estimarily oroductesorcino	tion of to be "Biotic ed and sphate s >290 inlight. mated in the cion of bl (CAS

Source: US EPA (2014)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

The assessment of the US EPA for those parameters that have been identified as being of "High" or "Very High" concern was as follows (US EPA, 2014):

- **Acute toxicity**: based on measured EC<sub>50</sub> values for daphnia. Measured values for fish and algae are higher than the water solubility limit, suggesting no effects at saturation (NES)
- Chronic aquatic toxicity: based on an experimental 21-day NOEC 0.021 mg/L in Daphnia magna. Estimated chronic values suggest a high hazard with the n = 1 oligomer (CAS No. 57583-54-7) of 0.0093 mg/L for fish
- **Bioaccumulation**: the estimated BCF value for the n=1 component (CAS No. 57583-54-7) has high potential for bioaccumulation. The higher molecular weight oligomers that may be found in this mixture (n=2, 3, 4...) are expected to have moderate or low potential for bioaccumulation based on their large size and low solubility according to the polymer assessment literature.

Hydroxy-RDP, dihydroxy-RDP, resorcinol diphenyl phosphate, and hydroxyl-resorcinol diphenyl phosphate, resorcinol, resorcinol conjugates, resorcinyl glucuronide and resorcinyl sulphate were identified as metabolites. Environmental degradation of RDP has been demonstrated in experimental studies; however, the degradation products have not been identified. Degradation of RDP by sequential dephosphorylation could produce phenol, diphenyl phosphate or resorcinol. The importance of dephosphorylation relative to possible competing pathways has not been demonstrated in a published study, according to the US EPA (US EPA, 2014).

One issue worth noting is that commercial RDP contains up to 5% TPP. TPP raises concerns of aquatic toxicity, but the presence of TPP in the commercial product is generally low.

#### Available monitoring data

There are no data available on the occurrence of RDP, or its degradation products, in the environment. Analysis of samples from the vicinity of manufacturing and processing plants is as necessary as analysis on house dust in houses, in which consumer goods such as electronic devices containing RDP are found. There is evidence that RDP containing fumes and aerosols are released during the application of RDP at production sites (van der Veen & de Boer, 2012).

#### **Conclusion on Alternative 8**

The following table summarises the conclusions from the above information on the feasibility and suitability of RDP as a replacement for DecaBDE.

Table 5-73: Conclusions on suitability and feasibility of RDP (CAS No. 57583-54-7; 125997-21-9)							
Category	Conclusion						
Suitability	<b>Environmental hazards</b> : RDP does not meet all PBT criteria but it shows signs of persistence in the environment; its biodegradation products are yet unclear. In addition, there is uncertainty about its bioaccumulation. The US EPA expressed concerns over its aquatic toxicity <b>Human health hazards</b> : the substance has no hazard classification but recent analyses by the US EPA have raised some "moderate" concern over carcinogenicity, developmental, neurological and repeated dose effects						
Technical feasibility	RDP appears to be suitable for replacing DecaBDE in plastic blends, primarily for E&E						
	applications where the use of DecaBDE has been eliminated under the RoHS Directive						

Table 5-73: Conclusions on suitability and feasibility of RDP (CAS No. 57583-54-7; 125997-21-9)							
Category	Conclusion						
Economic feasibility	RDP may nowadays require lower loadings than DecaBDE and it appears to have a lower price per kg and it does not require the use of ATO, but requires a change to the resin (e.g. from HIPS to a blend). Literature has described these changes as "affordable". Substitution cost estimates in polymers vary and in PC/ABS a cost saving has been estimated. For PPO/HIPS, costs may range between €45 and 46 million per year or ca. €3,000/kg emissions avoided						
Overall conclusion	RDP's hazard profile raises concerns with regard to persistence, bioaccumulation,						
	degradation and aquatic toxicity, yet the substance appears to have been a successful replacement for DecaBDE in E&E polymer applications						

# 5.5.9 Alternative 9: Bisphenol-A bis(diphenyl phosphate) (BDP/BAPP) (CAS No. 5945-33-5; 181028-79-5)

# Technical feasibility issues

#### Relevant applications

BAPP is a mixture of three components: two components with bisphenol-A as a major constituent (>97%) and TPP (3%) (Department of Ecology State of Washington, 2008):

- Phosphoric acid, (1 -methylethylidene) di-4, 1-phenylene tetraphenyl ester (CAS No. 5945-33-5)
- Phosphoric acid, bis[4-[1-[4-[(diphenoxyphos-phinyl)oxy]phenyl]-1-methylethyl]phenyl] phenyl ester (CAS No. 83029-72-5)
- TPP (CAS No. 115-86-6).

There are several literature sources describing the applicability of BDP/BAPP as a FR. A summary is provided overleaf.

Table 5-74: Applications for bisphenol-A bis(diphenyl phosphate) (BDP/BAPP) (CAS No. 5945-33-5; 181028-79-5)										
Application	Material - substrate	Notes	Source							
Enclosures	PC/ABS, PPE/HIPS	Superior flammability performance and lower volatility than is obtainable with conventional triaryl phosphates	Danish EPA (2006)							
Transportation: Dashboard instruments, instrument panels, instrument cluster housing, speaker grilles, gear knobs, and other parts	ABS, PC/ABS		PINFA (2010b)							
Automotive foams	Not specified		PINFA (2010b)							
Automotive E&E components	PC/ABS (4:1)		PINFA (2010b)							
E&E – UL94V0	PC, PC/ABS, PPE/HIPS, TPU		Troitzsch (2011)							

Table 5-74: Applications for bisphenol-A bis(diphenyl phosphate) (BDP/BAPP) (CAS No. 5945-33-5; 181028-79-5)										
Application	Material - substrate	Notes	Source							
Wire & cable, E&E housings	HIPS, PC, PU		Arcadis & EBRC (2011)							
Textiles, furniture		Textiles is a niche application								
Flooring										
Electronics	PC, PC/ABS, PPE/HIPS		US EPA (2014)							

A comparison between the technical characteristics of BDP/BAPP and DecaBDE in polymer applications has been provided by a consultee and this is presented in detail in the Confidential Annex.

# Economic feasibility issues

#### Loading

Several literature sources refer to the loadings of BDP, as shown in **Table 5-75**.

Table 5-75: Loadings for bisphenol-A bis(diphenyl phosphate) (BDP/BAPP) (CAS No. 5945-33-5; 181028-79-5)									
Loading	Material	FR grade	Source						
10-14%	PC/ABS PPE/HIPS	V-0	Danish EPA (2006)						
12-13% (max.15%)	PPE/HIPS	V-0	Landa (2009)						
15-16%	PPE/PS		Takamura et al., (2013)						
12.3%	PC/ABS	V-0	PINFA (2010)						
14%	4:1 PC/ABS	V-0	Papazoglou (2004)						
9%	8:1 PC/ABS	V-0							
20%	PPE/HIPS	V-0							

Consultation suggests that the substance's loading does not differ to that of DecaBDE in PC/ABS and mPPE. It also does not require the presence of ATO.

#### Price issues

Information from the Alibaba.com online marketplace would suggest that BDP/BAPP may have a market price per kg ca. 50% lower than that of DecaBDE (see **Table 10-3**), but this is not supported by information from consultation. By way of comparison, HELCOM (2013) presents the price of bisphenol-A at €4.5/kg.

Some additional information on how investment and operating costs may change from a transition from DecaBDE to BDP/BAPP in polymer formulation is provided in the Confidential Annex. It can be disclosed that investment costs are an important consideration when comparing the affordability of the two substances.

#### Substitution cost calculations

The following table summarises the relevant information for BDP/BAPP, based on the analysis presented in Section 5.4.

Table 5-76: S	Table 5-76: Substitution cost calculations for BDP/BAPP (CAS No. 5945-33-5; 181028-79-5)										
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes							
Polymers	A1	Not relevant	Not relevant								
	B1	HFFR full: <50 million HFFR mix: <15 million	<2,100	BDP assumed to be a 'member' of the HFFR group							
	C1	PC/ABS: -7 million to +10 million PPO/HIPS: 42-48 million	PC/ABS: -<500 to +<10 PPO/HIPS: 2,8000-3,200								
	D1	Not relevant	Not relevant								
Textiles	A2	Not relevant	Not relevant								
	C2	Not relevant	Not relevant								

# Hazard profile

# REACH Registration and C&L data

The table that follows summarises the hazard profile of BDP/BAPP based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-77: REACH Registration data for BDP/BAPP (CAS No. 5945-33-5; 181028-79-5)									
Category	Parameter	BDP/BAPP	Notes						
Physical state		Liquid							
Classification for environmental	Acute hazards to the aquatic environment	N/A							
hazards	Long-term hazards to the aquatic environment	Aquatic Chronic 4 - H413 Aquatic Chronic 2 - H411	Registration dossier Self-notified (C&L Inventory)						
Classification for human health	Carcinogenicity  Mutagenicity	N/A N/A							
hazards	Reproductive toxicity Acute toxicity	N/A N/A							
	Irritation	N/A							
	Sensitisation Specific target organ toxicity	N/A N/A							
PBT assessment	Persistence	Inconclusive but registrant recommends no concern							
	Bioaccumulation	Not B							
	Toxicity	Not T							
	Conclusion	Not a PBT							

Table 5-77: REACH	Table 5-77: REACH Registration data for BDP/BAPP (CAS No. 5945-33-5; 181028-79-5)									
Category	Parameter	BDP/BAPP	Notes							
Key	Partition coefficient	≥6	Weight of Evidence							
physicochemical	Water solubility	ca. 0.415 mg/L (20 °C)								
properties	Vapour pressure	ca. 0.00000112 kPa (25 °C) estimated ca. 0.0775 kPa (50 °C) calculated								
Ecotoxicological	PNEC aqua (freshwater)	0.04 mg/L	AF: 10							
information	PNEC aqua (marine water)	0.004 mg/L	AF: 100							
	PNEC aqua (intermittent releases)	0.004 mg/L	AF: 100							
	PNEC STP	100 mg/L	AF: 10							
	PNEC sediment (freshwater)	29.6 mg/kg sediment dw	Extrapolation method: partition coefficient							
	PNEC sediment (marine water)	29.6 mg/kg sediment dw	Extrapolation method: partition coefficient							
	PNEC soil	10 mg/kg soil dw	AF: 100							
	PNEC oral predators	66.67 mg/kg food	AF: 300							

# Past PBT hazard assessments

The following table summarises information on the assessment of the PBT properties of BDP/BAPP. The substance does not meet the PBT criteria.

Table 5-78: PBT properties	Table 5-78: PBT properties of BDP/BAPP (CAS No. 5945-33-5; 181028-79-5)									
Persistence	Bioaccumulation	Toxicity	Source							
Persistent	Uncertain bioaccumulation. Reported log Kow between 4 and> 6	Has a low to moderate acute aquatic toxicity. Studies in rats have shown low acute and sub-chronic toxicity. A full assessment of the environmental and health effects is not possible due to limited data	(Keml, 2009)							
Half –life (T%) at pH 4.0 > 1 year @ 25 °C, T% at at pH 7.0 > 1 year @ 25 °C, T% at pH 9.0 > 1 year at 25 °C.  T <sub>1/2</sub> also reported to be between 1 day and 1 year	LogKow ≥ 6 at 25 ° C (measured). Experimentally derived LogKow = 4.5 with a calculated BCF = 3.16	Low acute toxicity (>2,000 mg/kg rat) Low subchronic toxicity NOAEL ca. 2,000 mg/kg; not mutagenic Ames test. No chronic bioassays	JRC (2007)							

The ENFIRO assessment of BDP/BAPP has concluded that the substance has low to high ecotoxicity and persistence, see also **Table 5-33**.

#### Other hazard assessments

judgement

The Arcadis & EBRC report for the European Commission includes an assessment of risks to human health from the consumer uses of BDP/BAPP. A number of scenarios were considered, including service life of clothes, PVC, flooring and furniture. First tier exposure assessments to BDP/BAPP have been performed using the ECETOC TRA Consumer tool with a simple refinement for a more plausible inhalation exposure assessment using the saturated vapour concentration. This tentative risk assessment using conservative exposure estimations showed a risk with respect to the dermal and oral exposure to textiles and the dermal exposure to PVC flooring and furniture. It was stated by industry that the latter two applications are not relevant for the domestic environment. Additionally, the use in textiles was confirmed as being a niche application. No risk was identified for the other applications and routes considered (Arcadis & EBRC, 2011).

In its recent assessment of alternatives to DecaBDE, the US EPA provided some information on the substance. This is summarised below. The table provides a summary of findings for the one parameter that has been marked of "moderate" concern. On the other hand, parameters of "high" concern are discussed in more detail after the table.

Table	Table 5-79: US EPA Assessment of BDP/BAPP (CAS No. 5945-33-5; 181028-79-5)													
	Human Health Effects									Aqı Toxi	uatic city <sup>**</sup>		ronme   Fate	
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive								Bioaccumulation			
L	М	L	L	L	L	L	L		L	L	L	L	Н	Н
Carcin	BDP/BAPP may have low potential for carcinogenicity based on expert judgment; there were no structural alerts in the molecule. However, there is uncertainty regarding the carcinogenicity of BDP/BAPP due to the lack of data for this substance. Carcinogenic effects cannot be completely ruled out							the						
VL =	Source: US EPA (2014)  VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard  Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black													

The assessment of the US EPA for those parameters that have been identified as being of "High" or "Very High" concern was as follows (US EPA, 2014):

italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional

• Persistence: experimental studies were on the commercial mixture, which is estimated to contain approximately 85% BAPP. BAPP is not readily biodegradable. In a Japanese Ministry of International Trade and Industry (MITI)-I (OECD Test TG 301C) test, 6% biodegradation occurred over 28 days in sewage sludge. BAPP does not contain chromophores that absorb at wavelengths >290 nm, and therefore is not expected to be susceptible to direct photolysis by sunlight. The atmospheric half-life of BAPP is estimated to be 5.5 hours, although it is expected to exist primarily in the particulate phase in air. Enzymatic or basic hydrolysis leading to the production of phenol (CAS No 108-95-2), diphenyl phosphate (CAS No 838-85-7), and bisphenol-

A (CAS No 80-05-1) through sequential dephosphorylation is theoretically possible but has not been demonstrated

Bioaccumulation: although measured BCF values for the components of the polymeric mixture
result in a Moderate bioaccumulation hazard designation, the overall bioaccumulation
designation for BAPP is high, based on an estimated BAF value. The estimated BAF of 1,100 for
the predominant component of the mixture with a MW <1,000 daltons suggests that BAPP may
bioaccumulate in higher trophic levels.</li>

Some further analysis has been provided in reports prepared by certain US States (Maine, Illinois and Washington). An assessment by the State of Maine concluded that BDP/BAPP was not a suitable alternative to DecaBDE because of its persistence and degradation to bisphenol-A. Similarly, Washington State did not recommend BDP/BAPP as a suitable alternative for DecaBDE over concerns about the endocrine disrupting effects of bisphenol-A as a breakdown product. A 2007 report by the Clean Production Action's Green Screen analysis of BDP/BAPP concluded it was a chemical of high concern due the high toxicity concern associated with bisphenol-A. Two of the constituents of the commercial BDP/BAPP product are reported by Clean Production Action as giving bisphenol-A and phenol as degradation products<sup>57</sup>, while diphenyl phosphate may also be formed. Bisphenol-A was noted for its potential endocrine disruption effect and its irritant properties, while phenol was suggested to raise concerns over systemic effects and irritation(Clean Production Action, 2007).

The US EPA also noted in its recent report that degradation of BAPP has been demonstrated in experimental studies. The importance of dephosphorylation relative to possible competing pathways has not been demonstrated in a published study. Therefore, the hazards of the theoretical degradation products were not considered in the latest US EPA hazard assessment (US EPA, 2014).

### Available monitoring data

No information has been obtained.

#### Conclusion on Alternative 9

The following table summarises the conclusions from the above information on the feasibility and suitability of BDP/BAPP as a replacement for DecaBDE.

Table 5-80: Conclusions on suitability and feasibility of BDP/BAPP (CAS No. 5945-33-5; 181028-79-5)				
Category	Conclusion			
Suitability	Environmental hazards: while BDP/BAPP does not meet all PBT criteria, significant concerns have been expressed on its degradation and the products of such degradation by dephosphorylation (namely, bisphenol-A and phenol). Although no conclusive research has been identified, some analyses by EU State and other organisations consider BDP/BAPP an unsuitable replacement for DecaBDE. In addition, a classification for chronic aquatic toxicity is suggested both in the registration dossier and the C&L Inventory  Human health hazards: no significant concen has been identified; the US EPA highlighted the lack of information on carcinogenicity			

Bisphenol A and phenol are described not only as degradation products but also as contaminants.

Table 5-80: Conclusi	Table 5-80: Conclusions on suitability and feasibility of BDP/BAPP (CAS No. 5945-33-5; 181028-79-5)				
Category	Conclusion				
Technical feasibility	BDP/BAPP appears to be feasible for replacing DecaBDE in plastic blends, with textiles being a niche application				
Economic feasibility	BDP/BAPP appears to be used at loadings similar to DecaBDE and its per kg price is assumed to be comparable to DecaBDE, but it does not require the use of ATO. However, its use may require a change to different resin and notable investment costs. Substitution cost estimates in polymers vary and in PC/ABS a cost saving or a modest cost of €10 million or <€10/kg emissions avoided can be estimated. For PPO/HIPS, costs may range between €43 and 48 million per year or €2,800-3,200/kg emissions avoided				
Overall conclusion	BDP/BAPP may not be a suitable replacement for DecaBDE due to its persistence, aquatic toxicity and potential degradation products. Its use in polymer applications may increase production costs				

# 5.5.10Alternative 10: Substituted amine phosphate mixture (P/N intumescent systems) (CAS No. 66034-17-1/Proprietary)

# Technical feasibility issues

#### Relevant applications

The commercial product is a mixture of piperazine pyrophosphate (diphosphoric acid compound with piperazine (1:1), CAS No. 66034-17-1) and a substituted amine phosphate with a proprietary CAS No. The substituted amine phosphate mixture comprises approximately 50% of piperazine pyrophosphate (US EPA, 2014). There are several literature sources describing the applicability of this mixture as a FR. A summary is provided below.

Table 5-81: Applications for substituted amine phosphate mixture (P/N intumescent systems) (CAS No. 66034-17-1/Proprietary)				
Application	Material - substrate	Source		
Wires & cables	PP, PE	Danish EPA (2006)		
Wires & cables	EPDM, PP, TPU, PE/EVA	PINFA (2010c)		
Unspecified solid thermoplastics	EVA copolymer, PP, PE, TPU, Rubber elastomers			
Unspecified thermosets	Epoxy resins, UPE, vinyl esters, acrylic resins			
Not specified	Textile backcoating, intumescent coatings, hot melts, latex adhesives			
E&E – UL94 V-0	PP, PE, Thermoplastic styrene-block copolymers (TPE-S)	Troitzsch (2011)		
Not specified	PP, PE, EVA copolymers, thermoplastic elastomers, UPE, EPDM, TPU, PE/EVA	UK HSE (2012)		
Electronics	Elastomers, PP, PE, TPU	US EPA (2014)		
Wires & cables	Elastomers, EVA, PP, PE, TPU			
Public buildings	Elastomers, EVA, PP, PE, TPU			
Construction materials	Elastomers, EVA, PP, PE, TPU			
Automotive	Elastomers, EVA, PP, PE, TPU			
Aviation	Elastomers, EVA, PP, PE, TPU			
Storage and distribution	Elastomers, PP, PE			

Consultation suggests that this alternative may find applications in (unspecified) polymers used in electronics (including the housing of electrical appliances), wire and cable, public buildings, construction materials, automotive, aviation, storage and distribution products. Consultation with a supplier (shown in the Confidential Annex) appears to suggest that the alternative may perform to a similar or better performance level as DecaBDE.

# Economic feasibility issues

#### Loading

Information from consultation suggests that in PE/PP the loading of this alternative may be 20-30% higher.

#### Price issues

Consultation suggests that this alternative has a price per kg higher than that of DecaBDE (but it does not require the presence of ATO). The overall price increase for the final article is estimated as considerable compared to DecaBDE-based articles. Certain operating costs are also likely to change, as described in the Confidential Annex.

#### Substitution cost calculations

The substance has not been included in the substitution costs calculations in Section 5.4.

#### Hazard profile

#### REACH Registration and C&L data

This product is a mixture of piperazine pyrophosphate and a substituted amine phosphate. Only for the former is a REACH registration available. Its limited contents are summarised below.

Table 5-82: REACH Registration data for diphosphoric acid compound with piperazine (CAS No. 66034-17-1)					
Category	Parameter	Diphosphoric acid compound with piperazine	Notes		
Physical state		Solid			
Classification for environmental	Acute hazards to the aquatic environment	N/A			
hazards	Long-term hazards to the aquatic environment	Aquatic Chronic 3 (H412)			
Classification for	Carcinogenicity	N/A			
human health	Mutagenicity	N/A			
hazards	Reproductive toxicity	N/A			
	Acute toxicity	N/A			
	Irritation	Eye Irrit. 2 H319: Causes serious eye irritation			
	Sensitisation	N/A			
	Specific target organ toxicity	N/A			

Table 5-82: REACH	Table 5-82: REACH Registration data for diphosphoric acid compound with piperazine (CAS No. 66034-1					
Category	Parameter	Diphosphoric acid	Notes			
		compound with piperazine				
PBT assessment	Persistence	No PBT assessment made	A test under OECD 301D showed that the substance is not readily biodegradable			
	Bioaccumulation	No PBT assessment made				
	Toxicity	No PBT assessment made				
	Conclusion	No PBT assessment made				
Key physicochemical properties	Partition coefficient	Could not be determined	A buffer with a pH of 10.83 or 0.52 is needed to un-dissociate piperazine or pyrophosphate. When using these high or low buffers the ion-ration in the solution is so much disturbed, that the buffer will not be able to produce the non-ionized form of the test substance. Buffer solutions which have to buffer at these high or low pH's are also difficult to prepare			
	Water solubility	12.24 ± 0.16 g/L at 20 °C ± 0.5 °C				
	Vapour pressure	< 0.000006 Pa at 25 °C				
Ecotoxicological	Vapour pressure PNEC aqua (freshwater)	< 0.000006 Pa at 25 °C  No values given	Available study results:			
information	PNEC aqua (marine water) PNEC aqua (intermittent releases) PNEC STP PNEC sediment (freshwater) PNEC sediment (marine water) PNEC soil		Zebrafish 96h-LC <sub>50</sub> = >100 mg/L Daphnia magna 48h-EC <sub>50</sub> = 42 mg/L Algae ErC <sub>50</sub> = 93 mg/L Microorganisms NOEC = 100 mg/L			
	PNEC oral predators					

# Past PBT hazard assessments

No PBT assessments have been identified in the literature.

#### Other hazard assessments

In its recent assessment of alternatives to DecaBDE, the US EPA provided some information on this FR. This is summarised below. The table provides a summary of findings for those parameters that have been marked as being of "moderate" concern. On the other hand, parameters of "high" concern are discussed in more detail after the table.

	Table 5-83: US EPA Assessment of substituted amine phosphate mixture (P/N intumescent systems) (CAS No. 66034-17-1/Proprietary)													
Human Health Effects							_	Aquatic Toxicity**		onme Fate				
										TOAL	leity	IItaii	ate	
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitisation	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
Н	М	М	М	М	L	М	L	М	M	VL	М	L	Н	L
	nogenic		The carcinogenicity hazard potential for the substituted amine phosphate mixture is estimated to be "moderate" based on the substituted amine phosphate component. There is evidence that oral exposure to the substituted amine phosphate component causes carcinogenicity in experimental animals. However, there is no evidence located as to the substituted amine phosphate component's carcinogenicity to humans. Tumour formation in animals appeared to happen in a mechanical nature under conditions in which it produced bladder calculi. No data were located as to the carcinogenic potential of the substituted amine phosphate mixture or salts. The International Agency for Research on Cancer (IARC) classifies the substituted amine phosphate component as <i>Group 3: not classifiable as to its carcinogenicity to humans</i> Estimated based on positive results for chromosomal aberrations <i>in vivo</i> in mice exposed to the substituted amine phosphate component and positive results for gene mutations following <i>in vitro</i> exposure to the piperazine component in mouse lymphoma assays. There were also positive results <i>in vitro</i> for DNA synthesis-inhibition in Hela S3 cell and genetic toxicity in Escherichia coli WP2s in a microscreen assay following exposure to the substituted amine phosphate component. No data were located for the substituted											
Repro	ductive	2	amine phosphate mixture salts regarding the genotoxicity endpoint  Hazard potential for reproductive toxicity of the substituted amine phosphate mixture is estimated to be "moderate" based on data for the piperazine moiety from piperazine dihydrochloride; rats exposed to 300 mg/kg/day had decreased litter size in both generations. The NOAEL is identified at 125 mg/kg/day; there is uncertainly if effects could occur at doses between 125 and 250 mg/kg/day (the criteria cut-off dose for a Low hazard designation is >250 mg/kg/day). There were no adequate reproductive toxicity data located for the substituted amine phosphate mixture or substituted amine phosphate component of the mixture											
Devel	opmen	tal	Hazard potential for developmental toxicity of the substituted amine phosphate mixture is estimated to be "moderate" based on data for piperazine moiety from piperazine phosphate and professional judgement. There is uncertainty if effects could occur at doses between 94 and 250 mg/kg/day because a LOAEL was not identified (the criteria cut-off dose for a Low hazard designation is >250 mg/kg/day). Embryotoxicity was reported in conjunction with maternal toxicity and was considered to be a secondary effect. Data for the substituted amine phosphate component showed no developmental effects in rats exposed during gestation to doses up to 1,060 mg/kg-day. A conservative approach was used since there were no measured values for the substituted amine											
Repea	ated do	se	Repeat based of compositiones	phosphate mixture  Repeated dose effects from the substituted amine phosphate mixture is estimated based on effects following repeated oral exposure to the substituted amine phosphate component in rats. Decreased body weight gain and feed consumption along with stones and diffuse epithelial hyperplasia in the urinary bladder were reported at a dose of 72 mg/kg/day. No data were located for the substituted amine phosphate							sphate g with			

	Table 5-83: US EPA Assessment of substituted amine phosphate mixture (P/N intumescent systems) (CAS No. 66034-17-1/Proprietary)					
Respiratory sensitisation	Respiratory sensitisation hazard potential for the substituted amine phosphate mixture is estimated to be "moderate" based on analogy to the piperazine-containing compounds					
Eye irritation	Based on indications of mild to moderate eye irritation in rabbits for both the substituted amine phosphate and piperazine pyrophosphate components of the mixture. In addition, eye irritation hazard due to the substituted amine phosphate mixture is estimated to be "moderate" based on data for a confidential analogue showing eye irritation in rabbits					
Acute aq. toxicity	Acute toxicity hazard for the substituted amine phosphate mixture is estimated based on an experimental LC <sub>50</sub> value of 21 mg/L in Daphnia magna for the piperazine moiety of the ionised mixture which represents the most conservative value. Although measured toxicity values for the substituted amine phosphate free base indicate a Low hazard designation for this component of the mixture, a conservative approach was used since there are no measured values for the substituted amine phosphate mixture					

Source: US EPA (2014)

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

The assessment of the US EPA for those parameters that have been identified as being of "High" or "Very High" concern is as follows (US EPA, 2014):

- Acute mammalian toxicity: using a conservative approach, acute toxicity hazard potential for
  the substituted amine phosphate mixture is estimated based on toxicity for inhalation exposure
  to the piperazine moiety in rats. The hazard is estimated to be low for oral and dermal routes of
  exposure to the substituted amine phosphate and piperazine components of the mixture
- **Persistence**: the substituted amine phosphate mixture is estimated to show high persistence in the environment based on experimental data for the organic components. The persistence of the inorganic phosphate components of this mixture were not considered a factor in the assignment of this hazard designation. The organic component of the confidential substituted amine phosphate undergoes biodegradation according to measured results; however, the rates of removal are slow. The organic portion of the substituted amine phosphate component is considered inherently biodegradable, not readily biodegradable.

#### Available monitoring data

No information has been retrieved.

#### **Conclusion on Alternative 10**

The following table summarises the conclusions from the above information on the feasibility and suitability of the substitute amine phosphate mixture as a replacement for DecaBDE.

Table 5-84: Conclusions on suitability and feasibility of substituted amine phosphate mixture (P/N intumescent systems) (CAS No. 66034-17-1/Proprietary)					
Category	Conclusion				
Suitability	<b>Environmental hazards</b> : the very limited information available does not highlight any areas of concern with the exception of persistence based on experimental data for the organic components <b>Human health hazards</b> : some concern on the acute toxicity of the substituted amine phosphate mixture has been raised by the US EPA. "Moderate" concern was also raised for carcinogenicity (based on the substituted amine phosphate component), genotoxicity (based on both components), reproductive effects (based on piperazine), developmental effects (based on piperazine), repeated dose effects (based on the substituted amine phosphate component), respiratory sensitisation (based on the substituted amine phosphate component), and eye irritation (based on both components)				
Technical feasibility	Suitable for polymer applications in a variety of areas; example resins include elastomers, EVA, PP, PE and TPU				
Economic	Higher loadings and price per kg combined with changes to operating costs. It does not				
feasibility	require the use of ATO				
Overall conclusion	Limited information on hazards and increased production costs for polymer applications				

# 5.5.11Alternative 11: Red phosphorous (CAS No. 7723-14-0)

# Technical feasibility issues

Relevant applications

There are several literature sources describing the applicability of red phosphorous as a FR. A summary is provided below.

Table 5-85: Applications for red phosphorous (CAS No. 7723-14-0)				
Application	Material - substrate	Source		
Automotive textiles	Cotton-based and cotton-rich textiles	RPA (2003)		
Unspecified	PE/PP, PS, PVC, ABS, UPR, Epoxy, PU	Keml (2005)		
Connectors	PA	Danish EPA (2006)		
Wires	PE	1		
Unspecified	PP/PE, PS, PVC, ABS, PA, PC, SAN, UPR, Epoxy, PU, rubber	KemI (2009)		
Transportation insulation materials	PIR	PINFA (2010b)		
Sealants (flame-retardant and/or fire-resistant)	PUR, acrylics, epoxy, elastomers, PVC			
Cables	Used in fire-resistant coatings for cables			
	Polyolefins			
	Elastomers			
	Thermoplastic Elastomers (TPE) Polypropylene (PP)			

Table 5-85: Applications for red phosphorous (CAS No. 7723-14-0)				
Application	Material - substrate	Source		
E&E components	PA 6,6 + glass fibre			
E&E – UL94V0	PE, PET, epoxy resins	Troitzsch (2011)		
Unspecified	PA, PE	UK HSE (2012)		
Semi-durable finishes	Cotton, polyester	EFRA (2012)		
Electronics	Epoxy, PA, PA6,6 GF, PP	US EPA (2014)		
Wires & cables	Elastomers, PA, PP			
Automotive	Emulsions, epoxy resins			
Aviation	Epoxy resins, PA			
Waterborne emulsions	Emulsions, epoxy resins			
and coatings				
Small parts for electronic	PBTE, PET, PA	German MSCA		
appliances				

Red phosphorous is an active FR as a single additive in nitrogen and/or oxygen-containing polymers, such as polyamides (particularly glass-filled PA), polyesters, polyurethanes, epoxies, polyisocyanates, polycarbonates and ethylene-vinyl acetate, while it has to be applied with spumific and carbonific agents and/or with inorganic hydroxides in polyolefins, styrenics and rubbers. Its use is restricted on due to colour issues – it cannot be used for white or light coloured final articles but is widely applicable for items from black to medium grey (Gatti, 2002).

Another drawback of the use of red phosphorus is the formation of toxic phosphine gas during combustion and long-term storage (SFT, 2009). Precautions against degradation have to be taken (PINFA, 2010). The disproportionation of red phosphorus to phosphine and phosphoric acids occurs in the presence of moisture at elevated temperatures. Significant disproportionation can only take place in the injection moulding process if the residual moisture content in the polymer is too high (Uske & Ebenau, 2013). Industry claims that phosphine is very reactive and is readily oxidised in the environment, leading to the production of harmless phosphates (Gatti, 2002). Improved techniques in the production process and increased expertise in compounding red phosphorous means that phosphine problems may be controlled (Gatti, 2002). For example, efficient pre-drying can be used as a counter-measure (Uske & Ebenau, 2013).

The red phosphorous market has been historically limited mainly because of product flammability and has been regulated as potentially hazardous material in transportation, feeding and processing. In order to improve the safe handling of red phosphorous powder at the workplace, it is usual to stabilise it, microencapsulate the surface with thermoset resins, and add dust suppressant agents. However, even when stabilised and coated, red phosphorous powder is still flammable and always represents a hazard in handling and transportation. Consequently, the safest and most convenient way of handling and processing red phosphorous is the use of concentrates/masterbatches in a wide range of polymers (Gatti, 2002).

#### **Economic feasibility issues**

### Loading

Red phosphorous is the most concentrated source of phosphorus; therefore, it is an effective FR additive at a concentration ranging from 2-10% by weight (Gatti, 2002).

In glass fibre reinforced PA 6,6, red phosphorous is used at 5 to 8% addition level, where its high efficiency at low loading guarantees to maintain the excellent mechanical and electrical properties of the polymer while obtaining the highest flame-proofing characteristics (PINFA, 2010).

Table 5-86: Red phosphorous loadings in different polymers					
Material Red phosphorous content for UL-94 V-0 ra					
PC	1.2%				
PET	3%				
Filled phenolic resin	3%				
PA	7%				
PE 10%					
PS	15%				
Source: Papazoglou (2004)					

#### Price issues

Information from the Alibaba.com online marketplace would suggest that red phosphorous might have a price per kg that is ca. 20% lower than DecaBDE's (see **Table 10-3**). Additional information from consultation is not available. The substance does not require the use of ATO.

#### Substitution cost calculations

The following table summarises the relevant information for red phosphorous, based on the analysis presented in Section 5.4.

Table 5-87: Substitution cost calculations for red phosphorous (CAS No. 7723-14-0)						
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)	Notes		
Polymers	A1	Not relevant	Not relevant			
	B1	HFFR full: <50 million HFFR mix: <15 million	<2,100	Red phosphorous assumed to be a 'member' of the HFFR group		
	C1	PA: -11 to -13 million	PA: -700 to -850			
	D1	Not relevant	Not relevant			
Textiles	A2	Not relevant	Not relevant			
	C2	Not relevant	Not relevant			

# Hazard profile

# REACH Registration and C&L data

The table that follows summarises the hazard profile of red phosphorous based on information from the ECHA Dissemination Portal and the C&L Inventory.

Table 5-88: REACH Registration data for red phosphorous (CAS No. 7723-14-0)			
Category	Parameter	Red phosphorous	Notes
Physical state		Solid	
Classification for environmental hazards	Acute hazards to the aquatic environment	N/A	
	Long-term hazards to the aquatic environment	Aquatic Chronic 3 - H412	
Classification for human health hazards	Carcinogenicity	N/A	
	Mutagenicity	N/A	
	Reproductive toxicity	N/A	
	Acute toxicity	N/A	
	Irritation	N/A	
	Sensitisation	N/A	
	Specific target organ toxicity	N/A	
Classification for physicochemical hazards	Physicochemical hazards	Flam. Sol. 1 - H228	Harmonised classification
PBT assessment	Persistence	Р	
	Bioaccumulation	Not B	
	Toxicity	Not T	
	Conclusion	Not a PBT	
Key	Partition coefficient	Not relevant	
physicochemical	Water solubility	< 0.3 mg/L (20 °C)	
properties	Vapour pressure	Very low	
Ecotoxicological information	PNEC aqua (freshwater)	10.5 μg/L	AF: 1000
	PNEC aqua (marine water)	1.05 μg/L	AF: 10000
	PNEC aqua (intermittent releases)	105 μg/L	AF: 100
	PNEC STP	10 mg/L	AF: 100
	PNEC sediment (freshwater)	100 mg/kg sediment dw	AF: 10
	PNEC sediment (marine water)	10 mg/kg sediment dw	AF: 100
	PNEC soil	12.5 mg/kg soil dw	AF: 10

### Past PBT hazard assessments

The following table summarises information on the assessment of the PBT properties of red phosphorous. The substance does not meet the PBT criteria.

Table 5-89: PBT properties of red phosphorous (CAS No. 7723-14-0)					
Persistence	Bioaccumulation	Toxicity	Source		
Red phosphorus is an inorganic compound, and biodegradation is thus not a relevant parameter. Based on experimental determination of hydrolysis products of red phosphorus the substance is considered to meet the persistent (P) and very persistent (vP) criteria	No data describing bioaccumulation of red phosphorus are available	Based on the available data, red phosphorus does not meet the T criteria at a screening level, as the lowest L(E)C <sub>50</sub> value reported is 0.63 mg/L ( <i>Daphnia magna</i> , measured concentrations of total P), but further data are required for assessment of the T criterion	Danish EPA in JRC (2007)		

#### Other hazard assessments

The German Federal Environmental Agency (Umweltbundesamt) published a study in 2001 in which red phosphorous was one of 13 FRs assessed. The study described red phosphorous as unproblematic on the basis of environmentally relevant properties (toxicity and ecotoxicity data), main applications (including electrical and electronic, such as insulation, printed circuit boards and enclosures for electrical appliances, as well as textiles for upholstered furniture), and the conditions of use of the polymer articles<sup>58</sup>.

In its recent assessment of alternatives to DecaBDE, the US EPA provided some information on the substance. This is summarised in the table overleaf. The table provides a summary of findings for those parameters that have been marked of "moderate" concern. On the other hand, the one parameter of "high" concern is discussed in more detail separately.

The assessment of the US EPA for the parameter that has been identified as being of "High" or "Very High" concern is as follows (US EPA, 2014):

• **Persistence**: red phosphorus is estimated to display high persistence in the environment. Elemental red phosphorous is relatively non-reactive under typical environmental conditions. Measured data indicate that red phosphorous will slowly undergo hydrolysis under environmental conditions (<3% in 4 months) and will eventually convert to phosphine and hypophosphorous acid. Subsequent oxidation of these hydrolysis products will lead to the formation of phosphoric oxides and acids.

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Available at <a href="http://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/1988.pdf">http://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/1988.pdf</a> (accessed on 7 February 2014).

Table	Table 5-90: US EPA Assessment of red phosphorous (CAS No. 7723-14-0)													
	Human Health Effects					Aquatic Toxicity**		Envir ntal I	onme Fate					
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Reproductive Developmental Neurological Skin Sensitization Sensitization Eye Irritation Chronic Chronic Bioaccumulation						Bioaccumulation				
L	L	М	L	L	L	L	L	No data	M	M	L	L	Н	L
Genot	Genotoxicity  Uncertain potential for mutagenicity based on expert judgement. There is a lack of gene mutation data, genotoxic effects cannot be ruled out. Negative results for both chromosomal aberrations and gene mutation assays are required for a categorisation of "low"													
Eye ir	Exposure to red phosphorus may cause corneal injury													
	al irrita	tion PA (201	not a sk			n red ph nea pigs	•	s may c	ause sl	kin irrit	tation.	Red ph	osphori	us was

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

Information available from the New Zealand Environmental Protection Agency suggests potential hepatotoxicity from oral exposure to the substance (New Zealand Environmental Protection Agency, undated). Rabbits and guinea pigs were not killed by a dosage of 0.66 mg/kg/day but they developed a cirrhosis-like condition. Additionally, the same source refers to a 42-h test in Daphnia magna with a NOEC of 6.9 µg/L, which would support a classification as Aquatic Chronic 1 (as opposed to Aquatic Chronic 3, shown in the registration data).

#### Other hazard information

Notably, red phosphorous is often contaminated with yellow and white phosphorus, which are considerably more toxic forms of phosphorus (Keml, 2009).

#### Conclusion on Alternative 11

The following table summarises the conclusions from the above information on the feasibility and suitability of red phosphorous as a replacement for DecaBDE.

Table 5-91: Conclusions on suitability and feasibility of red phosphorous (CAS No. 7723-14-0)				
Category	Conclusion			
Suitability	Environmental hazards: red phosphorous may be considered persistent in the environment but as an inorganic compound cannot be subject to the PBT criteria. It is accompanied by an Aquatic Chronic 3 classification (but test data could suggest a more severe classification might be warranted)  Human health hazards: with the exception of irritant properties and some uncertainty over genotoxicity and hepatoxicity, no significant concerns for human health appear to			

Table 5-91: Conclusions on suitability and feasibility of red phosphorous (CAS No. 7723-14-0)			
Category	Conclusion		
	exist. Its physico-chemical hazards and the risk of disproportionation products are reduced through encapsulation and stabilisation		
Technical feasibility	Suitable for polymer applications (PA, PE/PP, Epoxy, etc.) in dark colours and semi-		
	durable finishes on cotton-rich textiles, generally unsuitable for man-made fibres		
Economic	Limited information available indicates lower loadings and lower per kg price than		
feasibility	DecaBDE. It does not require the use of ATO.		
	Substitution cost estimates in PA indicate a potential cost saving		
Overall conclusion	Generally of limited concern as regards hazards; its strong FR properties make it		
	suitable for a number of specific applications		

# 5.5.12Alternative 12: Ethane-1,2-bis(pentabromophenyl) (EBP) (CAS No. 84852-53-9)

## Technical feasibility issues

Relevant applications

There are several literature sources describing the applicability of EBP as a FR. A summary is provided below.

Table 5-92: Applications f	Table 5-92: Applications for ethane-1,2-bis(pentabromophenyl) (EBP) (CAS No. 84852-53-9)					
Application	Material - substrate	Notes	Source			
Enclosures	HIPS, ABS, PC/ABS, PPE/HIPS	EBP is claimed to	Danish EPA (2006)			
Connectors	PA, PBTE/PET	have better				
Wires	PP, PE	bloom resistance, UV stability and physical properties				
E&E – UL94V0	PE, PP, HIPS, ABS, PET, PBTE, PC, PC/ABS, PPE/HIPS, Epoxy resins, Unsaturated polyester resins (UP), Thermoplastic styreneblock copolymers (TPE-S) Thermoplastic polyurethanes (TPU) Thermopolyolefins (TPO)		Troitzsch (2011)			
Wires and cables – VW 1	Thermoplastic polyester elastomers (TPE-E)					
Not specified	ABS, HIPS, PA, PBTE/PET, PC, PP, PE, SAN, PC/ABS, HIPS/PPO, thermoplastic elastomers, silicone, PVC, EPDM, TPU, PE/EVA, thermosets (epoxy and phenolic resins, unsaturated polyesters)		UK HSE (2012)			
Thermoplastics	ABS, HIPS, PA, Polyester, PC, PP, PE/copolymer, SAN, PC/ABS, PPO/HIPS, Elastomers, PVC		Albemarle (2013)			
Foams	Polyolefin, PVC/Nitrile, Elastomers					

Table 5-92: Applications for ethane-1,2-bis(pentabromophenyl) (EBP) (CAS No. 84852-53-9)						
Application	Material - substrate	Notes	Source			
Wire & cable	Silicone, EPDM, PP, PE/EVA,					
	TPU, PVC					
Thermosets	Epoxy, phenolic, UPR, vinyl					
	esters, PU/CASE, latex					
Adhesives, sealants and			Chemtura (2013)			
coatings						
Automotive						
Aviation						
Public, mass transit						
Wire and cable						
Roofing membrane and						
flooring						
Textile backcoating						
HIPS, PE, PP, ABS,		FR efficiency,	ICL Industrial Products			
PBTE, UPE, Epoxy, Nylon		exceptional	(2013b)			
6, Textiles		thermal stability				
El	005 00 05 51	and multi-purpose	110 504 (2044)			
Electronics	CPE, PP, PE, Elastomers, HIPS,		US EPA (2014)			
	Engineering thermoplastics,					
	thermosets					
Wire & cable	CPE, PP, PE, Elastomers,					
5 L II L II II	Engineering thermoplastics					
Public buildings	Elastomers, PE, thermosets					
Construction materials	Elastomers, PP, thermosets					
Automotive	Elastomers, engineering					
	thermoplastics, PP, PE					
Storage and distribution	Elastomers, PP, PE					
products						
Textiles	Emulsions					
Waterborne emulsions	CPE, emulsions, engineering					
and coatings	thermoplastics					

According to consultation, EBP is being marketed as a direct "drop-in" replacement for DecaBDE. One supplier of the substance confirmed that it can be used in a wide variety of plastics, including thermoplastics (HIPS, ABS, polyolefins, TPU, polyesters (PBTE), PA), thermosets and in coatings. Available information shows that technical parameters, such as strength properties and flame resistance performance (LOI), are very similar and can be achieved with the same loading. ATO is still used at the same loading as well. An example is its application in technical textiles where EBP may act as a replacement for DecaBDE without process changes and with the same FR performance, as shown in the Confidential Annex.

The assertion that EBP is becoming/will become the main replacement for DecaBDE has also been supported by information provided during consultation by the US EPA and Environment Canada (US EPA, 2014b) (Environment Canada, 2014), as discussed in Section 5.3.3.

## Economic feasibility issues

### Loading

The following table replicates information presented by the Danish EPA on the relative loading of DecaBDE and EBP in different matrices. This information suggests that the two substances require identical loading (including the loading of the ATO synergist).

Table 5-93: EBP loading rates in different matrices					
Material/Fire	DecaBDE content	ATO content	EBP content	ATO content	
rating					
HIPS V-0	12-13%	4-5%	12-13%	4-5%	
PBTE V-0	10.4%	4%	10.4%	4%	
PA V-0	16-18%	6-7%	16-18%	6-7%	
ABS V-0	13-15%	5%	N/A	N/A	
Polyolefins V-0	20-30%	6-10%	20-30%	6-10%	
Source: Danish EPA	A (2006)				

#### Price issues

Information from the Alibaba.com online marketplace would suggest that EBP might have a price per kg which is ca. 20% higher than that of DecaBDE (see **Table 10-3**). Consultation would appear to be in some agreement with this estimate. A price difference of 5-20% has been suggested which, based on an assumed price for DecaBDE of €4/kg, would mean that EBP may cost €4.2-4.8/kg.

#### Substitution cost calculations

The following table summarises the relevant information for EBP, based on the analysis presented in Section 5.4.

Table 5-94: Substitution cost calculations for EBP (CAS No. 84852-53-9)					
Application area	Approach	Substitution cost (€/y)	Cost per kg DecaBDE emission avoided (€/kg)		
Polymers	A1	<1 million	<50		
	B1	EBP full: <1 million EBP mix: <1 million	<40		
	C1 HIPS: <1 to 3 million		HIPS: <50 to <200		
	D1	Not estimated per alternative substance	Not estimated per alternative substance		
Textiles	A2	<1 million	<50		
	C2	Full: <1 million Mix: <0.5 million	<50		

## Hazard profile

## REACH Registration and C&L data

**Important note**: The substance is included in the CoRAP and is currently undergoing evaluation by the UK authorities. This process is expected to generate additional information on the hazard profile of the substance. In the meantime, a manufacturer of the substance has generated information, some of which has been shared with the study team. This is presented here without prejudice to the outcome of the substance evaluation process and without claiming that the information shown is complete.

The table that follows summarises the hazard profile of EBP based on information from the ECHA Dissemination Portal and the C&L Inventory and informed by submissions made to the study team by a manufacturer of the substance.

Table 5-95: REACH	HRegistration data for EBP (	CAS No. 84852-53-9)	
Category	Parameter	EBP	Notes/Source
Physical state		Solid	
-	Acute hazards to the aquatic environment	Not classified	(Albemarle, 2013b)
Classification for environmental hazards	Long-term hazards to the aquatic environment	Not classified in registration dossier  Aquatic Chronic 4 - H413 in C&L Inventory	Registration dossier  Self-notified (C&L Inventory)
	Carcinogenicity	Not classified	(Albemarle, 2013b)
	Mutagenicity	Not classified	(Albemarle, 2013b)
Classification for	Reproductive toxicity	Not classified	(Albemarle, 2013b)
human health	Acute toxicity	Not classified	(Albemarle, 2013b)
hazards	Irritation	Not classified	(Albemarle, 2013b)
liazarus	Sensitisation	Not classified	(Albemarle, 2013b)
	Specific target organ toxicity	Not classified	(Albemarle, 2013b)
PBT assessment	Persistence	vP Biodegradation testing to date indicates EBP is not readily biodegradable over 28 d (METI test), does not undergo aerobic degradation by a mixture of soil/sludge over 90 d or anaerobic biodegradation by digester sludge over 60 days. The later 2 tests were performed with 14C-EBP and both specific and nonspecific measures of degradation were evaluated. No evidence of metabolites was observed in radiometric chromatograms of the matrixes; 14C-label was detected in one peak, which had the retention time of the parent EBP molecule.	EBP is considered very persistent and there is at present no evidence for any degradation involving formation of degradation products (Albemarle, 2013b)

Table 5-95: REACH	HRegistration data for EBP (	CAS No. 84852-53-9)	
Category	Parameter	ЕВР	Notes/Source
		EBP is not expected to undergo abiotic degradation based on its structure, and its negligible water solubility and vapour pressures and high binding to particulates indicate abiotic degradation would not be a significant route of environmental degradation. Further soil and sediment degradation studies were planned and will be performed during the REACH substance evaluation process	
	Bioaccumulation	Not B	Based on weight of evidence, inter alia: Measured LogKow = 3.55 low octanol solubility: 0.85 mg/L( <0.002 mM/L) (MW 972), BCF lower than 2000 (estimated from a study with limited reliability), toxicokinetic data in mammals indicating negligible absorption. No effects in several repeated dose studies at the limit dose of 1000 mg/kg bw/d (see box below). (Albemarle, 2013b)
	Toxicity	Not considered as fulfilling the T criterion of Annex XII, EC <sub>10</sub> / NOEC ≥ 0.01 mg/L for marine / freshwater organisms (long-term toxicity): EBP is not acutely toxic to 3 freshwater species (fish, daphnia, algae) at the limits of its water solubility. These studies, conducted via the Water Accommodated Fraction method indicate no effects at a load rate of 110 mg/L. An 8-wk fish bioconcentration study performed at concentrations in excess of its water solubility showed no toxicity. Chronic sediment organism toxicity tests in 2 species had NOELs of 5000 mg/kg dry sediment. Thus, EBP is not T.	(Albemarle, 2013b)

Table 5-95: REACH	I Registration data for EBP (	CAS No. 84852-53-9)	
Category	Parameter	ЕВР	Notes/Source
		Substance is not classified as carcinogenic (category 1 or 2), mutagenic (category 1 or 2), or toxic for reproduction (category 1, 2 or 3) according to Directive 67/548/EEC (or the DSD) or carcinogenic (category 1A or 1B), germ cell mutagenic (category 1A or 1B), or toxic for reproduction (category 1A, 1B or 2) according to Regulation EC No 1272/2008 (or CLP Regulation). No other evidence of chronic toxicity, as identified by the classifications: T, R48, or Xn, R48 according to Directive 67/548/EEC or specific target organ toxicity after repeated exposure (STOT RE category 1 or 2) according to Regulation EC No	
	Conclusion	1272/2008 Not a PBT or vPvB	(Albemarle, 2013b)
Кеу	Partition coefficient	3.55 measured by generator column method, Calculated values vary between 7.8 and 14	(Albemarle, 2013b) (Environment Agency, 2007)
physicochemical properties	Water solubility	0.54-0.72 μg/L at 25 °C	(Albemarle, 2013b) (Environment Agency, 2007)
	Vapour pressure	< 0.0001 Pa (20 °C)	(Albemarle, 2013b)
	PNEC aqua (freshwater)	No effects were observed at the solubility limit. Therefore, no meaningful PNEC values can be derived. A further study will be performed following the substance evaluation under REACH	(Albemarle, 2013b) (Environment Agency, 2007)
Ecotoxicological	PNEC aqua (marine water)	No effects were observed at the solubility limit. Therefore, no meaningful PNEC values can be derived	
information	PNEC aqua (intermittent releases)	No effects were observed at the solubility limit. Therefore, no meaningful PNEC values can be derived	
	PNEC STP	≥1mg/L*	AF: 10 (Albemarle, 2013b)
	PNEC sediment (freshwater)	≥100 mg/kg sediment dw**	AF: 50 (Albemarle, 2013b) (Environment Agency, 2007)

Table 5-95: REACH Registration data for EBP (CAS No. 84852-53-9)					
Category	Parameter	EBP	Notes/Source		
			AF: 500		
	PNEC sediment (marine	≥10 mg/kg sediment dw***	(Albemarle, 2013b)		
	water)	210 mg/kg sediment dw · · ·	(Environment Agency,		
			2007)		
	PNEC soil	≥ 156 mg/kg soil dw†	AF: 10		
	FINEC SUII	2 130 Hig/kg Soli UW1	(Albemarle, 2013b)		
	PNEC oral predators	≥ 222 mg/kg food††	(Albemarle, 2013b)		

<sup>\*</sup> information provided by industry: "For deriving the PNEC STP, the REACH Guidance indicates a test for nitrification inhibition is more sensitive than respiration inhibition. An assessment factor of 1 is applied to an NOEC. A soil nitrification inhibition test determined a NOEC of 2,500 mg/kg (AF=1). An STP respiration inhibition test determined an NOEC of 10 mg/kg dry sludge, the highest dose tested (AF=10). The PNEC STP derived from the soil nitrification inhibition NOEC is 2,500 mg/kg while the PNEC STP derived from the respiration inhibition NOEC is 1 mg/kg" (Albemarle, 2014b)

- \*\* information provided by industry: "Two long-term toxicity tests have been performed with freshwater sediment-dwelling organisms. No statistically significant effects were observed with either Chironomus or Lumbriculus at the highest concentrations tested (5000 mg/kg dry weight in both cases). The PNEC sediment is therefore ≥ 100 mg/kg dry weight, based on this unbounded NOEC and an assessment factor of 50" (Albemarle, 2014b)
- \*\*\* information provided by industry: "The PNEC marine sediment was calculated as recommended by the REACH Guidance. An assessment factor of 500 was applied to the results from 2 long-term freshwater sediments. Thus, the PNEC marine sediment was 5000/500 = 100 mg/kg dw" (Albemarle, 2014b)
- $\dagger$  information provided by industry: "The REACH Guidance states that when deriving a PNEC SOIL, the applied assessment factors (AFs) range from a factor of 1 to 1,000. The choice of AF depends on the level of information available. Since EBP was evaluated using three species from three trophic levels, a 10-fold AF was applied to the lowest NOEC that is, the height and dry weight NOEC of 1,563 mg/kg soil (dw) identified with onions. PNEC SOIL = 1,563 mg/kg  $\div$  10 AF = 156.3 mg/kg soil (dw)" (Albemarle, 2014b)
- †† information provided by industry: "EBP has a low potential for bioaccumulation based on its pharmacokinetics, measured properties, and reports in the literature. Further, test data from multiple repeated dose studies indicates low potential for toxic effects even if bioaccumulation were to occur. Therefore, a PNEC-oral for secondary poisoning is not needed. However, a PNEC-oral was calculated for illustrative purposes. The PNEC-oral was calculated using the REACH Guidance and based on a rat oral 90-d NOAEL of 1000 mg/kg bw/d. The NOEC mammal-food-chronic of 0.02 kg/kg bw/d was derived by multiplying the rat 90-d NOAEL (0.001 kg/kg bw/d) by the conversion factor (20) given for rats > 6 weeks of age. This value was converted to the PNEC-oral by dividing by the assessment factor of 90 (based on a study of 90 d duration). The PNEC-oral was 222 mg/kg food" (Albemarle, 2014b)

## Past PBT Hazard assessments

The following table summarises information on the assessment of the PBT properties of EBP. The substance does not meet the PBT criteria but there are still uncertainties over its PBT characteristics.

Table 5-96: PBT properties of EBP (CAS No. 84852-53-9)							
Persistence	Bioaccumulation	Toxicity	Source				
Found in increasing concentrations in the environment	The criterion is not fulfilled (reported BCF values <200)	Studies in rats and rabbits indicate low toxicity. Very limited data applicable to	(Keml, 2009)				

Persistence	Bioaccumulation	Toxicity	Source
Available evidence indicates EBP as	Measured BCF not significant (e.g., < 25 L/kg	environmental and health properties, but EBP suspected to have similar characteristics in the environment to DecaBDE Aquatic acute/chronic toxicity studies not	Environment Agency (2007) in JRC (2007)
cotentially P. EBP is not susceptible to abiotic degradation (e.g., nydrolysis) and is not readily biodegradable under aerobic conditions in the aquatic environment (viz: 2% according to OECD 301C). Persistence is linked to ow water solubility (0.72 ug/L)	at 0.05 mg/L) but not reliable due to, e.g.: flow through, not dietary, study water solubility limit exceeded dispersant used Assuming aquatic concn = 0.72 µg/L (i.e., solubility limit) then worst case BCF would be 1600 (i.e., < 2,000 threshold criterion for B). Measured LogKow = 3.55 (i.e., < 4.5 threshold criterion for B (but considered an estimate only, due to analytical uncertainties) QSAR prediction of BCF (modelled on LogKow) in the range 100-200. B potential for EBP: low but currently insufficient reliable data with which to quantify the bioaccumulation potential of DBDPE in both aquatic and	available. In view of low water solubility and low bioaccumulation potential, EBP not expected to meet threshold criterion for T (i.e., chronic NOEC < 0.01 mg/L)	

The Environment Agency indicated that EBP is not readily biodegradable, and there was no information available at the time to assess the likely significance of any degradation pathway. Some hypothetical breakdown products could be more toxic and bioaccumulative than the parent substance. The Environment Agency identified gaps in the following areas (Environment Agency, 2007):

- Data to provide more reliable information about bioaccumulation potential
- Data to provide information on actual products of degradation and metabolism and their rate of formation.

Information from industry on the PBT properties of EBP

Industry has provided views on the PBT profile of EBP. These are presented below, as submitted to RPA.

According to a registrant of DecaBDE, a weight of evidence approach suggests that EBP does not fulfil Annex XIII criteria. Further data are being generated following the substance evaluation under REACH.

#### Screening criteria

EBP is exceptionally limited in both its octanol and water solubility, and which combined, resulted in its measured LogKow of 3.55 (Albemarle, 2014b).

The final reports on the octanol-water partition coefficient studies of DecaBDE and EBP were directly compared. The same personnel using the same, e.g. generator column, methodology and the same analytical method conducted both studies at the same contract laboratory. The studies were performed approximately 2 years apart. Substantial sources of variability in the measured values are reduced or eliminated due to these shared attributes. Comparison of the results is more reliable than if the studies were conducted at different laboratories by different methods and means of analysis (Albemarle, 2014b).

The measured water and octanol concentrations and calculated LogKow values determined in the two studies are shown in the table below. Compared to EBP, DecaBDE's saturated concentration in the octanol stock solution was ca. 38 times higher, whereas DecaBDE's concentration in the aqueous column eluate was ca. 14 times lower. The measured concentration of DecaBDE in the aqueous eluate, 0.04  $\mu$ /L, was in line with its measured water solubility, <0.1  $\mu$ g/L, reported by the same laboratory using a similar analytical method. The measured concentration of EBP in the aqueous eluate was also consistent with EBP's measured water solubility, ca. 0.72  $\mu$ g/L, reported by the same laboratory using a similar analytical method. Both EBP's measured water solubility and measured concentration in the aqueous column eluate were between the analytical method's LOD and LOQ (Albemarle, 2014b).

Measurements of octanol solubility for DecaBDE and EBP under the same experimental conditions resulted in ca.  $80,000\mu g/L$  for DecaBDE and ca.  $850~\mu g/L$  for EBP. Albemarle used a different analytical method from the prior water solubility and octanol-water partition coefficient studies. Nonetheless, EBP's concentration in the saturated octanol stock solution measured by the contract laboratory in the LogKow study and its octanol solubility measured by Albemarle are similar (Albemarle, 2014b).

DecaBDE had a higher saturated octanol concentration, and a lower concentration in the aqueous eluate, than EBP. The magnitude of the difference in the two chemicals' concentrations is much greater for octanol than water. An Albemarle organic chemist suggested DecaBDE's higher octanol solubility may be related to the oxygen bridge, which allows a limited opportunity for hydrogen bonding with solvent. The higher octanol solubility of DecaBDE drives its higher LogKow, whereas the very low solubility in both octanol and water drive EBP's LogKow value (Albemarle, 2014b).

The measured octanol solubility of EBP is below the value, 0.002 mmol/L, which is considered in the REACH guidance as an indicator of low bioaccumulation potential. EBP's measured solubility in octanol indicates a low bioaccumulation potential. A low potential for bioaccumulation is consistent with the measured LogKow and an estimated very low bioavailability. However, the LogKow for

substances like EBP that are highly hydrophobic and of very low solubility in water and organic solvents should be used with caution in any modelling approaches. Therefore, most bioaccumulation models that are based on LogKow as one of the determining parameters need to be used with caution for these types of chemicals.

#### Other evidence of non-B / non-vB properties

Oral rat pharmacokinetic studies indicate negligible, if any, absorption of a single dose. Background levels of radioactivity were detected in blood, plasma, bile, urine and tissues. Elimination was via the faeces as the parent molecule (Albemarle, 2014b).

After 90 days oral administration of 100 mg/kg bw/d, rat liver contained only ca.  $4.7 \times 10^{-6}\%$  of the cumulative dose. Multiple repeated dose studies indicate oral NOEL/NOAELs of  $\geq$  1000 mg/kg/d bw or diet. These repeat dose studies include subchronic (28 and 90-d), prenatal developmental (rat and rabbit), and reproductive (20-wk) studies in rats, rabbits and/or birds. EBP was not detected (LOQ=1 mg/g w/w) in egg yolk or albumin after administration of 1000 ppm in the feed for up to 20 weeks to male and female bobwhite. An 8-wk fish bioconcentration study performed at concentrations in excess of its water solubility showed no toxicity. These studies indicate accumulation to toxic levels did not occur (Albemarle, 2014b).

An 8-wk fish study conducted at 2 concentrations higher than EBP's water solubility using a dispersant produced BCF values of <2.5 and <25. Of the 16 measured values in fish, only 1 (at week 2 of exposure) was above the minimal limit of determination of 1.27 µg/g. The remaining 15 values were non-detectable. Because the water concentrations were higher than EBP water solubility, this study has been considered not to be useful for hazard assessment. In any case, exposure via water is unlikely to be an important exposure route given EBP's negligible water solubility and binding to particulates. EBP's propensity for particulate binding was demonstrated by He et al. (2012) where the ratio of EBP's dissolved-to-particulate water concentration was 0.00000079. Some literature data (e.g. (Law & al, 2006b; He & al, 2012)) report on field studies on EBP, but due to various deficiencies no reliable conclusions on bioaccumulation can be drawn from these studies. Further studies will be performed following the substance evaluation under REACH. A recent publication (Xiao & al, 2013) confirmed the negligible absorption efficiency of EBP in fish when given via the diet. They propose to use EBP as benchmark chemical for a non-absorbable compound. In four independent experiments, EBP was only found in the faeces, but not in the fish tissues 5 days after single dietary exposures of juvenile rainbow trout (Albemarle, 2014b).

\*\*\* Additional information on the potential bioaccumulation and differences between DecaBDE and EBP is provided in Annex 5, as provided by Albemarle\*\*\*

#### <u>Additional considerations</u>

The identification of DecaBDE as a PBT substance was related to concerns about certain degradation products that had been identified in a few studies and some of the degradation products were previously identified as POPs. This is not the case for EBP as an alternative for DecaBDE. Several considerations indicate that degradation of EBP under environmental and physiological conditions is unlikely. These include the very limited bioavailability, and several structural features that have been investigated. So far, degradation products have not been identified, and further investigations will be performed following the substance evaluation under REACH (Albemarle, 2014b).

#### Other hazard assessments

The German Federal Environmental Agency (Umweltbundesamt) published a study in 2001 in which EBP was one of 13 FRs assessed. The study was not able to make a recommendation on the substance due to lack of data<sup>59</sup>.

In 2007, the Environment Agency for England and Wales undertook a risk evaluation study for EBP in the UK. The Environment Agency concluded that it was not possible to derive a meaningful PNEC for EBP for surface water from these data as no toxic effects were seen in any of the tests with EBP, indicating that the substance is not acutely toxic at concentrations up to its water solubility limit in these species. No risks were identified for surface water, wastewater treatment plants, the atmosphere, predators or humans following environmental exposure. The formulation and application of textile backcoatings might lead to a possible risk for sediment and soil organisms.

In their 2011 analysis for the European Commission, Arcadis & EBRC used one consumer exposure scenario (vapour inhalation) and no risk was identified (Arcadis & EBRC, 2011).

In its 2013 review of FRs, the Danish EPA referred to a study by Nakari & Huhtala (2010) which suggests that EBP may be acutely toxic to Daphnia magna (48h-EC $_{50}$  of 0.019 mg/L) and may affect reproduction in fish at relatively low concentrations, although these results are based on nominal concentrations and the actual water solubility of EBP may be lower than these values (Danish EPA, 2013). The Danish EPA also reported on a study by Wang et al. (2012) which has shown that EBP may have the potential to undergo photolytic debromination reactions; however, the environmental significance of such reactions is currently unknown (Danish EPA, 2013).

Finally, in its recent assessment of alternatives to DecaBDE, the US EPA provided some information on the substance. This is summarised in the table below. The table provides a summary of findings for the one parameter that has been marked of "moderate" concern. On the other hand, parameters of "high" or "very high" concern are discussed in more detail after the table.

Table	Table 5-97: US EPA Assessment of EBP (CAS No. 84852-53-9)													
	Human Health Effects								Aquatic Toxicity**		Environmental Fate			
Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation
L	М	L	L	Н	L	L	L	No data	VL	VL	L	L	VH	н
Carcin	Carcinogenicity  Potential for carcinogenicity based on analogy to DecaBDE and professional judgment. No experimental carcinogenicity data for exposure to EBP was located													
	Source: US EPA (2014)													
VL =	Very Lo	w haza	rd L = Lo	w hazar	d <b>M</b> = M	loderate	hazard	H = High	n hazar	d VH =	Very I	ligh haz	ard	

Available at <a href="http://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/1988.pdf">http://www.umweltbundesamt.de/sites/default/files/medien/publikation/long/1988.pdf</a> (accessed on 7 February 2014).

Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgement

The assessment of the US EPA for those parameters that have been identified as being of "High" or "Very High" concern is as follows (US EPA, 2014):

- Developmental toxicity: estimated to be "high" for developmental neurotoxicity based on analogy to DecaBDE. There were no maternal or foetal toxicity effects in rats or rabbits exposed during gestation to doses up to 1,250 mg/kg/day EBP. Some rodent developmental neurotoxicity studies of the analogue DecaBDE indicate adverse effects for the neurodevelopmental endpoint. There were no developmental neurotoxicity studies located for EBP. Due to the analogous properties of DecaBDE and EBP, neurodevelopmental toxicity is predicted
- **Persistence**: very high persistence of EBP is expected based on experimental biodegradation data. EBP was determined to not be readily biodegradable in a 28-day MITI test nor was it inherently degradable in a 90-day aerobic sewage/soil test using pre-exposed inoculum. It is not expected to undergo hydrolysis since it does not contain hydrolysable functional groups. The atmospheric half-life of EBP is estimated to be 4.5 days, although it is expected to exist primarily in the particulate phase in air. Laboratory studies have demonstrated photolysis of EBP, although the rate of this process under environmental conditions has not been established
- Bioaccumulation: the bioaccumulation hazard designation is estimated based on EBP monitoring data reporting detections in many different species, including those higher on the food chain. Although the estimated bioaccumulation factor is low, the persistence of EBP and its detection in many species from different habitats and trophic levels indicates high potential for bioaccumulation hazard in aquatic or terrestrial species.

## Available monitoring data

A comprehensive summary of monitoring data for EBP has been provided by EFSA and is reproduced below. The US EPA has also collected information on environmental monitoring and biological biomonitoring. The following table presents only results relating to biota.

Table 5-98: Monitoring da	ta for EBP (CAS No. 848	352-53-9) (based on EFSA, 2012)	
Sample	Location	Levels	Source
Insulating material for		4.8 mg/g polymer	Kierkegaard et al. (2004)
plastic water pipes			
Children's toys	Guangzhou city	Highest 117 μg/g polymer (mean 9 μg/g polymer). Calculated children's exposure as a result of contact with these materials to be around 1.3 to 15.1 ng/kg bw per day	Chen et al. (2009)

Ambient air  Ambient air highest concentrations were detected in air from the European Arctic anada and Spain  Ambient air from the European Arctic anada  Arctic Canada  Anology and the European Arctic frequency of detection: around 10 %) and the Hudson Bay (altection	Table 5-98: Monitoring da	nta for EBP (CAS No. 848	352-53-9) (based on EFSA, 2012)	
The highest concentrations were detected in air from the European continent and the lowest concentrations during periods with rather stagnant air over Southern Scandinavia  House dust  Five homes from three Swedish cities  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in t	Sample	Location	Levels	Source
House dust	Ambient air		0.077-7.9 pg/m <sup>3</sup>	Egebäck et al. (2012)
European continent and the lowest concentrations during periods with rather stagnant air over Southern Scandinavia			The highest concentrations	
lowest concentrations during periods with rather stagnant air over Southern Scandinavia			were detected in air from the	
House dust  Five homes from three Swedish cities  Five Great Lakes and in two Lakes in Canadta  Five Great Lakes and in two Lake			European continent and the	
House dust  Five homes from three Swedish cities  Five Great Lakes and in two Lakes in Canadta  Five Great Lakes and in two Lake			1 · · · · · · · · · · · · · · · · · · ·	
House dust  Five homes from three Swedish cities  Five discovery for the discovery for the discovery of detection: around 10 %) and the Furopean Arctic Hudson Bay and the European Arctic frequency: around 3 %)  Aquatic birds  Five homes from three Swedish cities  Five homes from three Swedish cities  Five homes from three Swedish cities  Five Great Lakes and fin two Lakes in Canadian  Three species of fish; nine Mud carps (Cirrhina mollotrealn), fifteen Nile tilapia (Oreochromis niloticus, and ten Plecostomus  Five Cosat  Five Great Lakes and in the Pearl River delta  Dongjiang River system, Southern  China  Five Great Alexand and Spark Eagle for the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase  Five Great Lakes and in two Lakes in Canadias  Canada  Five Great Lakes and in two Lakes in Canadias  China  Five Great Lakes and i			_	
House dust  Five homes from three Swedish cities on the Lathors allowed the vapour phase and Joseph Gaustier et al. (2007)  Zhu & Hittes (2006)  Zhu & Hittes (2007)  Zhu & Hittes (2006)  Sauthier et al., (2007, 2009)  Guerra et al. (2012)  Munschy et al., (2007)  Only detected in samples from the Canadian Arctic, (Frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Adjubse tissue of polar between the Canadian Arctic, (Frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Five Great Lakes and in the Pearl River delta on the Canadian Arctic (Frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Five Great Lakes and in the Danks in the Pearl River delta on the Canadian Arctic (Frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Five Great Lakes and in the Pearl River delta on the Canadian Arctic (Frequency of detection: around 10 %) and the Hudson Bay (detection frequency:			·	
three Swedish cities  three Swedish cities  three Swedish cities  three Swedish cities  Concentrations ranging from 20.8 to 121 ng/g dust.  The authors also analysed the vapour phase and found EBP in only one sample, 0.0229 ng/m³ (LOD = 0.00784 ng/m³)  (LOD = 0.00784 ng/m³)  Tree bark samples  USA  Identified in samples from only two out of 29 sites at concentrations ranging from 9.3 to 100 ng/g fat  Eggs from seven colonies of herring gulls  Eggs from peregrine falcon  Fench Atlantic  Canada and Spain  Juvenile common sole  Muscle and liver  Various fish species  Adipose tissue of polar bears  Arctic, Hudson Bay and Arctic (Hudson Bay and the European Arctic, Hudson Bay and the European Arctic Hudson Bay and the European Arctic frequency: around 3 %)  Aquatic birds  E-waste region in the Pearl River delta  Pearl River delta  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus, land ten Plecostomus (Hypostomus)	House dust	Five homes from		Karlsson et al. (2007)
concentrations ranging from 20.8 to 121 ng/g dust. The authors also analysed the vapour phase and found EBP in only one sample, 0.0229 ng/m³ (LOD = 0.00784 ng/m³)  Tree bark samples  USA  Identified in samples from only two out of 29 sites at concentrations ranging from 9.3 to 100 ng/g fat  Eggs from seven colonies of herring gulls  Eggs from peregrine falcon  Eggs from peregrine falcon  Eggs from peregrine falcon  Juvenile common sole  Muscle and liver  Various fish species  Adipose tissue of polar bears  Arctic, Hudson Bay and the European Arctic, Hudson Bay and the European Arctic, Hudson Bay and the European Arctic birds  E-waste region in the Pearl River delta maximum of 900 ng/g fat  Erwaste region in the Pearl River delta maximum of 900 ng/g fat  EBB was not found above the LOQ (0.020 ng/g)  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus), and ten Plecostomus (Hypostomus  Are value from the Canadian Place of the phase of the place of the p			,	,
20.8 to 121 ng/g dust.   The authors also analysed the vapour phase and found EBP in only one sample, 0.0229 ng/m³ (LOD = 0.00784 ng/m³)				
The authors also analysed the vapour phase and found EBP in only one sample, 0.0229 ng/m³ (LOD = 0.00784 ng/m³)  Tree bark samples  USA  Identified in samples from only two out of 29 sites at concentrations ranging from 9.3 to 100 ng/g fat  Eggs from seven colonies of herring gulls  Eggs from peregrine falcon  Eggs from peregrine falcon  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  Usenile common sole  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  Usenile common sole  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  Usenile common sole  Adipose tissue of polar bears  Adipose tissue of polar bears  Arctic, Hudson Bay and the European Arctic, Hudson Bay and the European Arctic  E-waste region in the Pearl River delta  E-waste region in the Pearl River delta  Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus, and ten Plecostomus  (Hypostomus  The authors ala found and family and from 37 to 110 ng/g fat bear and found above the LOQ (0.020 ng/g)  The authorized in samples from the Canadian Arctic (frequency of detection: around 10 %) and the Hudson Bay (detection)  Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus), and ten Plecostomus  (Hypostomus				
Vapour phase and found EBP in only one sample, 0.0229 ng/m³ (LOD = 0.00784 ng/m³)				
Tree bark samples  USA  USA  USA  Identified in samples from only two out of 29 sites at concentrations ranging from 9.3 to 100 ng/g fat  Detected in two out of seven pools showing concentrations at 9.3 and 44 ng/g w/w  Eggs from peregrine falcon  Eggs from peregrine falcon  Juvenile common sole  Muscle and liver  Various fish species  Adipose tissue of polar bears  Arctic, Hudson Bay and the European Arctic Hudson Bay and the European Arctic hudson Bay and the European Arctic  Aquatic birds  Eywaste region in the Pearl River delta in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus), and ten Plecostomus  (Hypostomus)  USA  Identified in samples from out of seven pools showing concentrations at concentrations at concentrations at concentrations at 9.3 to 100 ng/g fat  Detected in two out of seven pools showing concentrations at 9.3 to 100 ng/g fat  Detected in two out of seven pools showing concentrations at 9.3 to 100 ng/g fat  Uso 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  Onls to 3.90 ng/g fat  Only detected in samples from the Canadian Arctic (frequency of detection: around 10 %) and the Hudson Bay (detection: around 10 %) and the Hudson				
Tree bark samples  USA  Identified in samples from only two out of 29 sites at concentrations ranging from 9.3 to 100 ng/g fat  Eggs from seven colonies of herring gulls  Eggs from peregrine falcon  Eggs from peregrine falcon  Juvenile common sole  Muscle and liver  Various fish species  Adipose tissue of polar bears  Arctic, Hudson Bay and the European Arctic tic  E-waste region in the Pearl River delta  Pere species of fish; nine Mud carps ( <i>Cirrhina molitorella</i> ), fifteen Nile tilapia ( <i>Oreochromis niloticus</i> ), and ten Plecostomus ( <i>Hypostomus</i> )  IUSA  Identified in samples from only two out of 29 sites at concentrations ranging from 9.3 to 100 ng/g fat  Detected in two out of seven pools showing concentrations at 9.3 and 44 ng/g w/w  Detected in two out of seven pools showing concentrations at 9.3 and 44 ng/g w/w  Detected in two out of seven pools showing concentrations at 9.3 and 44 ng/g w/w  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  O.9 to 1.9 pg/g w/w.  O.08-1.01 mg/g fat  Only detected in samples from the Canadian Arctic (frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Ferwaste region in the Pearl River delta  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; nine Mud carps ( <i>Cirrhina molitorella</i> ), fifteen Nile tilapia ( <i>Oreochromis niloticus</i> ), and ten Plecostomus ( <i>Hypostomus</i> )  He et al. (2012)  The et al. (2012)  The et al. (2010)  The pool of grate and from 37 to 110 ng/g dry weight for the particulate phase				
Tree bark samples				
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Eggs from seven colonies of herring gulls  Lakes of North America  Eggs from peregrine falcon  Juvenile common sole  Various fish species  Adipose tissue of polar bears  Arctic, Hudson Bay and the European Arctic  Arctic Fequency: around 3 %)  Aquatic birds  E-waste region in the Pearl River delta  Three species of fish; nine Mud carps (Cirrhina molitorello), fifteen Nile tilapia (Orecchromis niloticus				
Eggs from seven colonies of herring gulls  Laurentian Great Lakes of North America  Eggs from peregrine falcon  Eggs from peregrine falcon  Juvenile common sole  Warious fish species  Adipose tissue of polar bears  Aquatic birds  E-waste region in the Pearl River delta  22 fish samples  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus), and ten Plecostomus (Hypostomus)				
Eggs from peregrine falcon  Eggs from peregrine falcon  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  Juvenile common sole  Muscle and liver  Various fish species  Adipose tissue of polar bears  Actic, Hudson Bay and He European Arctic  E-waste region in the Pearl River delta in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus (Face of the polar America)  Lake of North at 9.3 and 44 ng/g w/w  10.3 and 44 ng/g w/w  11. a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  10.18 to 3.90 ng/g fat  0.18 to 3.90 ng/g fat  0.19 to 1.9 pg/g w/w.  10.10 to 3.90 ng/g fat  10.10 to 1.9 pg/g w/w.  10.10 to 1.9 pg/g at 1.  10.10 to 1.0 pg/g fat  10.10 to	Eggs from soven colonies	Laurentian Great		Gauthior et al. (2007
Eggs from peregrine falcon  French Atlantic  Outset of Spark (Canada and Spain)  Adipose tissue of polar bears  Aquatic birds  French Atlantic  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile (Cincil of Spark) (Cincil of Spark), and ten Plecostomus  (Hypostomus  America  at 9.3 and 44 ng/g w/w  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  Outset of 20.8 1.0 ng/g fat  Outset of 0.9 to 1.9 pg/g w/w.  Outset of 0.9 pg/g of 0.9 pg/g of 0.9 pg/g fat  Outset of 0.9 pg/g of 0.9 pg/g fat  Outset of 0.9 pg/g w/w.  Outset of 0.9 pg/g w/w.  Outset of 0.9 pg/g of 0.9 pg/g fat  Outset of 0.9 pg/g w/w.  Outset of 0.9 pg/g w/w.  Outset of 0.9 pg/g w/w.  Outset of 0.9 pg/g of 0.9 pg/g fat  Outset of 0.9 pg/g of 0.9 pg/g fat  Outset of 0.9 pg/g of 0.9 pg/				-
Eggs from peregrine falcon  Canada and Spain  In a total of 25 eggs, EBP was detected in just one egg at 8.2 ng/g fat  Juvenile common sole  Muscle and liver  Various fish species  Cast  Coast  Coast  O.9 to 1.9 pg/g w/w.  Lake Winnipeg (Canada)  Alaska, the Canadian Arctic, Hudson Bay and the European Arctic  Arctic, Hudson Bay and the Pearl River delta  E-waste region in the Pearl River delta in two Lakes in Canada  Cast  Coast  O.9 to 1.9 pg/g w/w.  Coast  Only detected in samples from the Canadian Arctic (frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  E-waste region in the Pearl River delta maximum of 900 ng/g fat  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus), and ten Plecostomus  (Hypostomus  Canada and Spain detected in just one egg at 8.2 ng/g fat  D.18 to 3.90 ng/g fat  Coast  O.9 to 1.9 pg/g w/w.  Coast  O.9 to 1.9 pg/g w/w.  Coast  O.9 to 1.9 pg/g w/w.  Coast  Only detected in samples from the Canadian Arctic (frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Luo et al. (2009)  Three species of fish; or the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase  He et al. (2012)	or herring guils			2009)
falcon    detected in just one egg at 8.2   ng/g fat     Juvenile common sole   French Atlantic   Coast   O.18 to 3.90 ng/g fat     Muscle and liver   Coast   O.9 to 1.9 pg/g w/w.     Various fish species   Lake Winnipeg (Canada)     Adipose tissue of polar bears   Arctic, Hudson Bay and the European Arctic   Frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)     Aquatic birds   E-waste region in the Pearl River delta     22 fish samples   Five Great Lakes and in two Lakes in Canada     Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus (Hypostomus   Hypostomus	Fare from popularia			Cuarra et al. (2012)
Juvenile common sole  Juvenile common sole  Muscle and liver  Coast  O.18 to 3.90 ng/g fat  O.9 to 1.9 pg/g w/w.  Lake Winnipeg (Canada)  Adipose tissue of polar bears  Arctic, Hudson Bay and the European Arctic  Actic frequency: around 3 %)  Aquatic birds  E-waste region in the Pearl River delta  Tive Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  (Hypostomus)  Adipose tissue of polar back Winnipeg (Canada)  Alaska, the Canadian Arctic (frequency of detection: around 10 %) and the Canadian Arctic (frequency: around 3 %)  10-176 ng/g fat, with a maximum of 900 ng/g fat  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; one Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus), and ten Plecostomus  (Hypostomus  Munschy et al., (2007)  Mckinney et al., (2011)		Canada and Spain		Guerra et al. (2012)
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Adipose tissue of polar bears  Alaska, the Canadian Arctic, Hudson Bay and the European Arctic  Aquatic birds  E-waste region in the Pearl River delta in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus niloticus niloticus (Hypostomus)  Alaska, the Canadian Arctic (frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  10-176 ng/g fat, with a maximum of 900 ng/g fat  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; or the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase  He et al. (2012)				
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bears  Arctic, Hudson Bay and the European Arctic  Arctic  Aquatic birds  E-waste region in the Pearl River delta  22 fish samples  Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  (Hypostomus  Arctic, Hudson Bay the Canadian Arctic (frequency of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Luo et al. (2009)  Zhou et al. (2010)  Luo et al. (2010)  Three Species of fish; ophase and from 37 to 110 ng/g dry weight for the particulate phase  Arctic, Hudson Bay (detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Luo et al. (2010)  Zhou et al. (2012)  He et al. (2012)		· ·		
and the European Arctic  and the European Arctic  detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  E-waste region in the Pearl River delta  22 fish samples  Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  (Hypostomus  of detection: around 10 %) and the Hudson Bay (detection frequency: around 3 %)  Luo et al. (2009)  EBP was not found above the LOQ (0.020 ng/g)  Thou et al. (2010)  It at a 38 pg/L for the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase	Adipose tissue of polar			Mckinney et al., (2011)
Arctic the Hudson Bay (detection frequency: around 3 %)  Aquatic birds E-waste region in the Pearl River delta maximum of 900 ng/g fat.  22 fish samples Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus (Hypostomus  E-waste region in 10-176 ng/g fat, with a maximum of 900 ng/g fat  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; and in two Lakes in Canada  Three species of fish; and in two Lakes in Canada  China Three species of fish; and the Pearl River delta and in two Lakes and found above the LOQ (0.020 ng/g)  Three species of fish; and in two Lakes in Canada  China Three species of fish; and in two Lakes and from 37 to 110 ng/g dry weight for the particulate phase	bears	·		
Aquatic birds  E-waste region in the Pearl River delta  22 fish samples  Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  (Hypostomus  Five Great Lakes and in two Lakes in Canada  Five Great Lakes and in two Lakes in LOQ (0.020 ng/g)  Five Great Lakes and EBP was not found above the LOQ (0.020 ng/g)  Five Great Lakes and in two Log (0.020 ng/g)  Five Great Lakes and LOQ (0.020 ng/g)  Five Great Lakes and In two Log (0.020 ng/g)  Five G		and the European		
Aquatic birds  E-waste region in the Pearl River delta  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  E-waste region in the Pearl River delta  To-176 ng/g fat, with a maximum of 900 ng/g fat  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; nongjiang River system, Southern China  Three species of fish; nongjiang River system, Southern China  China  Three species of fish; nongjiang River system, Southern China  China  Luo et al. (2010)  Thou et al. (2010)  He et al. (2012)  He et al. (2012)		Arctic	the Hudson Bay (detection	
the Pearl River delta maximum of 900 ng/g fat  22 fish samples  Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  (Hypostomus  Five Great Lakes and in two Lakes in LOQ (0.020 ng/g)  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; no LOQ (0.020 ng/g)  Three specie			frequency: around 3 %)	
Five Great Lakes and in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus (Hypostomus  Five Great Lakes and in two Lakes in LOQ (0.020 ng/g)  EBP was not found above the LOQ (0.020 ng/g)  Three species of fish; no Log (0.	Aquatic birds	E-waste region in	10-176 ng/g fat, with a	Luo et al. (2009)
in two Lakes in Canada  Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  in two Lakes in LOQ (0.020 ng/g)  13 to 38 pg/L for the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase  13 to 38 pg/L for the dissolved phase and from 37 to 110 ng/g dry weight for the particulate		the Pearl River delta	maximum of 900 ng/g fat	
Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus  (Hypostomus  Canada  Dongjiang River system, Southern phase and from 37 to 110 ng/g dry weight for the particulate phase  13 to 38 pg/L for the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase	22 fish samples	Five Great Lakes and	EBP was not found above the	Zhou et al. (2010)
Three species of fish; nine Mud carps (Cirrhina molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus (Hypostomus  Dongjiang River system, Southern China  13 to 38 pg/L for the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase  13 to 38 pg/L for the dissolved phase and from 37 to 110 ng/g dry weight for the particulate phase		in two Lakes in	LOQ (0.020 ng/g)	
nine Mud carps ( <i>Cirrhina molitorella</i> ), fifteen Nile tilapia ( <i>Oreochromis niloticus</i> ), and ten Plecostomus ( <i>Hypostomus</i> )  system, Southern phase and from 37 to 110 ng/g dry weight for the particulate phase		Canada		
nine Mud carps ( <i>Cirrhina molitorella</i> ), fifteen Nile tilapia ( <i>Oreochromis niloticus</i> ), and ten Plecostomus ( <i>Hypostomus</i> )  system, Southern phase and from 37 to 110 ng/g dry weight for the particulate phase	Three species of fish;		13 to 38 pg/L for the dissolved	He et al. (2012)
molitorella), fifteen Nile tilapia (Oreochromis niloticus niloticus), and ten Plecostomus (Hypostomus		_ = =		
tilapia ( <i>Oreochromis</i> niloticus niloticus), and ten Plecostomus ( <i>Hypostomus</i>		·		
niloticus niloticus), and ten Plecostomus (Hypostomus	• •			
ten Plecostomus (Hypostomus			F	
(Hypostomus	· ·			
DICCOSCOTION	plecostomus)			

Table 5-98: Monitoring da	ta for EBP (CAS No. 848	352-53-9) (based on EFSA, 2012)	
Sample	Location	Levels	Source
Green mussel ( <i>Perna</i> viridis) and Blue mussel ( <i>Mytilus edulis</i> )	Cambodia, China, Hong Kong, India, Indonesia, Japan, Malaysia, the Philippines and Vietnam	<0.3 to 22 ng/g fat. The highest levels of EBP were detected in mussels from Japan and Korea	Ogawa et al. (2010)
Eels	Seven locations throughout Eastern Canada	EBP was quantified in only one sample at a concentration of 0.21 ng/g fat in a fish from Lake Ontario	Byer et al. (2010)
Three different species of fish Mud carp ( <i>Cirrhinus molitorella</i> ) (n = 12), Crucian carp ( <i>Carassius auratus</i> ) (n = 18) and Northern snakehead ( <i>Ophicephalus argus</i> ) (n = 6)	E-waste area	From LOD (not given, but LOQ = 0.38 ng/g fat) to 338 ng/g fat	Wu et al. (2010)
Chinese mystery snail (Cipangopaludina chinensis) (n = 43) and a prawn (Macrobrachium nipponense) (n = 7) and one reptile, Chinese Water Snake (Enhydris chinensis) (n = 2)		The mean concentration in the prawns was 84.3 ng/g fat, while in the remaining species no values were found above the LOD	
Watercock (Gallicrex cinerea) muscle, liver and kidney Carp (Cyprinus sp.), Bighead (Hypophthalmichthys nobilis) and Tilapia (Oreochromis sp.)	E-waste dismantling workshops in southern PR China	9.6-16.3, 13.7-54.6 and 24.5- 124 ng/g fat, respectively  Concentrations in liver and muscle were all <3.80 ng/g fat	Shi et al. (2009)
Thick-billed Murre ( <i>Uria</i> lomvia)		5.81 ng/g w/w Not detected in any other bird investigated, nor in capelin (mallotus villosus), ringed seal (pusa hispida), arctic fox (vulpes lagopus) or polar bear (ursus maritimus)	Klif (2010b)
100 composite samples of various food commodities		No sample contained EBP levels above the LOD (range as reported by the authors) of 0.9-3 (milk), 1.2- 2.7 (carcass fat), 1.42-7.97 (liver) and ND- 6.01 (eggs) ng/g fat	Tlustos et al. (2010)
Human plasma samples	Sweden	Could not be identified above the LOD (1.03 ng/g fat)	Karlsson et al. (2007)

Office cleaners, university students or policemen	Levels Not detected	Source Zhu et al. (2009)
university students	Not detected	Zhu et al. (2009)
Tianjin (Northern China)		
China	The levels found in the e-waste recycling area (17.7 and 24.2 ng/g dry weight for residents and exposed workers, respectively) were similar to those found in the urban area samples (17.8 ng/g dry weight), and higher than those found in the rural area (9.57 ng/g dry weight)	Zheng et al. (2011)
	China)	China)  The levels found in the e-waste recycling area (17.7 and 24.2 ng/g dry weight for residents and exposed workers, respectively) were similar to those found in the urban area samples (17.8 ng/g dry weight), and higher than those found in the rural area (9.57

Additionally, a recent Norwegian monitoring report has been quoted as saying, "Polybrominated diphenyl ether (PBDE) 47 and decabromodiphenyl ethane, DBDPE (84852-53-9) were the most frequently detected BFR compounds within this study. An interesting and new finding from the screening was that DBDPE levels exceeded the levels of PBDE 47 in numerous samples, including the Arctic samples" (information from consultation with the Norwegian authorities).

#### **Conclusion on Alternative 12**

The following table summarises the conclusions from the above information on the feasibility and suitability of EBP as a replacement for DecaBDE.

Table 5-99: Conclusi	ions on suitability and feasibility of EBP (CAS No. 84852-53-9)
Category	Conclusion
Suitability	Environmental hazards: EBP is very persistent and, while concerns have been raised on bioaccumulation (see the recent US EPA assessment), it does not meet the B/vB criterion. Reductive debromination has been discussed in the past and, while some indication of it happening may have been published (Wang et al, 2012), the significance of photolytic debromination reactions and the identities of degradation products are not clear. It is premature to reach a conclusion while the substance evaluation process is under way and more studies are to be performed. A manufacturer asserts that EBP does not behave like DecaBDE and has provided relevant information in support of this. An aquatic toxicity classification has been self-notified but is not present in the registration dossier for the substance. Finally, the substance has been detected in many species from different habitats and trophic levels  Human health hazards: neurodevelopmental toxicity is predicted and carcinogenicity concerns have been raised in the recent US EPA assessment due to the analogous properties of EBP and DecaBDE
Technical feasibility	EBP is marketed as a drop-in replacement for DecaBDE across its entire range of applications
Economic	EBP needs to be used at the same loading as DecaBDE and with the same presence of
feasibility	ATO. Its price is estimated to be 5-20% higher than DecaBDE's. The estimated

Table 5-99: Conclusi	Table 5-99: Conclusions on suitability and feasibility of EBP (CAS No. 84852-53-9)					
Category	Conclusion					
	substitution cost for both polymer and textile applications is in the <€1 million/y range or generally <€200 per kg emissions avoided					
Overall conclusion	EDP is a drop-in replacement for all applications of DecaBDE. Its cost is moderately					
	higher than DecaBDE and its hazard profile is still under investigation					

## 5.6 Conclusions

The following table summarises the analysis presented above and identifies which of the shortlisted alternatives would, in principle, make suitable replacements for DecaBDE. Currently, only brominated FRs would appear to be able to act as drop in replacements for a wide range of applications, and indeed EBP is widely regarded as the substance most suitable to replace DecaBDE. Nevertheless, many substances have a role to play and may act as suitable, reasonably priced alternatives for specific areas of DecaBDE's current use. It must not be disregarded that this shortlist of 12 substances represents a small proportion of all potential alternatives that have been found in the literature and which may find real use as substitutes for DecaBDE.

	Potential	FR			Technical		Economic feasibility		
No.	alternative substance	category	CAS No	Hazard profile	feasibility	Loading	Price (€) per kg	Subs cost (€/kg emission)	
1	Triphenyl phosphate (TPP)	HFFR	115-86-6	Aquatic toxicity (acute and chronic, H400/410) Repeated dose toxicity Carcinogenicity (? – based on modelling) Neurotoxicity (?) Endocrine disruption (? - CoRAP) SVHC: Potentially	Polymers only	PP: 8-14% PC/ABS: 13-20% ATO: No	6	100-4,000 depending on polymer type	
2	Magnesium hydroxide	HFFR	1309-42-8	Persistence (inorganic substance)  SVHC: No	Wide range, but inefficient	PA: 45-50% Text: 5× ATO: No	1	-1,250 to -1,300 polymers -<250 textiles	
3	Tris(1,3- dichloro-2- propyl) phosphate	HFR	13674-87-8	Persistence (P) Aquatic toxicity (H411) Acute toxicity (H302) Carc Cat 2 (H351, self-classified) Neurotoxicity (?) Female fertility effects (?) SVHC: No	Textiles, limited range	Text: 1.2× ATO: No	3.2	-<500 textiles	
4	Aluminium trihydroxide	HFFR	21645-51-2; 8064-00-4	Persistence (inorganic substance) Neurotoxicity (?) SVHC: No	Wide range, but inefficient	PP: 50-60% Text: 3× ATO: No	0.5	-1,350 to -1,450 polymers -<1,100 textiles	

	Potential	FR			Technical		<b>Economic feasibility</b>	
No.	alternative substance	native CAS No Hazard profile	feasibility	Loading	Price (€) per kg	Subs cost (€/kg emission)		
5	Tetrabromobi sphenol-A bis (2,3- dibromopropy I ether)	BFR	21850-44-2	Persistence (vP) Bioaccumulation (?) Unfavourable degradation products (TBBPA) which may further degrade to bisphenol-A (potential endocine dsruptor) and tetrabromobisphenol-A bis(methyl ether) (potential vPvB) Carcinogenicity (?) SVHC: Potentially	Mostly polymers	HIPS: 5% PP: 8-10% ATO: 3-5%	2.4	-800 to <3,200 depending on polymer type
6	Ethylene bis(tetrabrom ophthalimide)	BFR	32588-76-4	Persistence (vP) Bioaccumulation (B) Debromination in the environment (?) SVHC: Unclear	Drop-in replacement	HIPS: 12% Text: 1× ATO: 4%	5.6	<500 polymers <400 textiles
7	2,2'- Oxybis[5,5- dimethyl- 1,3,2- dioxaphospho rinane] 2,2'- disulphide	HFFR	4090-51-1	Persistence ( <b>P</b> or <b>vP</b> ) <b>SVHC</b> : No	Textiles (viscose fibres) only	Text: 10% ATO: No	>>4	Not estimated

	Potential	FR			Technical		Economic feasibility	1
No.	alternative substance	category	CAS No	AS No Hazard profile	feasibility	Loading	Price (€) per kg	Subs cost (€/kg emission)
8	Resorcinol bis(diphenylp hosphate) (RDP)	HFFR	57583-54-7; 125997-21-9	Persistence (P/vP under screening criteria) Bioaccumulation (?) Degradation products (?) Aquatic toxicity (acute & chronic) (?) The US EPA raised some concern over carcinogenicity, developmental toxicity, neurotoxicity, repeated dose toxicity SVHC: Potentially, uncertain	Polymeric blends	PC/ABS: 8-11% PPE/HIPS: 16- 20% ATO: No	3.5	-250 to <3,000 depending on polymer type
9	Bisphenol-A bis(diphenyl phosphate) (BDP/BAPP)	HFFR	5945-33-5; 181028-79-5	Persistence (?) Bioaccumulation (?) Chronic aquatic toxicity (H413 or H411, self-classified) Degradation products (bisphenol-A, potential endocrine disruptor & phenol,) SVHC: Potentially	Polymeric blends	PC/ABS: 10-14% PPE/HIPS: 10- 20% ATO: No	2-4	-<500 to <3,200 depending on polymer type
10	Substituted amine phosphate mixture (P/N intumescent systems)	HFFR	66034-17-1	Persistence (piperazine, ?) Aquatic toxicity (piperazine, chronic, H412) Acute toxicity (piperazine, ?) Genotoxicity, reprotoxicity, repeat dose toxicity, eye irritation (amine phosphate, ?) SVHC: Uncertain	Polymers and textiles	PP: ca. 25% ATO: No	>4	Not estimated

No.	Potential alternative substance	FR category	CAS No	Hazard profile	Technical feasibility	Economic feasibility		
						Loading	Price (€) per kg	Subs cost (€/kg emission)
11	Red phosphorous	HFFR	7723-14-0	Persistence (P) Aquatic Chronic 3 (H412) (but tests results would support Aq Chr 1) Eye & dermal irritation Hepatotoxicity & genotixicity (?) SVHC: No	Certain polymers, cotton-rich textiles	PA: 5-8% ATO: No	3.2	-850 to <2,500 depending on assumptions
12	Ethane-1,2- bis(pentabro mophenyl)	BFR	84852-53-9	Persistence (vP) Degradation products (photolytic debromination - ?) Neurodevelopmental toxicity & carcinogenicity (?) SVHC: Uncertain, under investigation (CoRAP). Industry argues less hazardous than DecaBDE	Drop-in replacement	HIPS: 12% Same as DecaBDE in range of polymers Text: 1× ATO: 4%	4.2-4.8	<40 to<200 for polymers <50 for textiles



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#### 7 Annex 1 – Consultation Statistics

#### 7.1 Methodology

In order to collect information for this report, a consultation exercise was undertaken by RPA. The initial approach involved contacting industry associations, in order to inform them about the situation with DecaBDE, the goals and requirements of the project and what was requested of them. The associations would then forward our request to the appropriate persons in their members. After a few weeks, a reminder was sent to those that had not responded to the initial e-mail, also informing them that we would contact their members individually.

Individual companies were also contacted. These came from the following sources:

- Lists of members of EU-wide associations<sup>60</sup>
- Companies that have submitted a registration dossier, notification for SiA or C&L notification to ECHA, according to information supplied to RPA by ECHA, including those that responded to ECHA's call for evidence on DecaBDE
- Non-EU manufacturers of DecaBDE or relevant articles, found through online search or information submitted by IPEN in the SC call for evidence.

Reminders were also sent to the companies, twice to those considered particularly important for filling the data gaps in RPA's and ECHA's assessment. On a number of occasions, phone calls were held in order to collect the missing information.

The companies that responded to the questionnaire were further contacted with follow-up questions in order to clarify some of their answers and to request further information, where necessary.

There were also responses by e-mail, most of them in order to state that DecaBDE is not relevant to the company. In cases where it was decided that useful information could be extracted, follow-up e-mails were sent asking for specific information, tailored to the consultee.

At the same time, ECHA uploaded the questionnaire for the Competent Authorities in the CIRCA BC database and informed them about it.

#### 7.2 Industry statistics

In total, 51 associations and 252 separate companies were contacted. **Figure 7-1** shows a breakdown of these stakeholders by sector of activity. **Figure 7-2** and **Figure 7-3** show the breakdown of contacted associations and companies per sector.

 $<sup>^{60}</sup>$  It should be noted that some national associations were also included in these

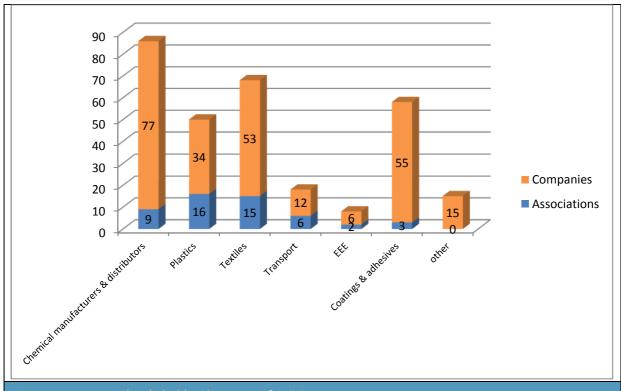
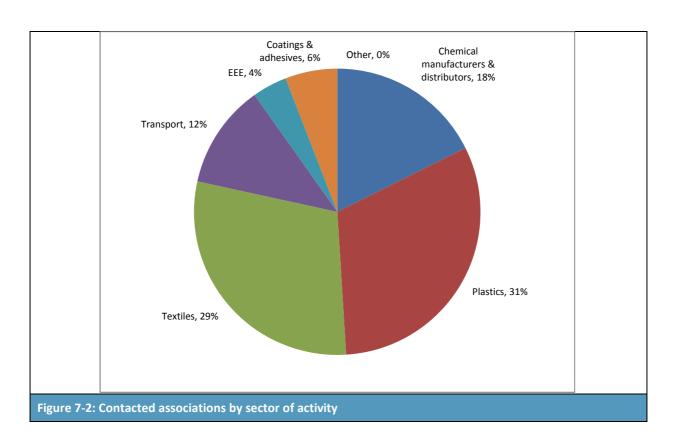


Figure 7-1: Contacted stakeholders by sector of activity



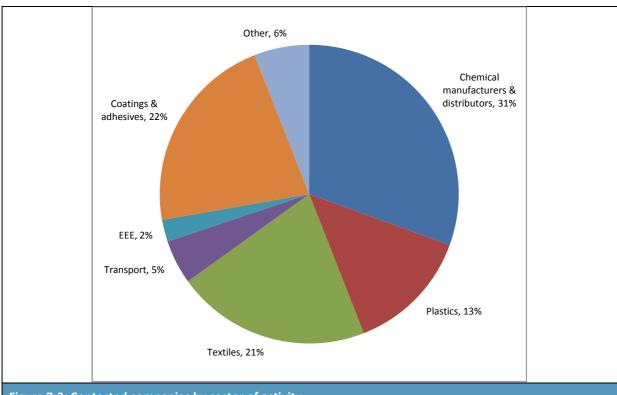
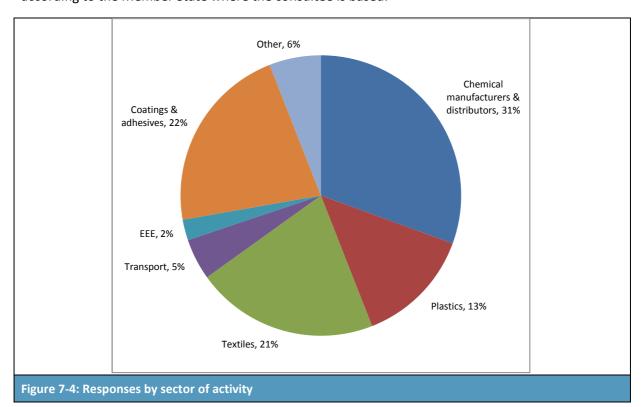
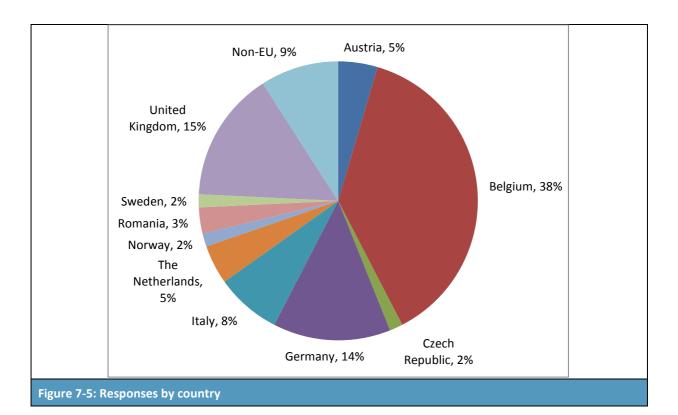


Figure 7-3: Contacted companies by sector of activity

The total number of responses was 66, with some associations and companies being contacted more than once, in an iterative way, both by e-mail and by teleconference. **Figure 7-4** shows the breakdown of the overall responses by sector of activity and **Figure 7-5** breaks the responses down according to the Member State where the consultee is based.





The vast majority of respondents are based in Belgium, with Germany and the UK following. The prominence of Belgium is due to the large number of European Associations and multinational companies having their headquarters in the country. The number of UK-based stakeholders is explained by the importance of DecaBDE for the textile and furniture industry, while Germany is one of the largest industrial economies in Europe. Non-EU stakeholders are based in Asia and the USA.

The final results were 10 completed questionnaires and useful information received through the other contacts. More specifically:

- 1 questionnaire from an importer of DecaBDE in the EU
- 1 questionnaire from a downstream user of DecaBDE for textile applications
- 2 questionnaires from distributors, who supplied DecaBDE in a mixture to be used in plastic, textile and coating applications
- 3 questionnaires from former users of DecaBDE, including one former non-EU manufacturer
- 3 questionnaires from suppliers of alternatives to DecaBDE, two of which supply the market with Inherently Flame Retardant Fibres (IFRF) and one with mixtures

From the companies that have participated in REACH mechanisms (registration, SiA notification, C&L notification), the response rate was as follows:

- 1 out of the 5 registrants finally submitted a questionnaire, while the rest did not provide input
- 2 out of the 4 SiA notifiers responded during consultation, one of which finally submitted a
  questionnaire
- 11 out of the 104 contacted C&L notifiers responded, two of which finally submitted a questionnaire
- The rest of the stakeholders who responded were associations or individual companies contacted independently.

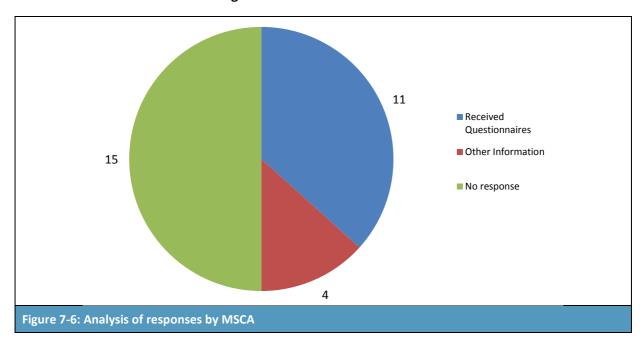
Analysing this information, it seems that the main interested parties were those that have either stopped using DecaBDE or are producing alternatives. There was a clear intention to showcase the properties of the alternatives on offer.

#### 7.3 Competent Authorities statistics

The total number of responses from MSCA was 15, which amounts to a 50% response rate. Of these:

- 11 included a completed (to various degrees) questionnaire
- 2 commented that DecaBDE import or consumption are not relevant to their country
- 1 responded that a study on PBDE levels in the environment is due later this year, but could not supply any information
- 1 requested additional time for the completion of the questionnaire, but had not submitted one at the time of writing this report

The above can be summarised in Figure 7-6.





## 8 Annex 2 – Descriptors

Activity	Chemical product category (PC)	Process category (PC)	Environmental release category (ERC)	Sector of use category (SU)	Article category (AC)
Formulation of flame retardant preparation		PROC 5	ERC 2		
Thermoplastic production (masterbatch and compound)	PC 32	PROC 1, 2, 3, 4, 5, 8b, 9, 14	ERC 3		
Converting	PC 32	PROC 4, 6, 7, 8a, 8b, 9, 10, 13, 14, 15, 21, 22, 24, 25	ERC 2, 3, 4, 5		
Foam production for construction	PC 32	PROC 3, 21	ERC 3, 10a, 11a		
Formulation Polyester and S102E>liquid filled dispersion	PC 32	PROC 3, 4, 5, 8a, 8b, 9, 15, 26	ERC 2, 3, 5, 6b:		
Filled dispersion used in construction	PC 32	PROC 1, 3, 5, 6, 7, 10, 11, 13, 19, 21	ERC 3, 4, 5, 6b, 6d, 8f, 10a, 10b		
Filled dispersion used for transportation	PC 32	PROC 1, 3, 5, 6, 7, 10, 11, 13, 19, 21	ERC 3, 4, 5, 6b, 6d, 8f, 10a, 10b		
Recycling	PC 32	PROC 1, 2, 3, 14, 21, 24	ERC 2, 3, 4, 5		
Coating used in textile	PC 1,8, 9a, 18, 20, 26, 28, 32, 35	PROC 5, 7, 9, 10, 11, 13, 21	ERC 2, 3, 4, 5, 6b, 7, 8a, 8c, 8d		
Formulation coating preparation	PC 32	PROC 3, 4, 5, 8b, 9, 15	ERC 2		
Coatings – Industrial application coatings		PROC 5, 8b, 9, 10, 13, 15	ERC 2, 5, 6d		
Manufacturing VE resins	PC 32	PROC 1, 3, 4, 5, 8b, 9, 15	ERC 2		
Manufacturing of formulated resins (gelcoats, putties, etc.)	PC 32	PROC 1, 3, 4, 5, 8b, 9, 115	ERC 2		
Industrial composites manufacturing	PC 32	PROC 1, 3, 4, 5, 7, 8b, 10, 13, 14, 15	ERC 2, 6d		
Adhesive & sealants	PC 1	PROC 3, 4, 5, 8a, 8b, 9	ERC 2, 8c		
Coating and inks formulation	Pc 1, 9a, 9b, 18, 23, 24, 31, 32, 35, 39	PROC 1, 2, 3, 4, 5, 7, 8a, 8b, 9, 10, 14, 15	ERC 2		

Activity	Chemical product	Process category (PC)	Environmental	Sector of use	Article category
	category (PC)		release category (ERC)	category (SU)	(AC)
Coatings and inks application – industrial covers the use in coatings (paints, inks, adhesives, etc.) including exposures during use	PC 1, 9a, 9b, 18, 23, 24, 31, 32, 35, 39	PROC 1, 2, 3, 4, 5, 7, 8a, 8b, 9, 10, 13, 15, 19	ERC 2, 4, 5		
Use at industrial sites					
Converting	PC 32	PROC 4, 6, 7, 8a, 8b, 9, 10, 13, 14, 15, 16, 21, 22, 24, 25	ERC 2, 3, 4, 5	SU 10, 12	
Thermoplastic used in construction	PC 32	PROC 14, 21	ERC 10a, 11a	SU 12	
Wood plastic composite	PC 32	PROC 14, 21	ERC 10a, 11a	SU 12	
Foam production for construction	PC 32	PROC 3, 21	ERC 3, 10a, 11a	SU 12	
Formulation Polyester and S102E > liquid filled dispersion	PC 32	PROC 3, 4, 5, 8a, 8b, 9, 15, 26	ERC 2, 3, 5, 6b	SU 10	
Filled dispersion used in construction	PC 32	PROC 1, 3, 5, 6, 7, 10, 11, 13, 19, 21	ERC 3, 4, 5, 6b, 6d, 8f, 10a, 10b	SU 12	
Filled dispersion used in transportation	PC 32	PROC 1, 3, 5, 6, 7, 10, 11, 13, 19, 21	ERC 3, 4, 5, 6b, 6d, 8f, 10a, 10b	SU 12	
Transformation	PC 32	PROC 3, 4, 5, 6, 7, 8a, 8b, 10, 12, 14, 21, 25	ERC 5, 10a, 11a	SU 5, 12	
Recycling	PC 32	PROC 1, 2, 3, 14, 21, 24	ERC 2, 3, 4, 5		
Coating used in textile backcoating	PC 34	PROC 3, 6, 7, 8b, 9, 10, 13, 19	ERC 5, 11a		
Coating used in textile	PC 1, 8, 9a, 18, 20, 26, 28, 32, 35	PROC 5, 7, 9, 10, 11, 13, 21	ERC 2, 3, 4, 5, 6b, 7, 8a, 8c, 8d	SU 5, 6b, 10, 19	
Coatings – Industrial application of coatings		PROC 5, 8b, 9, 10, 13, 15	ERC 2, 5, 6d		
Industrial composites manufacturing	PC 32	PROC 1, 3, 4, 5, 7, 8b, 10, 13, 14, 15	ERC 2, 6d	SU 12	
Adhesive & sealants	PC 1	PROC 3, 4, 5, 8a, 8b, 9	ERC 2, 8c	SU 10, 19	
Coating and inks application – industrial: covers the use in coatings (paints, inks, adhesives, etc.) including exposures during use	PC 1, 9a, 9b, 18, 23, 24, 31, 32, 35, 39	PROC 1, 2, 3, 4, 5, 7, 8a, 8b, 9, 10, 13, 15, 19	ERC 2, 4, 5	SU 11, 12, 14, 15, 16, 17, 19	

Activity	Chemical product category (PC)	Process category (PC)	Environmental release category (ERC)	Sector of use category (SU)	Article category (AC)
Wire and cable used in automotive	PC 32	PROC 14, 21	ERC 10a, 11a	SU 12	
Thermoplastic used in automotive	PC 32	PROC 14, 21		SU 12	
Used by professional workers	1		•	•	-
Professional application of coatings		PROC 5, 8a, 9, 10, 13, 19	ERC 8c		
Professional composites manufacturing	PC 9b, 32	PROC 19	ERC 8c, 8f	SU 12	
Coating and inks application - professional: covers the use in coatings (paints, inks, adhesives, etc.) including exposures during use	PC 1, 9a, 9b, 18, 23, 24, 31, 32, 35, 39	PROC 1, 2, 3, 4, 5, 7, 8a, 8b, 9, 10, 11, 13, 15, 19	ERC 8c, 8f, 10a, 11a	SU 11, 12, 14, 15, 16, 17, 19	
Consumer uses	1		-	•	-
Coating and inks application - consumer: covers the use in coatings (paints, inks, adhesives, etc.) including exposures during use	PC 1, 9a, 9b, 18, 23, 24, 31, 32, 35, 39		ERC 8c, 8f, 10a, 11a		
Article service life	•		1	1	1
Converting		PROC 14, 21, 22, 24, 25	ERC 2, 3, 4, 5		AC 2, 13
Thermoplastic used in construction		PROC 14, 21	ERC 11a		AC 1
Wire and cable used in automotive		PROC 14, 21	ERC 10a, 11a		AC 1
Wood plastic composite		PROC 14, 21	ERC 10a, 11a		AC 11, 13
Foam production for construction		PROC 21	ERC 3, 10a, 11a		AC 13
Filled dispersion used in construction		PROC 21	ERC 3, 4, 5, 6b, 6d, 8f, 10a, 10b		AC 13
Filled dispersion used for transportation		PROC 21	ERC 3, 4, 5, 6b, 6d, 8f, 10a, 10b		AC 1
Transformation		PROC 14, 21, 25	ERC 5, 10a, 11a		AC 5, 13
Recycling		PROC 14, 21, 24	ERC 2, 3, 4, 5	AC 1, 5, 10, 13	
Coated used in textile backcoating			ERC 5, 11a	AC 1, 5, 10, 13	

Activity	Chemical product category (PC)	Process category (PC)	Environmental release category (ERC)	Sector of use category (SU)	Article category (AC)
Coating used in textile		PROC 21	ERC 2, 3, 4, 5, 6b, 7, 8a, 8c, 8d	AC 5, 6, 10	
Coatings and inks formulation		PROC 14	ERC 2	AC 1, 2, 5, 6, 8, 10, 13	
Coatings and inks application – professional: covers the use in coatings (paints, inks, adhesives, etc.) including exposures during use			ERC 2, 4, 5	AC 1, 2, 5, 6, 8, 10, 13	
Coatings and inks application—professional: covers the use in coatings (paints, inks, adhesives, etc.) including exposures during use			ERC 8c, 8f, 10a, 11b	AC 1, 2, 5, 7, 8, 10, 13	

# 9 Annex 3 – Background information on alternatives (literature)

### 9.1 Analysis in the Risk Reduction Strategy (RPA, 2003)

**Table 9-1** presents an overview of the suitability of the potential alternative FRs for textiles that was presented in the Risk Reduction Strategy for the substance. An indication of their relative cost compared to DecaBDE is provided, alongside a brief description of their main advantages and disadvantages.

Table 9-1: Overview of suitability, cost, advantages and drawbacks of selected potential alternatives to DecaBDE in textiles (based on RPA, 2003) Suitability of alternative flame retardants Relative Domestic Contract cost sector sector (please **Automotive** Alternative flame retardant CAS No. note, this Main advantages Main drawbacks Upholstery (hospitals, Filters for may no coverings Blackout curtains textiles and wall Blinds longer be accurate) Ethane-1.2-Very similar to Possibly poor colour for white 100% ✓ ✓ 84852-53-9 DecaBDE; no air coatings; comparatively unknown bis(pentabromophenyl) (EBP) higher emissions technically Hexabromocyclododecane ✓ ✓ ✓ ✓ ✓ Some experience in its Less insoluble than DecaBDE; less 25637-99-4 50% higher (HBCD) effective on man-made fibres use Cotton: poor durability, non-Easy application; no Ammonium polyphosphate washable Similar compounding (APP) Man-made fibres: much higher necessary; quite cheap loads, poorer effects, non-durable 68333-79-9 Microencapsulated 100% ammonium polyphosphate ✓ ✓ Can be compounded Poor durability, not washable higher (mAPP) Tris(chloropropyl) phosphate Little effect as a FR. not chosen on (and similar phosphates) 13674-84-5 Used only as plasticiser safety grounds (TCPP) ✓ ? Limited use in seat fillers: 7723-14-0 Red phosphorous hazardous In-✓ Cheap filler, relatively Little real FR effect, potentially 106-78-1 Melamine expensive insoluble poor fabric handle ✓ Cheap filler, relatively Little real FR effect, potentially 21645-51-2 ✓ ✓ **√** Aluminium trihydroxide (ATH) Ininsoluble poor fabric handle

Table 9-1: Overview of suitability, cost, advantages and drawbacks of selected potential alternatives to DecaBDE in textiles (based on RPA, 2003)

		Suita Domestic sector		Contract sector				ants	Relative cost (please		
Alternative flame retardant	CAS No.	Upholstery	Filters for cookers	Blinds	Blackout curtains	Upholstery (hospitals, etc.)	Automotive textiles	Geotextiles and wall coverings	note, this may no longer be accurate)	Main advantages	Main drawbacks
									expensive		
N-hydromethyl-3 dimethylphosphonpropionami de	20120-33-6	✓				<b>✓</b>			Costly (multi- stage)	Good durability, innocuous on fibre	Only for 100% cotton; high volume waste; low fixation efficiency; air emissions worse than DecaBDE
Tetrakis methylhydroxy phosphonates	124-64-1					<b>✓</b>			Costly (multi- stage)	Good durability, innocuous on fibre; extensive toxicity data	Only for 100% cotton; needs curing,; poor fabric handle

Source: RPA (2003)

#### 9.2 Analysis by Keml – 2004, 2005, 2009

#### 9.2.1 Alternatives for plastics

KemI provided an extensive presentation of chemical alternatives to DecaBDE in polymer products (KemI, 2005). The general categories of alternatives have included:

- Halogenated FRs: these may include TBBPA, shortened TBBPA, hexabromocyclododecane (HBCD)
- Phosphorous containing FRs: these may include phosphines, phosphine oxides, phosphonium compounds, elemental red phosphorous and phosphates. It is noted that in some cases phosphorous/halogen compounds are used to increase the effectiveness of the FR or act (in parallel) as plasticisers. Relevant matrices for phosphoric acid esters, such as aryl phosphates and their alkyl-substituted derivatives, mentioned by Keml include PVC, PA and polyethylene ether (PPE). Phosphorinanes are used for transparent formulations, for example in polymethylmetacrylate (PMMA)
- **Inorganic non-phosphorous flame-retardants**: these include aluminium hydroxide and boron containing compounds that affect the combustion process of plastics by physical means
- Smoke suppressants: these are generally systems that lead to the formation of glassy coatings or intumescent foams or dilution of the combustible material, which prevents further formation of pyrolysis products and hence smokes. Such systems are of particular relevance to transportation applications of DecaBDE. Common additives are aluminium hydroxide, magnesium hydroxide and calcium carbonate.

The following table summarises the range of potential alternatives for DecaBDE in polymers by plastic material, as identified by Keml.

Table 9-2: Overvie	Table 9-2: Overview of alternative substances for polymer applications of DecaBDE by Keml (2005)					
Plastic material	Other commercial halogenated FRs	Commercial non-halogen FRs				
Polyolefins	Brominated paraffins	Alumina trihydrate				
(for instance	Brominated polystyrene	Ammonium polyphosphate				
polyethylene and	Chlorinated paraffins	Barium metaborate dithiopyrophosphate				
polypropylene)	Hexabromocyclododecane	Magnesium hydroxide				
	Octabromodiphenyl oxide	Neoalkoxy tri (dioctyl phosphate) titanate				
	Pentabromodiphenyl oxide	Red phosphorous (encapsulated)				
		Sodium antimonite				
		Zinc borate				

Table 9-2: Overvie	w of alternative substances for polymer	applications of DecaBDE by Keml (2005)
Plastic material	Other commercial halogenated FRs	Commercial non-halogen FRs
Polystyrene	Brominated polystyrene Chlorinated paraffins Chlorinated polystyrene Dibromoethyl dibromocyclohexane Hexabromocyclododecane Octabromodiphenyloxide Pentabromochlorocyclohexane Pentabromodiphenyl oxide Pentabromomethyl benzene Pentabromomethyl benzoate Trichloromethyltetrabromobenzene Tris(betachloropropyl) phosphate	Alumina trihydrate Ammonium polyphosphate Barium metaborate Cresyl diphenyl phosphate Magnesium hydroxide Neoalkoxy tri(dioctyl phosphate) titanate Octyl diphenyl phosphate Red phosphorous (encapsulated) Sodium antimonite Tributoxy ethyl phosphate Tributyl phosphate Tricresyl phosphate
	Tris(dichloropropyl) phosphate	Tris(isopropylphenyl) phosphate Trixylenyl phosphate Zinc borate
PVC (polyvinylchloride)	Brominated paraffins Chlorinated paraffins Pentabromodiphenyl oxide Tris(betachloropropyl) phosphate Tris(dichloropropyl) phosphate Vinyl bromide	Alumina hydrate Ammonium polyphosphate Barium metaborate T-butyl phenyl diphenyl phosphate Cresyl diphenyl phosphate Diisopropylphenyl phosphate Isodecyl diphenyl phosphate Magnesium carbonate Magnesium hydroxide Molybdic oxide Neoalkoxy tri(dioctyl phosphate) titanate Octyl diphenyl phosphate Red phosphorous (encapsulated) Sodium antimonite Tributoxy ethyl phosphate Tricresyl phosphate Tricresyl phosphate Tris(isopropylphenyl) phosphate Trioctyl phosphate Trioctyl phosphate Triphenyl phosphate Trixylenyl phosphate Trixylenyl phosphate Trixylenyl phosphate Zinc borate
ABS (acrylonitrile- butadiene-styrene terpolymer)	Brominated polystyrene Chlorinated paraffins Halogenated hydrocarbons Octabromodiphenyl oxide Pentabromodiphenyl oxide Pentabromomethyl benzene Pentabromophenyl benzoate Polyvinyl chloride Tetrabromobisphenol-A Trichloromethyl tetrabromobenzene Tris(tribromophenoxy)ethane	Alumina hydrate Ammonium polyphosphate Barium metaborate Magnesium hydroxide Octyl diphenyl phosphate Red phosphorous (encapsulated) Sodium antimonite Triphenyl phosphate Zinc borate

Table 9-2: Overview of alternative substances for polymer applications of DecaBDE by Keml (2005)					
Plastic material	Other commercial halogenated FRs	Commercial non-halogen FRs			
Unsaturated	Chlorinated paraffins	Alumina trihydrate			
polyesters	Chlorendic anhydride	Ammonium polyphosphate			
	Dibromoneophenyl glycol	Barium metaborate			
	Hexabromocyclododecane	Calcium sulphate			
	(Pentabromobenzyl)acrylate	Di-(polyoxoethylene) hydromethyl			
	Pentabromodiphenyl oxide	phosphonate			
		Magnesium carbonate			
		Magnesium hydroxide			
		Molybdic oxide			
		Neoalkoxy tri(dioctyl phosphate) titanate			
		Red phosphorous (encapsulated)			
		Sodium antimonite			
Epoxy resins	Brominated polystyrene	Alumina trihydrate			
	Chlorinated paraffins	Ammonium phosphate			
	Chlorendic anhydride	Barium metaborate			
	Dibromopentyl glycol	T-butyl phenyl diphenyl phosphate			
	Pentabromophenol	Cresyl phenyl phosphate			
	Pentabromodiphenyl oxide	Neoalkoxy tri(dioctyl phosphate) titanate			
	Tetrabromobisphenol-A	Octyl diphenyl phosphate			
	Tetrachlorobisphenol-A	Red phosphorous (encapsulated)			
	Tetrachlorophthalic anhydride	Sodium antimonite			
	Tribromophenol	Tributoxyethyl phosphate			
	Tris(betachloroethyl) phosphate	Tributyl phosphate			
	Tris(dichloropropyl) phosphate	Tricresyl phosphate			
		Tripropylphenyl phosphate			
		Trixylenyl phosphate			
		Zinc borate			
Polyurethanes	Brominated paraffins	Alumina trihydrate			
	Chlorendic anhydride	Aluminium hydroxide			
	Chlorinated paraffins	Ammonium polyphosphate			
	Dibromoethyl dibromocyclohexane	Ammonium bromide			
	Dibromoneopentyl glycol	Barium metaborate			
	Hexabromocyclododecane	T-butyl phenyl diphenyl phosphate			
	Hexachloroendomethylenetetrahydro-	Cresyl diphenyl phosphate			
	phthalic acid (HET acid)	O,O-diethyl-1-N-N bis(2-hydroxyethyl)			
	Pentabromodiphenyl oxide	aminomethyl phosphonate			
	Pentabromophenol	Di-(polyoxyethylene)hydroxymethyl			
	Tetrabromophthalic anhydride	phosphonate			
	Tetrachlorophthalic anhydride	Magnesium hydroxide			
	Tetrabromoneopentyl alcohol	Molybdic oxide			
	Tris(betachloroethyl) phosphate	Neoalkoxy tri(dioctyl phosphate) titanate			
	Tris(dichloropropyl) phosphate	Octyl diphenyl phosphate			
	Tris(chloropropyl) phosphate	Red phosphorous (encapsulated)			
	Trixenyl phosphate	Sodium antimonate			
		Tricresyl phosphate			
		Triethyl phosphate			
		Triethyl phosphate Triisopropyl phenyl phosphate			

#### 9.2.2 Alternatives for textiles

For textiles and alternatives to DecaBDE, one year earlier, KemI had also generated a similar analysis. According to KemI (2004), the key alternatives to DecaBDE could be grouped into the following categories:

- Organic phosphorus compounds or phosphorus chlorine compounds
- Aluminium and zinc hydrate
- Swelling (intumescent) systems
- New synergistic combinations, for example antimony bromine/phosphorus silicon
- Surface-active fibre systems
- Systems with graft copolymers.

KemI also suggested that, alternatively, the effect of the FR could be maximised by developing surface-active fibre systems, for example systems with graft copolymers which may have low flammability in themselves. KemI had found that, at the time, there were no established commercial effective total replacements, although the concentrations of antimony: DecaBDE could be reduced by partially replacing them with phosphorous-based systems. In some papers, it had been hypothesised that total replacement might be possible with phosphorous-based systems if they become liquid, either when they melt or by decomposing into liquid substances during the initial pyrolysis. This would mean that the textile substrate is wetted and the FR effect is transferred to the front of a back coating (KemI, 2004). Examples of alternatives are shown in **Table 9-3**.

Fibre	Protection against fire	Treatment
Natural fibres		
Cotton	Organophosphorous and nitrogen- containing monomers or	F
	reactive groups.	
	Antimony-organohalogen systems	F
	Examples: Dimethylphosphono (N-methylol) propionamide;	
	Tetrakis(hydroxymethyl)phosphonium urea ammonium salt	
Wool	Zirconium hexafluoride complex	F
Regenerated fibres	;	
Viscose	Flame-retardant additives: organophosphorous and	Α
	nitrogen/sulphur-containing;	
	polysilicic acid complex	Α
Synthetic fibres		
Polyester	Organophosphorous components	C/A
	Example: polyethylene terephthalate, with built-in phosphorus	
Modacrylic	Halogenated compounds (35-50 % w/w)	С
Polypropylene	Halo-organic compounds usually as bromine derivative	Α
Polyurethane	Tris(1-chloro-2-propyl) phosphate (TCPP)	
foams	Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)	
	Tris(2-chloroethyl) phosphate (TCEP)	
Polyamide	Additive phosphorus chemicals that are added at the time of fibre	
	spinning and are thus built into the polyamide from the start	
Flame-resistant fib	res	•
Polyhaloalkenes	Polyvinyl chloride	Н
	Polyvinylidene chloride	

Table 9-3: Overview	Table 9-3: Overview of alternative substances for textile applications of DecaBDE by Keml (2004)				
Fibre	Protection against fire	Treatment			
Poly(aramide- arimide)		Ar			
Polybenzimidazole		Ar			
Carbonised acrylic		Ar			

Source: Keml (2004) F: chemical post-treatment

A: additive in fibre melt spinning
C: modified copolymer. Copolymers are made up of two or more different monomers.

H: homopolymers constructed as a single type of monomer.

Ar: aromatic homo- or copolymer

KemI also provided information on intumescent (swelling) systems, which, it suggested, found applications in mattress covers, furniture upholstery and protective clothing. It was noted that the effect of intumescent systems in connection with fire depends on the type and added quantity of the intumescent system. Intumescence does not just relate to specific systems based on expanded graphite. This property also exists in a number of fibres present in textiles. Wool is an example (KemI, 2004).

Intumescent systems consist of three components:

- Acid source
- Carbon source
- Gas source.

The acid acts as a catalyst when the carbon source decomposes with the formation of gas, for example water vapour. The acid may also be a compound that forms acid in contact with heat. The carbon source consists of polyols (polyalcohols) that lose their hydrogen to form a "carbon foam" of suitable density and thickness to create good safety against continued spread of fire. The gas source is the third component. Gases are formed that are not combustible - for example hydrochloric acid, ammonia, water or carbon dioxide – depending on what the chemical system is like (Keml, 2004). The composition of intumescent systems depends on each specific situation (Keml, 2004):

- Desired flame-retardant properties
- Polymer composition in application concerned
- Any presence of fillers and additives in the polymer systems concerned.

The most common intumescent systems are listed in **Table 9-4** below.

Component	Example substance
Dehydrating substance:	Monoammonium phosphate
Carbonising substance that releases acid for esterification of	Diammonium phosphate
hydroxyl groups	Ammonium polyphosphate
nyuroxyr groups	Melamine phosphate
	Guanyl urea phosphate
	Urea phosphate
	Diammonium sulphate
	Ammonium tetraborate
Carbonising substance:	Polyols
Carbonising substance: Contains large quantities of carbon.	Erythritol
Thermal decomposition results in carbon skeleton	Pentaerythritol
Thermal decomposition results in carbon skeleton	Pentaerythritol dimer
	Pentaerythritol trimer
	Arabitol
	Sorbitol
	Inositol
	Polyhydrophenols
	Resorcinol
	<u>Sugars</u>
	Glucose
	Maltose
Gas sources:	Dicyandiamide
Produce non-combustible gases in connection with thermal	Melamine
decomposition	Guanidine
uecomposition	Glycin
	Urea
	Chloroparaffins

KemI noted that intumescent systems require special handling in application, for example on a backcoating, so that they work as intended. As the three-component system is stable and in solid form, it is important to find the best conditions and combinations of the three different components in an evenly and well-distributed dispersion in the textile application to achieve the desired flame protection (KemI, 2004).

#### 9.2.3 Later review of alternatives (2009)

In 2009, Keml reviewed a number of reports (by the Danish EPA, JRC, SFT, Washington State, Environment Agency for England and Wales, and Keml) and provided an overview of alternatives which is reproduced here as **Table 9-5**.

CAS Number	iew of alternative substances for Dec Alternative substance	Areas of application
	Aiternative substance	Areas of application
Inorganic FRs		
7723-14-0	Red phosphorous	Polyolefins, Polystyrene, PVC, ABS, Polyamide, Polycarbonate, SAN, Unsaturated polyester resin, Epoxy, Polyurethane, Rubber
68333-79-9	Ammonium polyphosphate	Polyolefins, Polystyrene, PVC, ABS, Polycarbonate, Unsaturated polyester resin, Epoxy, Polyurethane, Textile
1309-42-8	Magnesium hydroxide	Polyolefins, Polystyrene, PVC, ABS, Polycarbonate, Unsaturated polyester resin, Polyurethane, Rubber, Textile
21645-51-2	Aluminium hydroxide	Polyolefins, Polystyrene, PVC, ABS, Polycarbonate, Unsaturated polyester resin, Epoxy, Polyurethane, Textile
1332-07-6	Zinc borate	Polyolefins, Polystyrene, PVC, ABS, Polycarbonate, Polyurethane, Epoxy resin
	Zinc molybdates	PVC
1303-96-4	Other boron compounds, borax (sodium tetraborate)	Textile
13701-59-2	Barium metaborate	Polyolefin, Polystyrene, PVC, ABS, Polycarbonate, Unsaturated polyester resin, Epoxy, Polyurethane
16923-95-8	Potassium zirconium hexafluoride	Wool
12027-96-2	Zinc hydroxyl stannate	PVC, Epoxy resins, Polyurethane
12036-37-2	Zinc stannate	
Organic FRs		
868-85-9	Dimethyl hydrogen phosphite (DMHP)	Textile
18755-43-6	Dimethylpropanphosphonate (DMPP)	PUR, UPE
78-40-0	Triethyl phosphate	PVC, Polyurethane, Unsaturated polyester
68937-41-7	Aryl phosphates, such as Tris (isopropyl phenyl) phosphate	Polystyrene, PVC, Epoxy, Polyurethane paint and varnish, Textiles
57583-54-7	Resorcinol bis(diphenyl-	Polycarbonate, ABS
125997-21-9	phosphate) (RDP)	,
181028-79-5	Bisphenol-A bis (diphenyl	PC/ABS, PPE/HIPS, ABS,HIPS, PPE/PC
5945-33-5	phosphate) (BDP, BAPP)	
26444-49-5	Cresyl diphenyl phosphate	Polystyrene, Epoxy, Polyurethane, PC/ABS, PF
115-86-6	Triphenyl phosphate	PVC, PC/ABS, PPO, Phenolic resins
68937-40-6	Triaryl phosphate, butylated phosphinates	PVC, Epoxy resins, Polyurethane, PC/ABS
225789-38-8	Aluminium diethylphosphinate	Epoxy resins, PA, PBTE
115-96-8	Tris (2-chloroethyl) phosphate (TCEP)	Polystyrene, PVC, Epoxy resins, Polyurethane
13674-87-8	Tris (1,3-dichloro isopropyl) phosphate (TDCP)	Polystyrene, PVC, Epoxy resins, Polyurethane
13674-84-5	Tris (2-chloroisopropyl) phosphate (TCPP or TMCP)	Polystyrene, PVC,PC, Epoxy resin, Polyurethane, Textiles

CAS Number	Alternative substance	Areas of application
27104-30-9	Tetrakishydroximetyl- phosphonium chloride	Textile
218768-84-4	Melamine polyphosphate	PA, TPU
20120-33-6	Dimetylphosphonomethylol- propionamide	Textile
5301-78-0	Mixture of pentaerythritol	PP
41583-09-9	phosphate alcohol and	
14808-60-7	melamine phosphate and quartz	
5423-23-4	Diguanidine hydrogen phosphate	Textile
3194-55-6	Hexabromocyclododecane	Polyolefins, PS, Unsaturated polyester, Polyurethane
25637-99-4	(HBCD)	
84852-53-9	Decabromodiphenyl ethane	ABS, HIPS,PA, PBTE/PET, PC, PP, PE, SAN, PC/ABS, HIPS/PPE,TPU, Silicon, PVC, EPDM
37853-59-1	1,2-Bis (2,4,6 -	HIPS, ABS, PC, UPE
	tribromophenoxy) ethane	
58965-66-5	1,2,4,5-Tetra Bromo-3, 6 bis	ABS, HIPS, PA, PBTE/PET, PC, PP, PE, SAN, PC/ABS,
	(pentabromophenoxy) benzene	HIPS/PPE, Silicon, EPDM
79-94-7	Tetrabrombisphenol-A (TBBPA)	ABS, HIPS, PC, Epoxy resins
21850-44-2	Tetrabromobisphenol-A bis (2,3-dibrompropyleter)	HIPS, PP, PE, Crystalline PS
94334-64-2	Tetrabromobisphenol-A	PBTE/PET, PC, ABS, Polysulphone, SAN
71342-77-3	carbonate oligomers	
40039-93-8	Tetrabromobisphenol-A	
	epichlorohydrin polymer	
77098-07-8	Tetrabromophthalate diol	
68928-70-1	Brominated epoxy resin	PBTE, HIPS, ABS, PC/ABS, PA
88497-56-7	Brominated polystyrene	PS, ABS, PA, Epoxy resins
57137-10-7	, , ,	
148993-99-1		
59447-57-3	Poly (pentabromobenzyl acrylate)	PBTE/PET/PCT, PA, Styrene copolymer, PP, HIPS/PPC
593-60-2	Vinyl bromide	PVC
	Bromoalkyl phosphates	PUR
32588-76-4	Ethylene bis (tetrabromo phthalimide)	ABS, HIPS, PBTE/PET, PC, PP, PE, SAN, PC/ABS, HIPS/PPE, Thermoplastic elastomer, Silicon, PVC, EPDM
25713-60-4	Tris (tribromophenoxy) triazine	PE, ABS, HIPS
63449-39-8	MCCPs	Polyolefins, PS, PVC, ABS, UPE, Epoxy resins,
85535-85-9		Polyurethane
13560-89-9	Dodecachlorododeca hydrodimethanodibenzo cyclooctene (Dechlorane Plus)	PA, ABS, PP, Epoxy resins
108-78-1	Melamine	PUR, Textile
37640-57-6	Melamine cyanurate	PA, Thermoplastics, PUR

#### 9.3 Analysis by the Danish EPA – 2006

The Danish EPA undertook an extensive analysis of the market for alternative substances to DecaBDE. A summary of the applicability of the identified substances is shown in **Table 9-6**. The 'plus' signs indicate the perceived applicability/compatibility of different chemical alternatives to DecaBDE. It has to be noted that DecaBDE is not necessarily used in all polymer matrices shown in this table.

#### 9.4 Analysis by Troitzsch – 2011

An analysis of the availability of alternatives for DecaBDE in polymer was published by Troitzsch in 2011. **Table 9-7** summarises the relevant entries but is limited to alternatives that can achieve the maximum flame retardancy rate UL94 V-0. The table is dominated by E&E applications of DecaBDE which are mostly outside the scope of this analysis (due to the provisions of the RoHS Directive). Hence, they are marked in red colour.

#### 9.5 Analysis by the US EPA - 2012-2014

In 2012, the US EPA published the draft of an extensive study on alternatives for DecaBDE; the report was issued in its final form in 2014. An overview of the availability of alternatives by polymer matrix type and area of application is shown in **Table 9-8**. E&E applications which are currently covered by the provisions of the RoHS Directive have been marked in red colour.

#### 9.6 Analysis by the UK HSE – 2012

The proposal for inclusion of DecaBDE to the Candidate List by the UK HSE in 2012 included a list of alternatives that could potentially be considered as a replacement for DecaBDE. A table detailing the applicability and compatibility of each of a group of 28 alternatives is available and is reproduced here as **Table 9-9**. Because the UK HSE has used information from previously generated reports, some overlap with work undertaken by, e.g. the Danish EPA, is evident.

Table 9-6: Overview of alternative subs	stances	for po	lymer app	olicatio	ons of E	DecaBD	E by th	ne Dani	ish EP <i>A</i>	A (2006	5)								
Alternative substance	ABS	HIPS	Other PS	РА	PBTE/PET	PC	ЬР	PE	PC/ABS	HIPS/PPE	PPO	Engineering thermoplastics	PUR foams	Thermoplastic elastomers	EPDM	PE/EVA	PVC	PF	Silicone
Ethane-1,2-bis(pentabromophenyl)	+	+	SAN	+	PBTE /PET	+	+	+	+	+	-	-	-	+	+	-	+	-	-
Ethylene bis(tetrabromophthalimide)	+	+	SAN	-	PBTE /PET	+	+	+	+	+	-	-	-	+	+	-	+	-	+
Bis(tribromophenoxy)ethane	+	+	-	-	-	+	-	-	-	-	-	UPE	-	-	i	-	-	-	-
Tetradecabromodiphenoxybenzene	+	+	SAN	+	PBTE /PET	+	+	+	+	+	-	-	-	-	+	-	-	-	+
Tetrabromobisphenol-A (TBBPA)	+	+	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-
Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	-	+	Crystal PS	-	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-
Brominated polystyrene	-	-	-	+	PBTE /PET /PCT	-	+	-	+	-	-	-	-	-	-	-	-	-	-
Poly(dibromostyrene)	-	-	-	+	PBTE /PET	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Brominated epoxy polymer	+	+	-	-	PBTE	-	-	-	+	-	-	-	-	-	-	-	-	-	-
Poly pentabromobenzyl acrylate	-	-	Copoly mers	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol-A	+	-	SAN	-	+	+	-	-	+	-	-	Poly sulpho ne	-	-	ı	ı	ı	ı	-
Tris(tribromophenoxy) triazine	+	+	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-
Dodecachloro dodecahydro dimethano dibenzocyclooctene	+	-	-	+	-	-	+	-	ı	-	-	Ероху	-	-	-	ı	-	-	-
Resorcinol bis(diphenylphosphate) (RDP)	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
Bisphenol-A bis(diphenyl phosphate) (BAPP)	-	-	-	-	-	-	-	-	+	+	-	-	-	-	-	-	-	-	-

Alternative substance	ABS	HIPS	Other PS	РА	PBTE/PET	PC	рр	PE	PC/ABS	HIPS/PPE	ЬРО	Engineering thermoplastics	PUR foams	Thermoplastic elastomers	EPDM	PE/EVA	PVC	PF	Silicone
Bisphenol-A bis(diphenyl phosphate) (BDP)	+	+	-	-	-	PC/ PPE	-	-	-	-	-	-	-	-	-	-	-	-	-
Cresyl diphenyl phosphate (CDP)	-	-	-	-	-	-	-	-	+	-	-	Ероху	+	-	-	-	-	+	-
Triphenyl phosphate (TPP)	-	-	-	-	-	-	-	-	+	1	M o di fi e d	Phenoli c	-	-	-	-	-	-	-
Triaryl phosphates butylated	-	-	-	-	-	-	-	-	+	1	-	-	-	-	-	-	-	-	-
Magnesium hydroxide	-	_	-	-	-	-	+	+	-	-	-	+	-	+	+	+	+	-	-
Red phosphorous	-	-	-	+	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-
Ammonium polyphosphate	-	-	-	+	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-
Melamine polyphosphate	-	-	-	+	-	-	-	-	-	-	-	TPU	-	-	-	-	-	-	-
Melamine cyanurate	-	-	-	+	-	-	-	-	-	1	-	PUR	-	-	-	-	-	-	-
Organic phosphinates	-	-	-	+	PBTE	-	-	-	-	1	-	-	-	-	-	-	-	-	-
Reogard 1000	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-

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Category	Material	Area of application – FR standard met	Halogenated alternatives	Halogen-free alternatives
	Polyethylene (PE)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO Tris(bromoneopentyl) phosphate/ATO	Intumescent system based on phosphorous/nitrogen compounds Red phosphorous and halogen-free FR Red phosphorous
	Polypropylene (PP)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO TBBPA (2,3-dibromopropyl ether)/ATO Brominated epoxies/ATO Chloroparaffin/ATO	Intumescent system based on phosphorous/nitrogen compounds  Magnesium hydroxide
	High impact polystyrene (HIPS)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO Brominated epoxies /ATO Tetrabromobisphenol-A/ATO Chloroparaffin/ATO	
	Acrylonitrile/butadiene/ styrene (ABS)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO Brominated epoxies /ATO Tetrabromobisphenol-A /ATO	
	Polyethylene terephthalate (PET)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Brominated epoxies /ATO Ethylene bis(tetrabromophthalimide)/ATO TBBPA carbonate oligomer/ATO	Red phosphorous  Metal phosphinate
	Polybutylene terephthalate (PBTE)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO Brominated epoxies/ATO TBBPA carbonate oligomer/ATO	Metal phosphinate  Melamine poly aluminium and zinc phosphates
	Polycarbonate (PC)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO TBBPA carbonate oligomer/ATO Tetrabromobisphenol-A reactive	Sulphonate salts Triphenyl phosphate Resorcinol bis(diphenyl phosphate) Bisphenol-A bis(diphenyl phosphate) Polyphosphonates
	Polycarbonate/ABS blend (PC/ABS)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO	Resorcinol bis(diphenyl phosphate) Bisphenol-A bis(diphenyl phosphate)

Category	Material	Area of application – FR standard met	Halogenated alternatives	Halogen-free alternatives
			TBBPA carbonate oligomer/ATO Brominated epoxies/ATO	Triphenyl phosphate Polyphosphonates
	Polyphenylene ether/high impact polystyrene blend (PPE/HIPS)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO TBBPA carbonate oligomer/ATO	Resorcinol bis(diphenyl phosphate) Bisphenol-A bis(diphenyl phosphate) Triphenyl phosphate
Thermosets	Epoxy resins (EP)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO	Aluminium hydroxide Aluminium hydroxide/Ammonium polyphosphate Red phosphorous Phosphorous polyol
	Unsaturated polyester resins (UP)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO Tetrabromobisphenol-A reactive Chloroparaffin/ATO Hexachloroendomethylenetetrahydrophthalic acid, Tris(chloropropyl) phosphate	Aluminium hydroxide Aluminium hydroxide/ Red phosphorous Aluminium hydroxide/Ammonium polyphosphate Dimethylpropane phosphonate Dimethylpropane phosphonate+ Intumescent system based on ethylenediamino phosphate
Thermoplastic elastomers	Thermoplastic polyester elastomers (TPE-E)	Wires and cables – VW 1	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO	Melamine cyanurate Metal phosphinate Polyphosphonates
	Thermoplastic styrene-block copolymers (TPE-S)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO	Intumescent system based on phosphorous/nitrogen compounds
	Thermoplastic polyurethanes (TPU)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO Ethylene bis(tetrabromophthalimide)/ATO Tris(chloropropyl) phosphate/ Melamine cyanurate	Melamine cyanurate Expandable graphite Cresyldiphenyl phosphate Resorcinol bis(diphenyl phosphate) Bisphenol-A bis(diphenyl phosphate) Magnesium hydroxide
	Thermopolyolefins (TPO)	E&E – UL94 V-0	Decabromodiphenyl ethane/ATO	

Table 9-8: Overv	riew of alternative substances for polymer ap	plications of DecaBDE by the US EPA (2014	)		
Polymer category	Electronics	Cable and wire			
Chlorinated polyethylene (CPE)	<ul> <li>Bis(hexachlorocyclopentadieno) cyclooctane</li> <li>CONFIDENTIAL BROMINATED POLYMER</li> <li>Decabromodiphenyl ethane</li> </ul>	CONFIDENTIA     Decabromodij	ocyclopentadieno) cyclooctane L BROMINATED POLYMER ohenyl ethane etrabromophthalimide, EBTBI		
Polymer category	Electronics	Cable and wire	Public buildings		
	Aluminum diethylphosphinate     Bis(hexachlorocyclopentadieno) cyclooctane     CONFIDENTIAL BROMINATED POLYMER     Melamine polyphosphate (TPU)     Decabromodiphenyl ethane     Polyphosphonate     Poly[phosphonate-co-carbonate]     Substituted amine mixture (also TPU)     Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)     Zinc borate (EVA)	<ul> <li>Aluminum diethylphosphinate (also TPU)</li> <li>Alumina Hydroxide</li> <li>Ammonium polyphosphate</li> <li>Bis(hexachlorocyclopentadieno) cyclooctane</li> <li>CONFIDENTIAL BROMINATED POLYMER</li> <li>Decabromodiphenyl ethane</li> <li>Magnesium hydroxide (also EVA)</li> <li>Polyphosphonate</li> <li>Poly[phosphonate-co-carbonate]</li> <li>Red phosphorous</li> <li>Substituted amine mixture (also EVA, TPU)</li> <li>Zinc borate (EVA)</li> </ul>	Alumina hydroxide     Bis(hexachlorocyclopentadieno) cyclooctane     CONFIDENTIAL BROMINATED POLYMER     Melamine polyphosphate (TPU)     Decabromodiphenyl ethane     Magnesium hydroxide (also EVA)     Polyphosphonate     Poly[phosphonate-co-carbonate]     Substituted amine mixture (also EVA, TPU)     Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)     Zinc borate (EVA)		
Elastomers	Construction materials	Automotive	Aviation		
	Alumina hydroxide     Bis(hexachlorocyclopentadieno) cyclooctane     CONFIDENTIAL BROMINATED POLYMER     Melamine polyphosphate (TPU)     Decabromodiphenyl ethane     Ethylene bis-tetrabromophthalimide, EBTBI     Magnesium hydroxide (also EVA)     Polyphosphonate     Poly[phosphonate-co-carbonate]     Substituted amine mixture (also EVA, TPU)     Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)     Zinc borate (EVA)	<ul> <li>Aluminum diethylphosphinate</li> <li>Alumina hydroxide</li> <li>CONFIDENTIAL BROMINATED POLYMER</li> <li>Melamine polyphosphate (TPU)</li> <li>Decabromodiphenyl ethane</li> <li>Magnesium hydroxide (also EVA)</li> <li>Polyphosphonate</li> <li>Poly[phosphonate-co-carbonate]</li> <li>Substituted amine mixture (also EVA, TPU)</li> <li>Tetrabromobisphenol-A bis (2,3-dibromoprop ether)</li> <li>Zinc borate (EVA)</li> </ul>	<ul> <li>Aluminum diethylphosphinate</li> <li>Magnesium hydroxide (also EVA)</li> <li>Melamine polyphosphate (TPU)</li> <li>Polyphosphonate</li> <li>Poly[phosphonate-co-carbonate]</li> <li>Substituted amine mixture (also EVA, TPU)</li> <li>Zinc borate (EVA)</li> </ul>		

Polymer category	Electronics	Automotive	Waterborne and emulsion coatings		
Engineering Thermoplastic	<ul> <li>Aluminum diethylphosphinate (PA, PBTPBTE, PET)</li> <li>Bis(hexachlorocyclopentadieno) cyclooctane</li> <li>Brominated epoxy resin end- capped with tribromophenol (NYLON)</li> <li>Brominated polyacrylate (PA, PBT)</li> <li>Brominated polystyrene (PA, PBTE, PET, PES)</li> <li>CONFIDENTIAL BROMINATED POLYMER (ABS, HIPS)</li> <li>Melamine polyphosphate (PA, PBT)</li> <li>Resorcinol bis-diphenylphosphate, RDP (PC/ABS, PPE/HPS)</li> <li>Decabromodiphenyl ethane</li> <li>Ethylene bis-tetrabromophthalimide, EBTBI</li> <li>Polyphosphonate</li> <li>Poly[phosphonate-co-carbonate]</li> <li>Bisphenol-A bis-(diphenyl phosphate) (reaction products), BAPP, BDP or DPADP (PPE/HIPS, PC, PC/ABS)</li> <li>TBBPA glycidyl ether &amp; TBBPA polymers (NYLON, PBTE)</li> <li>Triphenyl phosphate (TPP) (PPE/HIPS, PC/ABS)</li> <li>Red phosphorous (PA, PA66 GF)</li> </ul>	<ul> <li>Aluminum diethylphosphinate (PA, PBTE, PET)</li> <li>Brominated polystyrene (PA)</li> <li>CONFIDENTIAL BROMINATED POLYMER</li> <li>Melamine polyphosphate (PA, PBTE)</li> <li>Decabromodiphenyl ethane</li> <li>Polyphosphonate</li> <li>Poly[phosphonate-co-carbonate]</li> <li>TBBPA glycidyl ether &amp; TBBPA polymers (NYLON, PBTE)</li> </ul>	<ul> <li>CONFIDENTIAL BROMINATED POLYMER</li> <li>Melamine polyphosphate (PA, PBTE)</li> <li>Decabromodiphenyl ethane</li> </ul>		
Polymer category	Electronics				
High-impact polystyrene (HIPS)	Bis(hexachlorocyclopentadieno) cyclooctane Brominated epoxy resin end- capped with tribrom CONFIDENTIAL BROMINATED EPOXY CONFIDENTIAL BROMINATED POLYMER Decabromodiphenyl ethane Ethylene bis-tetrabromophthalimide, EBTBI TBBPA glycidyl ether & TBBPA polymers (ABS, HIPS Tris(tribromophenoxy) triazine, Tris(tribromophen	5)			

Polymer category	Electronics	Cable and wire	Public buildings	Construction materials			
Polyethylene (PE)	Bis(hexachlorocyclopentadieno) cyclooctane CONFIDENTIAL BROMINATED POLYMER Decabromodiphenyl ethane Ethylene bistetrabromophthalimide, EBTBI Substituted amine mixture Zinc borate	<ul> <li>Alumina hydroxide</li> <li>Ammonium polyphosphate</li> <li>Bis(hexachlorocyclopentadieno) cyclooctane</li> <li>CONFIDENTIAL BROMINATED POLYMER</li> <li>Decabromodiphenyl ethane</li> <li>Ethylene bistetrabromophthalimide, EBTBI</li> <li>Magnesium hydroxide</li> <li>Substituted amine mixture</li> <li>Zinc borate</li> </ul>	Alumina hydroxide     Ammonium polyphosphate     Bis(hexachlorocyclopentadieno) cyclooctane     CONFIDENTIAL BROMINATED POLYMER     Decabromodiphenyl ethane     Ethylene bistetrabromophthalimide, EBTBI     Magnesium hydroxide     Substituted amine mixture     Zinc borate	Alumina hydroxide     Ammonium polyphosphate     Bis(hexachlorocyclopentadieno) cyclooctane     CONFIDENTIAL BROMINATED POLYMER     Decabromodiphenyl ethane     Ethylene bistetrabromophthalimide, EBTBI     Magnesium hydroxide     N-alkoxy hindered amine reaction products (thin films)     Substituted amine mixture     Zinc borate			
	Automotive	Aviation	Distribution and Storage				
	Alumina hydroxide     CONFIDENTIAL BROMINATED     POLYMER     Decabromodiphenyl ethane     Ethylene     bis(tetrabromophthalimide)     Magnesium hydroxide     Substituted amine mixture     Zinc borate	<ul><li>Magnesium hydroxide</li><li>Substituted amine mixture</li><li>Zinc borate</li></ul>	Ammonium polyphosphate     Brominated polyacrylate     CONFIDENTIAL BROMINATED EPO:     CONFIDENTIAL BROMINATED POLY     Decabromodiphenyl ethane     Ethylene bis-tetrabromophthalimic     Magnesium hydroxide     Melamine polyphosphate     Substituted amine mixture     Zinc borate	/MER			

Polymer category	Electronics	Cable and wire	Automotive		Distribution and Storage
Polypropylene (PP)	Ammonium polyphosphate     Bis(hexachlorocyclopentadieno) cyclooctane     Brominated polyacrylate     CONFIDENTIAL BROMINATED POLYMER     Decabromodiphenyl ethane     Ethylene bistetrabromophthalimide, EBTBP     Red Phosphorous     Substituted amine mixture     Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)     Tris(tribromoneopentyl) phosphate     Zinc borate	<ul> <li>Ammonium polyphosphate</li> <li>Bis(hexachlorocyclopentadieno) cyclooctane</li> <li>CONFIDENTIAL BROMINATED POLYMER</li> <li>Decabromodiphenyl ethane</li> <li>Ethylene bistetrabromophthalimide, EBTBP</li> <li>Magnesium hydroxide</li> <li>Red phosphorous</li> <li>Substituted amine mixture</li> <li>Zinc borate</li> </ul>	Ammonium poly     Brominated poly     CONFIDENTIAL B     POLYMER     Decabromodiphe     Ethylene bistetrabromophthe     Magnesium hydr     Substituted amir     Tetrabromobispledibromopropyl e     Zinc borate	acrylate BROMINATED enyl ethane alimide, EBTBP roxide ne mixture henol-A bis (2,3-	Ammonium polyphosphate     Brominated polyacrylate     CONFIDENTIAL BROMINATED POLYMER     Decabromodiphenyl ethane     Ethylene bistetrabromophthalimide, EBTBP     Magnesium hydroxide     Melamine polyphosphate     Substituted amine mixture     Zinc borate
Polymer category	Electronics	Public buildings		Construction	materials
Thermosets	Aluminum diethylphosphinate (EPC     Alumina hydroxide     Bis(hexachlorocyclopentadieno)     cyclooctane     Brominated polystyrene (thermose polyester)     CONFIDENTIAL BROMINATED POLY     Melamine polyphosphate (EPOXIES     Decabromodiphenyl ethane     Phosphonate oligomer     Red Phosphorous (EPOXIES)	Alumina hydroxide     Ammonium polyphospha     Bis(hexachlorocyclopent     CONFIDENTIAL BROMIN.     Melamine polyphosphat	adieno) cyclooctane ATED POLYMER e (EPOXIES,UPE) ane	<ul><li>Amm</li><li>Bis(he</li><li>CONF</li><li>Melar</li><li>Decak</li><li>Phosp</li></ul>	ina hydroxide onium polyphosphate exachlorocyclopentadieno) cyclooctane IDENTIAL BROMINATED POLYMER mine polyphosphate (EPOXIES,UPE) promodiphenyl ethane phonate oligomer A glycidyl ether & TBBPA polymers (UPE)

Table 9-9: Overview o	of alter	native	substa	ances f	or poly	mer a	pplicat	ions o	f Decal	BDE by	UK HS	E (201	2)							
Alternative substances	ABS	HIPS	PA	PBTE/PET	PC	ЬР	PE	SAN	PC/ABS	HIPS/PPO	Thermoplasti c Elastomers	Silicone	PVC	EPDM & rubbers	TPU	PE/EVA	Thermosets	Polysulphone	PUR	Hot melts
Ethane-1,2- bis(penta- bromophenyl); EBP	+	+	+	PBT E/PE T	+	+	+	+	+	+	+	+	+	+	+	+	Epoxy, Phenolics, UPE			
Ethylene bis(tetra- bromophthalimide)	+	+		PBT E/PE T	+	+	+		+	+	+	+	+	+	+	+	Epoxy, Phenolics, UPE			
Brominated epoxy oligomers/ polymers	+	+		PBT E/PE T					+											
Tetrabromobispheno I-A	+			PBT E/PE T	+												Epoxy, Phenolics, UPE, Vinyl esters			
Bis(tribromophenoxy ) ethane	+	+			+												UPE			
Tetrabromobispheno I-A bis (2,3- dibromopropyl ether); TBBPA-DBPE		+				+	+								+					
Tetrabromobispheno I-A carbonate oligomer	+			PBT E/PE T	+			+	+					+						
Tetradecabromodi- phenoxybenzene	+	+	+	PBT E/PE T	+	+	+	+	+	+		+		+						_
Tris(tribromophenox y) triazine	+	+		PBT E/PE T			+													
Brominated polystyrene			+	PBT E/PE T/PC T																

Table 9-9: Overview o	of alter	native	substa	ances f	or poly	mer a	pplicat	ions of	Decal	BDE by	UK HS	E (201	2)							
Alternative substances	ABS	HIPS	PA	PBTE/PET	PC	ЬР	PE	SAN	PC/ABS	HIPS/PPO	Thermoplasti c Elastomers	Silicone	PVC	EPDM & rubbers	TPU	PE/EVA	Thermosets	Polysulphone	PUR	Hot melts
Poly(pentabromo- benzyl acrylate); PBAM			+	PBT E/PE T					+	+										
Chloroparaffins: MCCPs LCCPs	+	+				+	+													
Dodecachlorododec a- hydrodimethanodi- benzocyclooctene; Dechlorane Plus	+		+			+											Ероху			
Tris (tribromoneopentyl) phosphate		+				+													+	
Resorcinol bis (diphenylphosphate) ; RDP		+	+	PBT E/PE T	+				+	+										
Bisphenol-A bis(diphenylphospha te); BDP; BAPP; BPADP					+				+	+					+					
Triphenyl phosphates; TPP Triaryl phosphates butylates									+	+							Phenolics			
Cresyl diphenyl phosphate; CDPP									+	+	+		Flexi ble				Phenolics			+

Alternative substances	ABS	HIPS	РА	PBTE/PET	PC	ЬР	PE	SAN	PC/ABS	HIPS/PPO	Thermoplasti c Elastomers	Silicone	PVC	EPDM & rubbers	TPU	PE/EVA	Thermosets	Polysulphone	PUR	Hot melts
Red phosphorous			+									+		+			Ероху			
Ammonium polyphosphate; APP						+	+									+	Epoxy, Phenolics, UPE, Acrylics, Vinyl Esters		+	
Diethylphosphinic acid, aluminium salt			+	PBT E/PE T							+				+		Ероху			
Diphosphoric acid compound with piperazine (1:1)						+	+				+			+	+	+	UPE			
Magnesium hydroxide						+	+				+	+	Flexi ble	+	+	+	Acrylic			
Aluminium trihydroxide; ATH							+				+	+	Rig/ Flexi ble	+	+	+	Epoxy, phenolics, UPE, vinyl esters, acrylic			+
Melamine cyanurate		+	+	PBT E		+				+					+	+	UPE			+
Melamine phosphate						+	+										Epoxy, phenolics, UPE			
Melamine polyphosphate		+	+	PBT E/PE T						+							Epoxy, phenolics, UPE, acrylics			
Expandable graphite											+			+						

# 9.7 EFRA Brochures – 2011, 2012

#### 9.7.1 Introduction

The European Flame Retardants Association (EFRA) has published a series of brochures on the use of FRs. These explain the applicability of different FR substances and could be construed to demonstrate the main alternatives to DecaBDE in applications such as:

- EEE
- Building and construction
- Textiles and upholstery.

The following tables summarise the useful information that may be extracted with a view to identifying technically feasible alternatives to DecaBDE.

#### 9.7.2 EEE

The relevant EFRA brochure includes overviews of the FRs that may potentially be used in applications such as:

- Cables and wires
- E&E enclosures
- Electronic connectors.

Only cables and wires are considered relevant to the replacement of DecaBDE and the relevant alternatives are shown in **Table 9-10**.

Table 9-10: Flame retardants that ma	y be used in cable	es and v	wires (l	pased o	n EFRA	(2011	))		
Potential alternative substance	CAS No.	PVC	NBR	SBR	Silicone rubber	EPDM	EVA	LDPE	рр
Isopropylated triphenyl phosphate based (IPPP)	28108-99-8	++	+	+	+				
Trixylyl phosphate (TXP)	25155-23-1	++							
Tricresyl phosphate (TCP)	1330-78-5	++							
Cresyl diphenyl phosphate (CDP)	26444-49-5		+	+	+				
Bisphenol-A bis(diphenylphosphate) (BDP)	181028-79-5; 5945-33-5		+	+	+				
Ethane bis(pentabromophenyl) (EBP)	84852-53-9	+	++	++	+	++	+	+	+
Ethylene bis(tetrabromophthalamide)	32588-76-4					++	+	+	+
Polybrominated styrene copolymers (PBS)	148993-99-1		++	++	++				
Polybrominated styrene homopolymers (PBS)	88497-56-7		++	++	++				
Brominated polystyrene (BPS)	-		+	+	+				
Bis (tribromophenoxy) ethane	37853-59-1		+	+	+				

Table 9-10: Flame retardants that ma	y be used in cabl	es and	wires (l	pased o	on EFRA	(2011	))		
Potential alternative substance	CAS No.	PVC	NBR	SBR	Silicone rubber	EPDM	EVA	LDPE	РР
Tetrabromophthalate ester	26040-51-7	+	++	++	++	++			
Antimony trioxide (ATO)	1309-64-4	+							
Aluminium tri-hydroxide (ATH)	21645-51-2	+			+	+	++	++	
Magnesium di-hydroxide (MDH)	13760-51-5	+				+	++	++	++
Zinc oxide containing products (ZnO)	1314-13-2	+							
Source: EFRA (2011) Note: the main applications of each su	ubstance are show	vn with	"++"						

# 9.7.3 Building and construction

A separate brochure by EFRA looks into FRs used in building and construction applications. Two areas are considered relevant to DecaBDE: roofing and cable, wire and piping. Insulation and flooring/wall coverings are omitted from the following table.

Table 9-11: Flame re	etardants that may be used in roofing a	nd cable/wiring	/piping
Application area	Potential alternatives	CAS No.	Relevant substrates
Roofing	Ethane-1,2-bis(pentabromophenyl) (EBP)	84852-53-9	Plasticised PVC/nitrile rubber blends or polyethylene
	Aluminium trihydroxide (ATH)	21645-51-2	Polyolefin-based synthetic roofs
Cable wiring and	Aluminium trihydroxide (ATH)	21645-51-2	PVC or polyolefin for cables
piping	Magnesium hydroxide (MDH)	1309-42-8	PVC or polyolefin for cables
	Ethane-1,2-bis(pentabromophenyl) (EBP)	84852-53-9	Various polymers
Sources: EFRA (2012	2b)		

# 9.7.4 Textiles and upholstery

A third brochure by EFRA looks into FRs used in textile and upholstery applications. One area is considered relevant to DecaBDE: semi-durable finishes. Foam fillings, durable and non-durable finishes, as well as interliners are not considered relevant and thus are omitted from the following table.

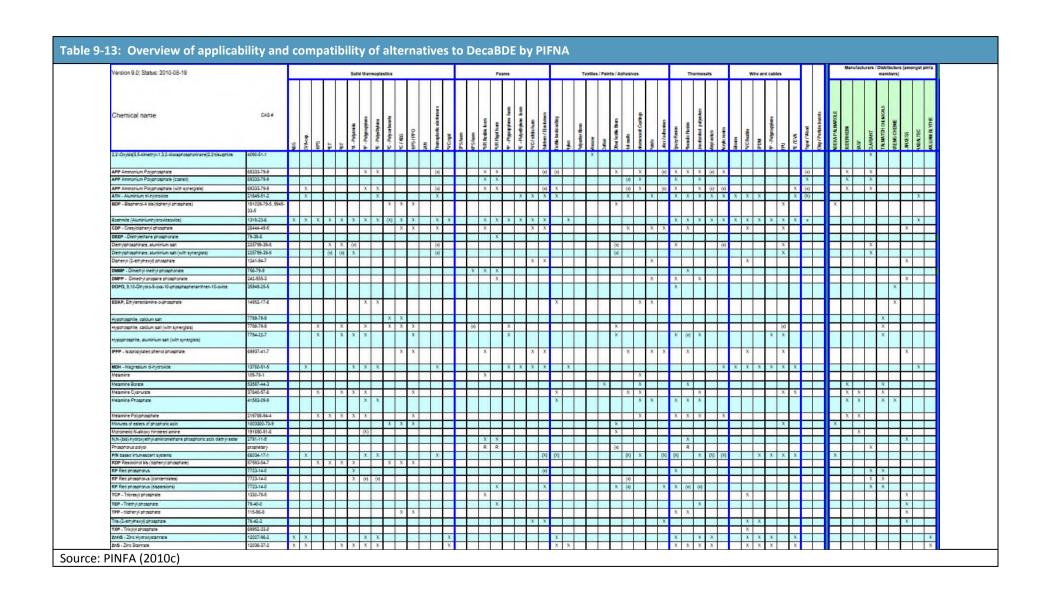
Table 9-12: Flame	retardants that may be used in semi-durable texti	le finishes	
Application area	Potential alternatives	CAS No.	Relevant substrates
Textiles – Semi- durable	Ethane-1,2-bis (pentabromophenyl) (EBP) + Antimony synergists	84852-53-9	Cotton, polyester,
	Tris(tribromophenyl)Triazine + Antimony synergists (TTBPT)	25713-60-4	acrylic, leather, leather imitation (PUR, PVC)
	2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate) (TL-10-ST)	38051-10-4	
	Aluminium tri-hydroxide (ATH)	21645-51-2	Cotton, polyester
	Ammonium polyphosphate (microencapsulated) (APP)	68333-79-9	

Table 9-12: Flame	retardants that may be used in semi-durable te	xtile finishes	
Application area	Potential alternatives	CAS No.	Relevant substrates
	Red phosphorous	7723-14-0	
	Melamine polyphosphate	218768-84-4	
	Melamine cyanurate	37640-57-6	
Sources: EFRA (20	12)		

# 9.8 PINFA Brochures – 2010, 2013

PINFA, which represents the manufacturers and users of non-halogenated phosphorus, inorganic and nitrogen FRs, has issued a series of publications in recent years on the availability and suitability of non-brominated alternatives for different FR applications (PINFA, 2010) (PINFA, 2010b) (PINFA, 2010c) (PINFA, 2013).

In the interest of brevity and space, the information presented in all these documents is not replicated here. Instead, the following table is presented which summarises the availability of phosphorous- and nitrogen-based alternatives and their suitability for different applications.



# 9.9 The ENFIRO Project

ENFIRO was a European Commission-funded project that was designed to run between 2009 and 2012 and was aimed at evaluating alternative FRs regarding their FR, environmental and toxicological properties, as well as their influence on the function of products once incorporated. The main objectives were to deliver a comprehensive dataset on viability of production and application, environmental safety, and a life cycle assessment of the alternative FRs and to recommend certain FR/product combinations for future study based on risk and impact assessment studies. ENFIRO evaluated viable substitution options for a number of BFRs (DecaBDE, TBBPA and brominated polystyrene) (Anonymous, undated).

ENFIRO identified 17 alternatives suitable for investigation. The following table summarises the relevant alternatives.

		ty and compatibility of alto caBDE is not explicitly men	ernatives to DecaBDE and ntioned are italicised)	other BFRs under
Polymer materials	Mainly used BFR	Applications	HFFR selected	HFFR shortlist
Epoxy resins	ТВВРА	Printed circuit boards, Electronic components encapsulations, Technical laminates	9,10-Dihydro-9-oxa-10- phosphosphaphenanthr ene oxide (DOPO), Aluminium hydroxide (ATH), Fyrol PMP	DOPO, ATH
Epoxy encapsulates	DecaBDE	Electrical Encapsulating & Casting	Melamine polyphosphate (MPP), Boehmite, Aluminium diethylphosphinate (Alpi), ATH, Zinc hydroxyl stannate (ZHS), Zinc stannate (ZS), Zinc borate (ZB)	MPP, Alpi, ATH, ZHS, ZS
HIPS/PPE	DecaBDE/ATO	Housings for business machines, dashboards, toys, equipment for refrigerator, telephones, and other consumer electronics	Resorcinol bis (biphenyl phosphate) (RDP), Bis phenol A bis (biphenyl phosphate) (BDP), Triphenyl phosphate (TPP)	RDP, BDP. Some hazard concern less desirable FRs
PC/ABS	DecaBDE/ATO	Housings for business machines, dashboards, toys, equipment for refrigerator, telephones, and other consumer electronics	RDP, BDP, TPP	RDP, BDP. Some hazard concern less desirable FRs
Polyamide 6 Polyamide 6,6	Brominated polystyrene (BPS)/ATO	Electrical & electronic equipment, connectors, switches etc.; encapsulated electronic components	Alpi, MPP , ZB, ZS, Melamine cyanuarate (MC)	Alpi, MPP, ZS
PBTE	Brominated polystyrenes/ ATO	Electrical & electronic equipment, connectors, switches etc.; encapsulated electronic components	Alpi, Nanoclay (organo- clays based on montmorillonite, nano- MMT)	Alpi

		y and compatibility of alte	ernatives to DecaBDE and optioned are italicised)	other BFRs under
Polymer materials	Mainly used BFR	Applications	HFFR selected	HFFR shortlist
EVA	DecaBDE / ATO	Wire & Cable	ATH, Magnesium hydroxide (Mg(OH) <sub>2</sub> . ATH coated with Zinc hydroxy stannate (ZHS), Boehmite	ATH, ATH coated with ZHS
Textile coatings	DecaBDE/ATO	Protective clothing, Carpets, curtains, upholstered fabrics, tents, interior in public transportation	Ammonium polyphosphate (APP), Pentaerythritol (PER), MPP, ZB	APP, PER, MPP
Intumescent Coating: HIPS	DecaBDE/ATO	Housings of electronic products	Novel application to attempt to reach V(0) for pure HIPS with intumescent coating based on APP, PER, MPP	Mixture of APP, PER, MPP. Novel application to attempt to reach V(0) for pure HIPS with intumescent coating
Source: Anonyr	nous (undated)			

# 9.10 Comparison of alternatives by Albemarle – 2013

Albemarle supplies both DecaBDE and a range of alternatives. It publishes a guide to its FR products, where the applicability and compatibility of alternative substances is compared to that of DecaBDE. A reproduction of a comparison table from a recent version of this guide is given in **Table 9-15**. It must be noted that some products are proprietary.

By way of summary, Albemarle offers the following alternatives (Albemarle, 2013):

- Brominated FRs: Decabromodiphenyl ethane, Ethylene bis(tetrabromophthalimide), HBCD,
   TBBPA, Tetrabromophthalic anhydride, Tetrabromophthalic anhydride diester/etheriol,
   Brominated polystyrene and proprietary brominated polymers (GreenArmor, GreenCrest)
- Inorganic FRs: aluminium and magnesium hydroxide.

The vast majority are used as additive FRs apart from TBBPA and its derivatives which may act as reactive FRs. The alternatives that find the widest range of applications as DecaBDE substitutes are decabromodiphenyl ethane, ethylene bis(tetrabromophthalimide) and a proprietary brominated polymer.

Table 9-15: Overview of applicability and compatibility of alternatives to DecaBDE by the manufacturer Albemarle (2013)

Application		EA	RTHWISE FAM	ILY OF PRODUC	TS		SAYTEX	SAYTEX 102E	SAYTEX BT-93	SAYTEX	SAYTEX	SAYTEX RB-	SAYTEX RB-	MARTINAL ON-310 ON-	MARTINAL ON-904 ON- 906 ON-908	MARTINAL OL-104LEO	MARTINAL OL-104 IO	MARTINAL OL-104 ZO		MAGNIFIN H-	MAGNIFIN H-5 IV	MAGNIFIN H-5 A	MAGNIFIN H- 5 GV H-5 HV
	GreenArmor	GreenCrest	SAYTEX HP-7010	SAYTEX HP-3010	SAYTEX HP-5010	SAYTEX 621	8010		BT-93W	HP-900P/G	CP-2000	49	79/BLENDS	313 ON-320 ON-4608	ON-921 ON- 935	OL-107LEO OL-111 LE	OL-107 IO	OL-107 ZO OL-104 RO	OL-104 C OL- 107 C	5 H-7 H-10	H-10 IV	H-10 A	H-5 MV H-10 MV
	Brominated polymer	Brominated polymer		Brominated polystyrene			DecaBDE ethane	DecaBDE	ЕВТВРІ	нвсо	ТВВРА	Tetrabromo phthalic anhydride	Tetrabromo phthalic anhydride diester/eth eriol	Aluminum hydorxide	Aluminum hydorxide	Aluminum hydorxide	Aluminum hydorxide	Aluminum hydorxide	Aluminum hydorxide	Magnesium hydroxide	Magnesium hydroxide	Magnesium hydroxide	Magnesium hydroxide
Thermoplastic	cs			•		•				•										•	•		
ABS	Α						Α	Α	Α		А												
HIPS	A						Α	Α	Α	A													
Polyamide	Α .		A	Α .	A		Α .	A													A		
Polyester Polycarbona	A		A	A	A	А	Α	А	A			-								<u> </u>	<b>—</b>		<b>  </b>
te	Α		Α	А	А		Α	А	Α		R												
Polypropyle	Α						Α	Α	Α														А
Polyethylen																							
e/Copolyme	Α						Α	Α	Α					Α		Α	Α			Α	Α		Α
SAN	A						A	Α	A														
Alloys (PC/ABS, HIPS/PPO)	Α		А	А			А	А	А														
Elastomers	Α						А	Α	Α					Α		Α		Α		Α		Α	Α
PVC	Α						А	А	Α					А		А				Α			А
Foams																							
Polyolefins	Α						Α	Α	А							A		A	A	Α		A	A
PVC/Nitrile	A						A	A	A							A		A	A	А		Α	A
Elastomers	A						Α	Α	A							Α		А	А				l
Wire and Cabl Silicone	ie						А	А	A							A		А			А		A
EPDM	A						A	A	A A					A		A		A		A		A	
Polypropyle	A						A	A	A														А
PE/EVA	А						А	А	А					А		А	А		А	А	А		А
XL PE/EVA	А						А	А	А									А	А			А	А
TPU	А						Α	А								А				А			А
PVC	А						А	А	А							А			А	А			А
Thermosets		ı	ı																				
Epoxy							A	A	A		R	R		A	A	A			A				
Phenolic Unsaturate							Α	Α	A		Α	R		A	A	A			A		-		
d Polyester							А	А	А		R	R		А	A	A		A	A				
Vinyl Esters							А	А	А		R	R		А	Α	А		А					
SMC/BMC								А	А			R		А	A	А		А					
PU/CASE							Α	А	A				R		A	А							
Latex		2042)	l				А	A	Α	A				A									

Source: Albemarle (2013)

# 9.11 Comparison of alternatives by Chemtura (Great Lakes) – 2013

The following table summarises information on commercial FR products placed on the market by Chemtura (Great Lakes Solutions) for areas of application that may be potentially relevant to DecaBDE.

Table 9-16: Overview of applicability and co Chemtura (2013)	mpatibility	of alter	natives t	o DecaBI	DE by the	e manufa	cturer 
Commercial alternative by Chemtura	Adhesives, sealants and coatings	Automotive	Aviation	Public, mass transit	Wire and cable	Roofing membrane and flooring	Textile backcoating
ATO and smoke suppressants	+	+	+	+		+	+
Firemaster® 2100R (EBP)							
(CAS No. 84852-53-9)	+	+	+	+	+	+	+
Firemaster® 504 (blend of PHT4-Diol™ flame							
retardant and phosphate ester)	+					+	
(Proprietary)							
Firemaster® 508 (blend of PHT4-Diol™ flame							
retardant and phosphate ester) (Proprietary)	+						
Firemaster® CP-44HF (Poly(dibromostyrene)							
copolymer)		+					
(CAS No. 88497-56-7)							
Firemaster® PBS-64HW							
(Polydibromostyrene)		+					
(CAS No. 88497-56-7)							
Firemaster® BZ-54 (Tetrabromobenzoate							
ester)	+						
(Proprietary)							
Reofos® 50 (Triaryl phosphate							
isopropylated)	+					+	+
(CAS No. 68937-41-7)							
Reofos® 65 (Triaryl phosphates Isopropylated)			+	+			
(CAS No. 68937-41-7)		+			+	+	+
Reofos® 95 (Triaryl phosphates							
isopropylated)					+	+	
(CAS No. 68937-41-7)							
Reofos® RDP (Resorcinol Bis-(Diphenyl							
Phosphate))					+		
(CAS No. 57583-54-7)							
Reofos® BAPP (Bisphenol-A Bis-(diphenyl							
Phosphate))					+		
(CAS No. 5945-33-5)							
Reofos® LF-50 (Phenol, tert-butylated							
phosphate (3:1)) (CAS No. 68937-40-6)						+	+
BC-52™ (Phenoxy-terminated carbonate							
oligomer of Tetrabromobisphenol-A)		+					
(CAS No. 94334-64-2)							

Commercial alternative by Chemtura	Adhesives, sealants and coatings	Automotive	Aviation	Public, mass transit	Wire and cable	Roofing membrane and flooring	Textile backcoating
BC-58™ (Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol-A) (CAS No. 71342-77-3)		+					
DP-45™ (Tetrabromophthalate ester) (CAS No. 26040-51-7)			+	+	+		
PDBS-80™ (Poly(dibromostyrene)) (CAS No. 1195978-93-8)		+					
Kronitex® CDP (Cresyl diphenyl phosphate) (CAS No. 26444-49-5)	+					+	
Kronitex® TCP (Triaryl phosphates butylated) (CAS No. 1330-78-5)	+						
ZB-467 (Zinc borate)		+	+	+	+		+
ZB-223 (Zinc borate)					+	+	+
Emerald Innovation™ 1000 (Proprietary brominated polymeric)	+	+	+	+	+	+	+
Emerald Innovation™ NH-1 (Proprietary phosphate ester)			+				

# 9.12 Comparison of alternatives by ICL Industrial Products – 2013

**Table 9-17** summarises information on commercial FR products placed on the market by ICL. The table compares the applicability of different alternatives to that of DecaBDE.

By way of summary, ICL offers the following alternatives (ICL Industrial Products, 2013):

- Brominated FRs
- Phosphorus-based FRs
- Inorganic FRs.

Table 9-17: (	Overview of applicability and	d compatibility of	f alter	native	s to D	ecaBD	E by t	he ma	nufac	turer l	ICL Inc	lustria	al Prod	ucts (	2013)						
Commercial product	Alternative substance	CAS No.	HIPS	EPS/XPS	ABS	PE	ЬР	PBTE/PET	PA (nylon)	PC/ABS	Alloys	PVC/ Flexible	Rubber / elastomers	Epoxy resins	Phenolic resins	UPE	Flexible PUF	Rigid PUF	Chip/ particle boards	Textile / fibres	Latex /
FR-1210	DecaBDE	1163-19-5	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+
FR-11	Ammonium bromide	12124-97-9																	+	+	
FR-122P	Polymeric FR	1195978-93-8		+																	
FR-245	Tris(tribromophenoxy) triazine	25713-60-4	+		+					+											
FR-370	Tris(tribromoneopentyl) phosphate	19186-97-1	+	+	+	+	+				+									+	+
FR-513	Tribromoneopentyl alcohol	36483-57-5															+	+			
FR-522	Tribromophenol	118-79-6														+		+			
FR-720	Tetrabromobisphenol-A - bis(2,3 dibromopropyl ether)	21850-44-2	+		+	+	+														
FR-803P	Brominated polystyrene	88497-56-7						+	+												
FR-1025	Brominated polyacrylate	59447-57-3				+	+	+	+		+										
FR-1206	Hexabromocyclo- dodecane	3194-55-6		+																	
FR-1410	Decabromodiphenyl ethane	84852-53-9	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+			
FR-1524	Tetrabromobisphenol-A	79-94-7			+					+				+	+						
F-2001	Brominated epoxy	68928-70-1		+										+		+					
F-2200HM	Brominated epoxy	3072-84-2 68928-70-1		+										+							
F-2016	Polymer				+					+											

Table 9-17: 0	Overview of applicability and	d compatibility o	f alter	native	s to D	ecaBD	E by t	he ma	nufac	turer l	ICL Inc	dustria	al Prod	ucts (	2013)						
Commercial product	Alternative substance	CAS No.	HIPS	EPS/XPS	ABS	PE	РР	PBTE/PET	PA (nylon)	PC/ABS	Alloys	PVC/ Flexible	Rubber / elastomers	Epoxy resins	Phenolic resins	UPE	Flexible PUF	Rigid PUF	Chip/ particle boards	Textile / fibres	Latex /
FR-1210	DecaBDE	1163-19-5	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+
F-2100, F- 2400	Polymer				+			+	+	+	+										
F-3014, F- 3020	End-capped brominated epoxy	158725-44-1 135229-48-0	+		+										+						
F-3100	End-capped brominated epoxy	135229-48-0			+			+	+	+	+										
Polyquel <sup>™</sup> 140						+	+	+	+	+	+										
Polyquel <sup>™</sup> 145						+															
Polyquel <sup>TM</sup> 240, Polyquel <sup>TM</sup> 241			+		+																
Safron 6605																		+			
Texfron series																				+	+
Fyrol FR- 2/Fyrol 38	Tris (1,3- dichloroisopropyl) phosphate	13674-87-8												+	+	+	+			+	
Fyrol HF-4	Proprietary halogen-free flame retardant																+				
Fyrol HF- 5/HF-5HP	Proprietary halogen-free FR additive																+				
Fyrol 6	Diethyl N,N bis (2-	2781-11-5												+				+			_

Table 9-17: (	Overview of applicability and	compatibility of	f alter	native	s to D	ecaBD	E by t	he ma	nufac	turer	ICL Inc	lustria	l Prod	ucts (	2013)						
Commercial product	Alternative substance	CAS No.	HIPS	EPS/XPS	ABS	PE	ЬР	PBTE/PET	PA (nylon)	PC/ABS	Alloys	PVC/ Flexible	Rubber / elastomers	Epoxy resins	Phenolic resins	UPE	Flexible PUF	Rigid PUF	Chip/ particle boards	Textile / fibres	Latex /
FR-1210	DecaBDE	1163-19-5	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+
	hydroxyethyl) aminomethylphosphonat e																				
Fyrol A300TB	Proprietary chloralkyl phosphate blend																+				
Fyrol PCF	Tris 2-chloroisopropyl phosphate	13674-84-5												+		+	+	+			
Fyrol P26	Proprietary					+	+	+	+					+							
Fyrol PNX	Oligomeric ethyl ethylene phosphate	184538-58-7															+				
Fyrol PNX- LE	Modified oligomeric ethyl ethylene phosphate	184538-58-7															+				
Fyroflex RDP/RDP- HP	Resorcinol bis(diphenyl phosphate)	125997-21-9	+							+				+	+					+	
Fyroflex Sol-DP	Proprietary aromatic phosphate		+		+					+			+								
Phosflex 4	Tributyl phosphate	126-73-8										+									+
Phosflex T- BEP	Tris(butoxyethyl) phosphate	78-51-3											+								+
Phosflex 31L/41L	Isopropylated triphenyl phosphate mixture	68937-41-7										+		+							
Phosflex 375	Proprietary plasticizer blend of alkyl diphenyl phosphate and triaryl											+		+							

Commercial product	Alternative substance	CAS No.	HIPS	EPS/XPS	ABS	PE	ЬР	PBTE/PET	PA (nylon)	PC/ABS	Alloys	PVC/ Flexible	Rubber / elastomers	<b>Epoxy resins</b>	Phenolic resins	UPE	Flexible PUF	Rigid PUF	Chip/ particle boards	Textile / fibres	Latex /
FR-1210	DecaBDE	1163-19-5	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+
	phosphate ester																				
Phosflex 71B	t-Butylated triphenyl phosphate mixture	56803-37-3 and 65652-41-7 and 78-33-1	+							+		+									
Lindol	Tri( <i>m,p</i> -cresyl) phosphate mixture	1330-78-5										+									
Lindol XP Plus	Tri( <i>m,p</i> -cresyl) phosphate mixture	1330-78-5										+									
FR-20	Magnesium hydroxide	1309-42-8				+	+		+			+	+								
FR1120 (synergist)	Calcium Borate on a silicate carrier	13701-64-9	+		+	+	+	+	+		+	+	+								

# 9.13 Other novel alternatives

Some information on novel alternative FRs was discussed in the 12 European Meeting on Fire Retardant Polymers in Poznan in  $2009^{61}$  and is summarised below.

Products	Application	Reference
(N-t-butyl-N'-1,2,2,6,6-pentamethylpiperidin-4-	PP, LDPE, HIPS	(Aubert, et al., 2012)
yl)diazene	, 251 2, 1111 3	(, labell, et al., 2012)
N-cyclohexyl-N'-1,2,2,6,6-pentamethylpiperidin-4-	PP, LDPE, HIPS	(Aubert, et al., 2012)
/l)diazene		, , , , , , , , , , , , , , , , , , , ,
Bis(1,2,2,6,6–pentamethylpiperidin-4-yl)diazene	PP, LDPE, HIPS	(Aubert, et al., 2012)
Bis(1-methoxy-2,2,6,6-tetramethylpiperidin-4-	PP, LDPE, HIPS	(Aubert, et al., 2012)
yl)diazene	, ==: =, 5	(**************************************
Bis(1-ethoxy-2,2,6,6-tetramethylpiperidin-4-	PP, LDPE, HIPS	(Aubert, et al., 2012)
yl)diazene	, ,	
Bis(1-propoxy-2,2,6,6-tetramethyl-4-yl)diazene	PP, LDPE, HIPS	(Aubert, et al., 2012)
		(Aubert, et al., 2011)
Bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-	PP, LDPE, HIPS	(Aubert, et al., 2012)
yl)diazene		
Bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-	PP, LDPE, HIPS	(Aubert, et al., 2012)
yl)diazene		
Bis(1-methoxy-2,2,6,6-tetramethyl-4-	PP, LDPE, HIPS	(Aubert, et al., 2012)
piperidone)azine	DA CC	(1 - 1 - 2011)
Ammonium sulfamate (AS) and dipentaerythritol	PA 66	(Lewin, 2011)
Melamine cyanurate (MC)	PA 66	(Lewin, 2011)
Pentabromobenzylacrylate in the momnomeric	PA 66	(Lewin, 2011)
(PMA) and the polymeric (PPA) form		
Nanosilica and SINK	Polystyrene based nanocomposite	(Yang & Nelson, 2011)
Nanocomposite based on polyprolylene and organic	Polypropylene	(Wang, et al., 2011)
Co/AI-layered double hydroxide		
Nanocomposites polypropylene/organoclay	Polypropylene	(Szustakiewicz, et al., 2011)
PP/OMMT)		
Ammonium polyphosphate in propylene	PP, PA 6	(Stec & Rhodes, 2011)
Mixture of organic aluminium phosphate and		
melamine polyphosphate in polyamide 6 and		
nanofillers	EVA	/Mars at al. 2011)
Composites of ethylene-vinyl acetate copolymer	EVA	(Wang, et al., 2011)
with two different layered double hydroxides	PC	(Hu, et al., 2011)
Poly(9,10-dihydro-9-oxa-10-phosphaphenanthrene- 10-oxide siloxane	PC PC	(nu, et di., 2011)
Diol 2-[4-(2-hydroxy-ethoxy)-3-(10-oxo-10-H9-oxa-	PBTE	(Sablong, et al., 2011)
Dioi 2-[4-(2-iiydi oxy-ethoxy)-5-(10-0x0-10-ii9-0xa- 10-λ5-phospha-phenanthrene-10-yl)-phenoxy]-	1512	(Japiong, et al., 2011)
ethanol		
Comonomers (e.g. diethyl-[2-(diethylphosphinyl)-4-	Vinyl polymers	(Dumitrascu & Howell, 2011)
vinylphenyl]phosphate) used in copolymerization	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
with styrene		
4,4,5,5-Tetra(3,5-dibromophenyl)-2,2-diphenyl-1,3-	Polymers	(Howell & Cho, 2011)
oxa-2-silole and related compounds		
Rheological additives (organic-modified	Styrene-butyl acrylate copolymer	(Bodzay, et al., 2011)
montmorillonite, palygoskite and sepiolite)		
Charring agent, ammonium polyphosphate and	PP	(Liu, et al., 2011)
organically-modified montmorillonite		
Epozeri AH-16, Epozerit T-58, D.E.R. 330, D.E.H. 24,	Fibre-reinforced epoxy resins	(Toldy, et al., 2011)
TEDAP		/=
Mercury vapour UV lamp and vinyl phosphonic acid	Cotton, Polyamide, Polyester	(Opwis, et al., 2011)
Elastic barriers (wool, flax FR)	Bast, wool and thermostable fibres	(Kozlowski, et al., 2011)
	(polyacrylate)	

<sup>&</sup>lt;sup>61</sup> 12<sup>th</sup> European Meeting on Fire Retardant Polymers Poznan, Poland, 31 August - 3 September 2009

#### 9.14 Information from consultation with Member State authorities

Some information has been submitted by Member State authorities during consultation for the present project. This is summarised here, as appropriate.

#### 9.14.1Norway

The following table includes some brominated substances which the Norwegian authorities have described as "newer brominated flame retardants in focus – some are/may be replacements for DecaBDE (both preferable and possibly unpreferable alternatives)".

Table 9-19: Potential brominate	d alternativ	es to DecaBDE by	the Norwegian authorities
Substances		CAS No	Use
Dibromoneopentyl glycol		3296-90-0	Unsaturated polyesters, elastomers, rigid polyurethane foams
2,4,6 Tribromphenol	2,4,6-TBP	118-79-6	Epoxy resins, phenolic resins, polyester resins, polyolefins
Ammonium bromide		12124-97-9	Wood
Tris-(2,3-dibromopropyl)- phosphate	TRIS, TrisBP	126-72-7	
Tribromoneopentylalcohol		1522-92-5	
2-ethylhexyl-2,3,4,5- tetrabromobenzoate	TBB, EHTBB	183658-27-7	Replaces pentaBDE
Tris(tribromoneopentyl)phosph ate		19186-97-1	Styrene, Polyurethane
1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 2-(2- hydroxyethoxy)ethyl 2- hydroxypropyl ester		20566-35-2	N/A
Tetrabrom A bis(2,3-dibrompropylether) *	TBBPA- DBPE	21850-44-2	Polyolefine resins, polystyrene
Tetrabromo - p - xylene	p - TBT	23488-38-2	
Tetrabrombisfenol A diallylether	TBBPAAE	25327-89-3	EPS, foamed polystyrene
2,4,6-tris(2,4,6- tribromophenoxy)-1,3,5-triazine		25713-60-4	N/A
Bis (2- ethylhexyl) tetrabromophthalate	TBPH, BEHTBP	26040-51-7	Replaces PentaBDE - PVC, Neoprene
Dibromostyrene		31780-26-4	Styrenic polymers, engineering plastics
Etylene, bis (tetrabromophthalimide)	EBTBPI	32588-76-4	HIPS, polyethylene, poly-propylene, thermoplastic polyesters, polyamide, EPDM, rubbers, polycarbonate, ethylene co- polymers, ionomer resins, textiles

Substances		CAS No	Use
2,4,6-tribromophenyl allyllether	ATE	3278-89-5	Expandable polystyrene (EPS), polystyrene foam
2,2-bis(bromomethyl)-1,3- propandiol		3296-90-0	Unsaturated polyesters, elastomers, rigid polyurethane foams
1,2-dibromo-4-(1,2- dibromoethylcyclohexane	TBECH	3322-93-8	
2,3-dibromopropyl- 2,4,6 tribromphenylether	DPTE	35109-60-5	
2,2-dimethylpropan-1-ol, tribromo derivative		36483-57-5	Polyurethane, rigid and flexible polyurethane foam
1,2-bis(2,4,6- tribromphenoxy)etan	BTBPE	37853-59-1	Replaces OctaBDE - Thermoplastics, Acrylonitrile Butadiene Styrene terpolymer (ABS), High Impact Polystyrene (HIPS)
Tetrabromobisphenol-A dimethyl ether	Me-TBBPA	37853-61-5	
2,3-dibrom-1-propanol- hydrogen phosphate		5412-25-9	
1,4- bis(pentabromophenoxy) tetrabromobenzene		58965-66-5	Engineering thermoplastics
Pentabromobenzyl acrylate		59447-55-1 (as monomer)	Polybutyleneterephatlate (PBTE), Polyethylene terephatale (PET), ABS
Poly(pentabromobenzyl) acrylate		59447-55-1 (as polymer)	Polypropylene, Polystyrene and others - polyamides, polyesters, polycarbonates, Polyamide
Polybrominated biphenyl	PBB	59536-65-1	
2,4,6-Tribromoanisole	ТВА	607-99-8	
Pentabromophenol	PBP	608-71-9	
1,1'-[ethane-1,2- diylbisoxy]bis[pentabromobenz ene]		61262-53-1	
Tetrabromphthalic anhydride	ТВРА	632-79-1	Unsaturated polyesters and rigid polyurethane foams, paper, textiles, epoxides, wool
2,2',4,5,5'-pentabromobiphenyl	PBB-101	67888-96-4	
1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-,mixed esters with diethylene glycol and propylene glycol		77098-07-8	N/A
Decabromodiphenyl ethane	DBDPE (EBP)	84852-53-9	Styrene

Table 9-19: Potential brominated alternatives to DecaBDE by the Norwegian authorities							
Substances		CAS No	Use				
Pentabromethylbenzene	PBEB	85-22-3	Unsaturated polyesters, styrene, butadiene copolymers, textile				
Hexabromobenzene	HBB	87-82-1	N/A				
Pentabromotoluene		87-83-2	Unsaturated polyesters, polyethylene, polypropylenes, polystyrene, SBR-latex, textiles, rubbers, ABS				

Source: Consultation

Notes: most of the information comes from the following sources

- Compilation-of-Norwegian-Screening-Data-for-Selected-Contaminants-2002 2012
- Literature-survey-Polybrominated-diphenyl-ethers-and-perfluorinated-compounds-in-the-Norwegian environment
  - http://www.miljodirektoratet.no/no/Publikasjoner/Statlig miljoovervakning/Kartlegging av nye milj ogifter/Rapporter/Literature\_survey\_Polybrominated\_diphenyl\_ethers\_and\_perfluorinated\_compounds in the Norwegianenvironment/
- Current state of knowledge and monitoring requirements Emerging "new" brominated flame
  retardants in flame retardant products and the environment
  <a href="http://www.miljodirektoratet.no/no/Publikasjoner/Statlig\_miljoovervakning/Kartlegging\_av\_nye\_miljogifter/Rapporter/Current\_State\_of\_Knowledge\_and\_Monitoring\_requirementsEmerging\_new\_Brominated\_flame\_retardants\_inflame\_retarded\_products\_and\_the\_environment/</a>

#### **9.14.2Germany**

The German authorities provided some information from past work on alternatives for brominated FRs. They referred to an UBA background paper on brominated FRs from 2008 according to which, in electrical/electronic devices, DecaBDE can usually be substituted by halogen-free organophosphorous FRs. This requires simultaneously the substitution of the plastics by hardly inflammable plastic mixtures with PC or PPE. For small components made from polyester plastics (PBTE, PET) or polyamide (PA), suitable alternative FRs are magnesium hydroxide, microencapsulated red phosphorus, melamines or organic phosphinates. In electrical/electronic equipment in the low voltage range, the amount of FRs used may often be reduced, because this equipment often contains more FR than necessary in order to fulfil fire protection requirements. Increasing flame proofing of electric/electronic equipment against external ignition sources results in increasing use of FRs. The German authorities pointed out that this needs to be discussed on a broader basis under technical and societal aspects in order to balance advantages and disadvantages.

Textiles do not have to be flame retardant when they are made from glass fibres or plastic types of low flammability (e.g. polyaramides). Another alternative for textiles is the use of chemically bound FRs, e.g. polyester fibres with covalently-bound phosphorous-containing FRs. Cellulose fibres may be permanently finished with reactive phosphorous FRs. A further possibility is the development of intumescence systems, which swell in case of fire and build barrier layers. Finally, the German authorities noted that the build-up and density of a fabric or upholstery have a decisive influence on the fire behaviour of a textile. The following table is a reproduction of a table that appears in the aforementioned UBA report.

		ties to the brominated flame retardants
DecaBDE, TBBPA and HBCD (UE Area of application	BA, 2008)  Bromated flame retardant (plastic/ fibre)	Technically suitable possibilities for substitution (examples)
		Substitute material and/or alternative material
Enclosures for electronic appliances	DecaBDE (ABS, HIPS) HBCD (HIPS) TBBA additive (ABS)	Phosphorus-containing, halogen-free FRs: RDP, BDP (PC, PC/ABS, PPE/HIPS)
Small parts for electronic appliances	DecaBDE (PBTE, PET, PA)	Red phosphorus (microencapsulated), magnesium hydroxide, melamine, metal phosphinate (PA) Metal phosphinate (PBTE, PET)
Printed circuit boards (PCBs)	TBBPA reactive (Epoxy resin)  TBBPA additive (Phenolic resin)	Phosphorus-containing, halogen-free FRs: DOPO/Aluminium-hydroxide (epoxy resin) Metal phosphinates/DOPO/Silicon dioxide (epoxy resin) Polymer phosphonate (epoxy resin) Flame-retardant thermosetting plastics
		Flame-retardant thermosetting plastics Flame-retardant thermoplastics (in development)
Textile back coatings	DecaBDE (various fibres)	Inherently flame-retardant synthetic fibres with woven-in FSM (PP, PE)
	HBCD (various fibres)	Flame-retardant synthetic fibres (polyaramide); glass fibre Permanent equipment with phosphonium compounds (cellulose) Intumescent-systems (various fibres)
Insulating materials made of	HBCD (EPS, XPS)	Mineral rock wool (except perimeter
polystyrene Source: (Umweltbundesamt, 20	008)	insulation)

In 2001, in a research project funded by UBA, Leisewitz et al. evaluated FRs and their alternatives. The researchers came to the following conclusions.

Application rejected	DecaBDE, TBBPA additive
Reduction sensible, substitution desired	TBBPA reactive, TCPP
Problematic properties, reduction sensible	HCBD, sodium borate decahydrate, ATO
Recommendation impossible due to lack of data	EBP, RDP, Pyrovatex CP new, melamine cyanurate
Application unproblematic	Red phosphorous, ammonium polyphosphate, aluminium trioxide

#### 9.14.3Sweden

The Swedish authorities (KemI) provided a link to the KemI (2009) report, which has been referred to elsewhere in this document.

#### 9.14.4France

The French authorities provided a reference to the US EPA assessment of alternatives to DecaBDE, which has been extensively used in the preparation of this document.

#### 9.14.5Denmark

The Danish EPA provided a copy of a recent Danish EPA report (2013) which, on the issue of alternatives for DecaBDE, relies significantly on the recent US EPA assessment and previous work by the Danish EPA itself.

# 10 Annex 4 – Screening of alternatives for the development of a shortlist

# 10.1 Steps 1 & 2 – Identification of alternatives and screening for technical feasibility

**Table 10-1** presents the publications in which each alternative is mentioned as having some potential for replacing DecaBDE in plastics (P), textiles (T) or coatings (C). The total number of references is presented as well as how many times each alternative has been mentioned for each use area, P, T or C. Information from consultation has also been included on the right hand side of the table.

For an individual alternative substance to be considered as having a 'minimum' level of technical feasibility, it must meet the following criteria:

- 1. Has been identified by consultees as relevant (i.e. it is actually used)
- 2. Appears to be suitable for all article categories (plastics, textiles, coatings) AND
  - appears in at least five different literature sources as potentially suitable for use in polymers, AND
  - appears in at least two different literature sources as potentially suitable for use in textiles, AND
  - appears in literature as potentially suitable for use in coatings (including, in the absence of detailed information, adhesives and sealants).
- 3. If a substance appears to be particularly relevant to plastics but not necessarily to textiles or coatings, i.e. it appears in **seven or more** different literature sources as potentially suitable for use in polymers, it is considered suitable for shortlisting.

The shortlisted alternative substances are shown in the table in bold type.

	: First screening step – Overview of					<u> </u>						Т							
CAS No.	Alternative substance	Kemi (2004), Kemi (2005). Kemi (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	Р	т	С
N/A	Brominated paraffins	Р															1	0	0
N/A	Penta bromophenyl benzoate	Р															1	0	0
N/A	Trichloromethyltetrabromobenzene	Р															1	0	0
N/A	Tris(tribromophenoxy)ethane	Р															1	0	0
N/A	Dibromoneophenyl glycol	Р															1	0	0
N/A	Chlorinated polystyrene	Р															1	0	0
N/A	Dithiopyrophosphate	Р															1	0	0
N/A	Tripropylphenyl phosphate	Р															1	0	0
N/A	Diisopropylphenyl phosphate	Р															1	0	0
N/A	Di-(polyoxoethylene) hydromethyl phosphonate	Р															1	0	0
N/A	Dibromopentyl glycol	Р															1	0	0
N/A	Tetrabromoneopentyl alcohol	Р															1	0	0
N/A	Brominated polymer (GreenArmor)													P, T			1	1	0
N/A	Phosphorus polyol							Р				P, T					2	1	0
N/A	Poly(1,3-phenylene methyl phosphonate)											Р					1	0	0
N/A	Sulphonates											Р					1	0	0
N/A	Cyclic phosphonates											Р					1	0	0
N/A	Oxaphosphorinane oxy-bis-dimethyl sulphide											Т					0	1	0
N/A	Potassium diphenyl sulphone sulphonate (KSS)											Р					1	0	0

Table 10-1: F	irst screening step – Overview of s	ibstanc	es or	reieva	nce to	tne rep	olacemo	ent of L			sence (	of alter	nativ	es in liter	ature				
CAS No.	Alternative substance	Kemi (2004), Kemi (2005). Kemi (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	Р	т	С
N/A	Silicon compounds											Р					1	0	0
N/A	Zinc molybdate compounds	Р															1	0	0
N/A	Bromoalkyl phosphates	Р															1	0	0
N/A	Other proprietary product (via consultation)															Р, Т	1	1	0
1003300-73-9	Mixtures of esters of phosphoric acid											P, T				Р	2	1	0
10361-65-6	Ammonium phosphate											Т					0	1	0
103850-22-2	Neoalkoxy tri (dioctyl phosphate) titanate	Р															1	0	0
108-78-1	Melamine	Р, Т					Р					Т			Р		3	2	0
115-27-5	Chlorendic anhydride	Р															1	0	0
115-28-6	Hexachloroendomethylenetetrahydro- phthalic acid (HET acid)	Р						Р									2	0	0
115-77-5	Pentaerythritol												Т				0	1	0
115-86-6	Triphenyl phosphate	Р	Р	Р	Р		Р	Р	Р	Р		Р	Р				10	0	0
115-88-8	Octyl diphenyl phosphate	Р															1	0	0
115-96-8	Tris(betachloroethyl) phosphate - Tris(2-chloroethyl) phosphate	Р															1	0	0
117-08-8	Tetrachlorophthalic anhydride	Р															1	0	0
118-79-6	Tribromophenol	Р												Р	Р		3	0	0
1195978-93-8	Poly(dibromostyrene)													Р			1	0	0
12027-96-2	Zinc hydrostannate	Р										Р, Т	Р				3	1	0
12036-37-2	Zinc stannate	Р										P, T	Р				3	1	0

Table 10-1: Fi	rst screening step – Overview of s	ubstanc	es of	releva	nce to	the rep	lacemo	ent of E	DecaB	BDE – Pre	sence (	of alter	nativ	es in lite	rature				
CAS No.	Alternative substance	Keml (2004), Keml (2005). Keml (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	P	т	С
12124-97-9	Ammonium bromide	Р												P, T	Wood		2	1	0
124-64-1	Tetrakis(hydroxymethyl) phosphonium chloride						Р		Т								1	1	0
1241-94-7	Diphenyl 2-ethylhexyl phosphonate											P, C					1	0	1
126-73-8, 6131- 90-4	Tributyl phosphate	Р												Р			2	0	0
12777-87-6	Expandable graphite								Р			Р					2	0	0
1303-96-4	Sodium tetraborate	Т													Р		1	1	0
1309-42-8; 13760-51-5	Magnesium hydroxide	Р, Т	Р		Р	P, C	Р		Р		P, C	P, T		Р	Р	Т	10	2	2
1313-27-5	Molybdic oxide	Р															1	0	0
1330-78-5	Tricresyl phosphate	Р					Р	Р			Р	Р		Р			6	0	0
135229-48-0; 158725-44-1	Brominated epoxy resin end-capped with tribromophenol				Р	Р		Р	Р					Р			5	0	0
13560-89-9	Dodecachloro dodecahydro dimethano dibenzocyclooctene	Р	Р		Р	P, C			Р								5	0	1
13674-84-5	Tri-(2-chloroisopropyl)phosphate	Р, Т												Р	Р, Т		3	2	0
13674-87-8	Tris(1,3-dichloro-2-propyl) phosphate	Р												Р, Т		Т	2	2	0
13701-64-9	Calcium metaborate													Р			1	0	0
138265-88-0; 1332-07-6	Zinc borate	Р		Р		Р	Р					P, T, C					5	1	1
139189-30-3	Resorcinol bis(2,6-dixylenyl phosphate)											Р					1	0	0
14728-39-9, 68333-79-9	Ammonium polyphosphate	Р, Т	Р		Р	P, T, C	Р		P, C		T, C	P, T, C	Т		P, T, C		8	6	5
14852-17-6	Ethylene diamine phosphate											P, T, C					1	1	1

Table 10-1: F	irst screening step – Overview of su	ubstanc	es of	releva	nce to	the rep	laceme	ent of C	DecaB	DE – Pre	sence (	of alter	nativ	es in liter	ature				
CAS No.	Alternative substance	Keml (2004), Keml (2005). Keml (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	Р	т	С
148993-99-1	Poly(dibromostyrene)	Р	Р		Р	Υ			Р		Р						5	0	0
1522-92-5	Tribromoneopentylalcohol														?		0	0	0
15432-85-6; 11112-10-0	Sodium antimonite	Р															1	0	0
16923-95-8	Potassium hexafluorozirconate								Т			Т					0	2	0
1806-54-8	Trioctyl phosphate	Р															1	0	0
183658-27-7	2-Ethylhexyl-2,3,4,5- tetrabromobenzoate														?		0	0	0
184538-58-7	Oligomeric and modified ethyl ethylene phosphate													Р			1	0	0
18755-43-6	Dimethylpropane phosphonate	Р						Р				Р					3	0	0
191680-81-6	N-Alkoxy hindered amine reaction products					Р			Т			Т					1	2	0
19186-97-1	Tris(tribromoneopentyl) phosphate					Р			P, T					P, T, A	Р		4	2	1
20120-33-6	N-Hydroxymethyl-3- dimethylphosphonopropionamide (DMPP)	Т							Т			Р			Т		1	3	0
20566-35-2	1,2-Benzenedicarboxylic acid, 3,4,5,6- tetrabromo-, 2-(2-hydroxyethoxy)ethyl 2-hydroxypropyl ester														?		0	0	0
21645-51-2, 8064-00-4, 1318-23-7	Aluminium trihydrate/Boehmite	Р, Т			Р	P, T, C	Р		Р		P, T, C	P, T, C	Р	P, T, C	P, T, C	Р	11	6	5
21850-44-2	Tetrabromobisphenol-A bis (2,3- dibromopropyl ether)	Р	Р	Р, Т	Р	Р		Р	Р					Р	Р		9	1	0
218768-84-4	Melamine polyphosphate	Р	Р		Р	Р			Р		Т	P, T, C	P, T				7	3	1

Table 10-1: I	First screening step – Overview of s	ubstanc	es of	releva	nce to	the rep	lacemo	ent of E	DecaB	DE – Pre	sence (	of alter	nativ	es in lite	rature				
CAS No.	Alternative substance	Keml (2004), Keml (2005). Keml (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	Р	т	С
225789-38-8	Organic phosphinates (diethylphosphinic acid, aluminium salt)	Р	Р		Р	Р, Т	Р	(P)	Р			Р, Т	Р		Р	Т	10	3	0
23488-38-2	Tetrabromo - p - xylene														?		0	0	0
25155-23-1	Trixylenyl phosphate	Р									Р						2	0	0
25327-89-3	Tetrabromobisphenol-A diallylether														Р		1	0	0
25713-60-4	Tris(tribromophenoxy) triazine	Р	Р		Р	Р			Р		Т			Р	?		6	1	0
26040-51-7	Tetrabromophthalate ester										Р			Р	Р		3	0	0
26124-86-7	Barium metaborate	Р															1	0	0
26248-87-3	Tris(chloropropyl) phosphate	Р						Р									2	0	0
26444-49-5	Cresyl diphenyl phosphate	Р	Р	Р	Р		Р	Р	Р	Р	Р	P, T, C		Р			11	1	1
27104-30-9	Tetrakis(hydroxymethyl)phosphonium chloride, oligomeric reaction products with urea (THPC-urea)	Т							Т								0	2	0
2781-11-5	O,O-diethyl-1-N-N bis(2-hydroxyethyl) aminomethyl phosphonate	Р										Р		Р			3	0	0
28108-99-8, 26967-76-0, 68937-41-7	Triisopropylphenyl phosphate	Р									Р						2	0	0
28774-93-8	Tetrabromobisphenol-A polycarbonate								Р								1	0	0
29420-49-3	Potassium perfluorobutane sulphonate (KPBS)											Р					1	0	0
29761-21-5	Isodecyl diphenyl phosphate	Р															1	0	0
30262-02-3	Dibromoethyldibromocyclohexane	Р															1	0	0
31780-26-4	Dibromostyrene														Р		1	0	0

Table 10-1:	First screening step – Overview of s	ubstanc	es or	reieva	nce to	tne rep	lacemo	ent of L	Јесав	DE – Pre	sence	of alter	nativ	es in liter	ature				
CAS No.	Alternative substance	Kemi (2004), Kemi (2005). Kemi (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	Р	т	С
3194-55-6, 25637-99-4	Hexabromocyclododecane	Р		P,T	Р										Р, Т		4	2	0
32588-76-4	Ethylene bis(tetrabromophthalimide)	Р	Р	Р	Р	Р, С		Р	P, (T)		Р			P, T, C	Р, Т		10	3	2
3278-89-5	2,4,6-Tribromphenyl allylether														Р		1	0	0
3296-90-0	Dibromoneopentyl glycol	Р													Р		2	0	0
3296-90-0	Dibromoneopentyl glycol														?		0	0	0
3322-93-8	1,2-Dibromo-4-(1,2- dibromoethylcyclohexane														?		0	0	0
35948-25-5	Dihydrooxaphosphaphenanthrene oxide (DOPO)											Р			Р		2	0	0
36483-57-5	1-Propanol, 2,2-dimethyl-,tribromo derivative														Р		1	0	0
37640-57-6	Melamine cyanurate	Р	Р		Р				Р		Т	Р, Т			Р		6	2	0
37853-59-1	Bis(tribromophenoxy)ethane	Р	Р	Р	Р				Р		Р				Р		7	0	0
38051-10-4	2,2-Bis(chloromethyl)trimethylene bis(bis(2- chloroethyl)phosphate)										Т						0	1	0
4090-51-1	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide											Т				Т	0	2	0
40039-93-8	Tetrabromobisphenol-A epichlorohydrin polymer (brominated epoxy resin)	Р		(P)	Р				Р								4	0	0
5301-78-0, 41583-09-9, 14808-60-7	Reogard 1000	Р	Р						Р								3	0	0
53587-44-3	Melamine borate											P, C					1	0	1
5412-25-9	2,3-Dibromo-1-propanol-hydrogen phosphate														?		0	0	0

Table 10-1: Fi	irst screening step – Overview of s	ubstanc	es of	releva	nce to	the rep	olacemo	ent of C	DecaB	DE – Pre	sence (	of alter	nativ	es in liter	ature				
CAS No.	Alternative substance	Keml (2004), Keml (2005). Keml (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	Р	т	С
5423-23-4	Guanidine phosphate	Υ										Т					0	1	0
546-93-0, 13717-00-5, 5145-48-2, 14457-83-1, 61042-72-6	Magnesium carbonate	Р															1	0	0
56803-37-3; 65652-41-7; 78- 33-1	t-Butyl phenyl diphenyl phosphate	Р												Р			2	0	0
57-13-6	Urea											Т					0	1	0
57583-54-7, 125997-21-9	Resorcinol bis(diphenylphosphate) (RDP)	Р	Р	Р	Р		Р	Р	Р	Р		Р	Р	Р, Т	Р		12	1	0
58965-66-5	Tetradecabromodiphenoxybenzene	Р	Р						Р					Р			4	0	0
593-60-2	Vinyl bromide	Р															1	0	0
59447-55-1	Pentabromobenzylacrylate monomer	Р	Р			Р		Р	P, T						Р		6	1	0
59447-57-3	Poly(pentabromobenzyl) acrylate	Р			Р				Р					Р			4	0	0
5945-33-5 181028-79-5	Bisphenol-A bis(diphenyl phosphate) (BDP/BAPP)	Р	Р	Р	Р		Р	Р	Р	Р	Р	P, T	Р	Р	Р	Р	14	1	0
59536-65-1	Polybrominated biphenyl														?		0	0	0
607-99-8	2,4,6-Tribromoanisole														?		0	0	0
608-71-9	Pentabromophenol	Р													?		1	0	0
61262-53-1	Decabromodiphenyl ethane														?		0	0	0
6145-73-9	Tris (betachloropropyl) phosphate - Tris(2-chloropropyl) phosphate	Р															1	0	0
632-79-1	Tetrabromophthalic anhydride	Р													Р, Т		2	1	0

Table 10-1: I	First screening step – Overview of s	ubstanc	es of	releva	nce to	the rep	lacem	ent of I	DecaB	BDE – Pre	sence (	of alter	nativ	es in liter	ature				
CAS No.	Alternative substance	Keml (2004), Keml (2005). Keml (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), ICL Industrial Products (2013b)	Member States consultation	Industry consultation	P	т	С
63449-39-8, 85535 85-9	Chlorinated paraffins	Р			Р			Р	Р								4	0	0
66034-17-1	Substituted amine phosphate mixture (P/N intumescent systems)					Р		Р	Р			P, T, C				Р	5	1	1
67888-96-4	2,2',4,5,5'-Pentabromobiphenyl														?		0	0	0
68664-06-2	Phosphonate oligomer, Polyphosphonate					Р		Р							Р		3	0	0
68928-70-1; 3072-84-2	Brominated epoxy polymer	Р	Р		Р	Р			Р					Р			6	0	0
68937-40-6, 56803-37-3	Triaryl phosphates butylated	Р	Р		Р				Р					Р, Т			5	1	0
68937-41-7	Triaryl phosphates isopropylated	P, T, C										P, T, C		Р, Т			3	3	2
68952-33-0	Trixylyl phosphate											Р					1	0	0
756-79-9	Dimethyl methyl phosphonate (DMMP)											Р					1	0	0
7585-20-8	Zirconium acetate											Т					0	1	0
77098-07-8	1,2-Benzenedicarboxylic acid, 3,4,5,6- tetrabromo-,mixed esters with diethylene glycol and propylene glycol														?		0	0	0
77098-07-8	Tetrabromophthalate diol	?															0	0	0
77226-90-5	Poly[phosphonate-cocarbonate]					Р											1	0	0
7723-14-0	Red phosphorous (encapsulated)	Р	Р		Р	P, C	Р		Р		Т	P, C		P, C			8	1	3
7778-18-9, 10034-76-1, 10101-41-4	Calcium sulphate	Р															1	0	0
7783-20-2	Ammonium sulphate											Т					0	1	0
7784-22-7	Aluminium hypophosphite											P, T					1	1	0

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CAS No.	Alternative substance	Kemi (2004), Kemi (2005). Kemi (2009)	Danish EPA (2006)	Washington State (2006)	JRC (2007)	US EPA (2012-2014)	Illinois EPA (2007)	Troitzsch (2011)	UK HSE (2012)	Lowell Center for Sustainable Production, (2005)	EFRA (2012, 2012b)	PINFA (2013, 2010, 2010b, 2010c)	ENFIRO	Albemarle (2013) Chemtura (2013b), Id Industrial Products (2013b)	Member States consultation	Industry consultation	P	т	С
7789-79-9	Calcium hypophosphite											P, T					1	1	0
78-38-6	Diethyl ethyl phosphonate (DEEP)											Р					1	0	0
78-40-0	Triethyl phosphate	Р										Р					2	0	0
78-43-3, 26604- 51-3, 13674– 87–8	Tris (dichloropropyl) phosphate	Р															1	0	0
78-51-3	Tributoxy ethyl phosphate	Р												Р			2	0	0
79-94-7	Tetrabromobisphenol-A	Р	Р	Р, Т	Р			Р	P, T					Р	Р		8	2	0
79-95-8	Tetrachlorobisphenol-A	Р															1	0	0
84402-58-4	Methyl phosphonic acid, amidino-urea compound											Т					0	1	0
84852-53-9	Ethane-1,2-bis(pentabromophenyl)	Р	Р	Р, Т	Р	P, T, C		Р	Р		P, T			P, T, C	P, T, C	P, T, C	11	6	4
85-22-3	Pentabromomethylbenzene														Р, Т		1	1	0
868-85-9	Dimethyl hydrogen phosphite (DMHP)	Т															0	1	0
87-82-1	Hexabromobenzene														?		0	0	0
87-83-2	Pentabromomethylbenzene	Р													Р, Т		2	1	0
87-84-3	Pentabromochlorocyclohexane	Р															1	0	0
88497-56-7; 57137-10-7	Brominated polystyrene	Р	Р		Р	Р		Р	Р		Р			Р			8	0	0
94334-64-2, 71342-77-3	Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol-A	Р	Р		Р		_	Р	Р		_			Р			6	0	0

The above approach results in a shorter list of **21 substances**, shown in **Table 10-2**. It should be noted that this approach provides only a rough estimate of the 'popularity' of each alternative. In particular, there is significant overlap of the analyses presented in literature resulting from sources often quoting, or otherwise relying upon other each other. It must also be noted that for specific applications, the most technically feasible alternative may be a more 'exotic' one. The result of this could be that the alternative does not appear in the table at all or perhaps it is included but shows incompatibility with many DecaBDE applications.

Table	10-2: Second sci	reening step – Technical feasibility of identified alt	ernatives for Dec	aBDE		
No	CAS No.	Alternative substance	Consultation with industry	Р	Т	С
1	N/A	Other proprietary product (via consultation)	Р, Т	1	1	0
2	1003300-73-9	Mixtures of esters of phosphoric acid	Р	2	1	0
3	115-86-6	Triphenyl phosphate		9	0	0
4	1309-42-8; 13760-51-5	Magnesium hydroxide		9	2	2
5	13674-87-8	Tris(1,3-dichloro-2-propyl) phosphate	Т	2	2	0
6	14728-39-9; 68333-79-9	Ammonium polyphosphate		7	4	4
7	21645-51-2; 8064-00-4; 1318-23-7	Aluminium trihydrate/Boehmite	Р	9	5	4
8	21850-44-2	Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)		8	1	0
9	218768-84-4	Melamine polyphosphate		7	2	1
10	225789-38-8	Organic phosphinates (Diethylphosphinic acid, aluminium salt)	Т	8	3	0
11	26444-49-5	Cresyl diphenyl phosphate		11	1	1
12	32588-76-4	Ethylene bis(tetrabromophthalimide)		9	2	2
13	37853-59-1	Bis(tribromophenoxy)ethane		7	0	0
14	4090-51-1	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	Т	0	2	0
15	57583-54-7; 125997-21-9	Resorcinol bis(diphenylphosphate) (RDP)		10	1	0
16	5945-33-5; 181028-79-5	Bisphenol-A bis(diphenyl phosphate) (BDP/BAPP)	Р	12	1	0
17	66034-17-1	Substituted amine phosphate mixture (P/N intumescent systems)	Р	5	1	1
18	7723-14-0	Red phosphorous (encapsulated)		8	1	2
19	79-94-7	Tetrabromobisphenol-A		7	2	0
20	84852-53-9	Ethane-1,2-bis(pentabromophenyl)	P, T, C	10	5	3
21	88497-56-7; 57137-10-7	Brominated polystyrene		8	0	0
		Number of 'relevant' alternatives per a	application area	21	19	9

The first substance in the list is a proprietary product the composition of which has not been disclosed; therefore, the analysis that may be offered on this alternative cannot be as full as for other shortlisted alternatives.

# 10.2 Step 3 – Screening for economic feasibility

#### 10.2.1 Introduction

There are two elements to this second screening process: (a) identifying those alternatives which are very costly, and (b) evaluating the substitution costs for each (remaining) alternative in terms of raw material and reformulation cost, investment cost and operating cost.

For the first element, three sources of information have been used in identifying which of the shortlisted substances are potentially too costly in comparison to DecaBDE, thus they might be less likely to find extensive use as alternatives to DecaBDE:

- Information from consultation on specific substances that has been undertaken in the period November 2013 – February 2014 – this has generally been limited, as the number of respondents to the RPA questionnaire (and the ECHA Call for Evidence) has been particularly low. Information that has been provided is shown in the Confidential Annex
- Information from literature this has focused on reviews of alternatives (mostly by regulatory authorities) that have been undertaken in the past
- Information from the Internet indicative prices for both DecaBDE and each of the shortlisted alternatives available from the large trading site <u>Alibaba.com</u>. It is recognised that the site is generally a gateway for Chinese suppliers to promote their products and is merely used to establish the relative prices of alternatives, so the very costly ones (if any) can be identified and screened out. Where the Alibaba.com website did not provide sufficient information, a series of other substances were consulted, including:
  - EC21 (link)
  - ECPlaza (<u>link</u>)
  - ICIS (link)
  - Made in China (link)
  - TradeEasy (<u>link</u>)
  - TradeKey (<u>link</u>).

For the second element, information has been sought primarily from consultation complemented by any readily available information in the open literature.

#### 10.2.2Information on cost of alternatives per tonne from online sources

For DecaBDE and each of the alternatives, CAS Numbers were used to identify suppliers on the Alibaba.com and other websites. For those who provided an indication of the price (per kg), tables were generated with the minimum, maximum and median prices. Subsequently, the average of all median prices of each alternative (and of DecaBDE) was calculated.

	0.00.01	All III	Online trad	ders price
No	CAS No.	Alternative substance	Vs. DecaBDE	Source
1	N/A	Other proprietary product (via consultation)	-	-
2	1003300-73-9	Mixtures of esters of phosphoric acid	No data	-
3	115-86-6	Triphenyl phosphate	-21%	Α
4	1309-42-8; 13760-51-5	Magnesium hydroxide	-75%	А
5	13674-87-8	Tris(1,3-dichloro-2-propyl) phosphate	-61%	-
6	14728-39-9; 68333-79-9	Ammonium polyphosphate	-54%	А
7	21645-51-2; 8064-00-4; 1318-23-7	Aluminium trihydrate	-88%	А
8	21850-44-2	Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	-44%	А
9	218768-84-4	Melamine polyphosphate	-18%	Α
10	225789-38-8	Organic phosphinates (Diethylphosphinic acid, aluminium salt)	No data	-
11	26444-49-5	Cresyl diphenyl phosphate	-47%	Α
12	32588-76-4	Ethylene bis(tetrabromophthalimide)	+40%	A/M
13	37853-59-1	Bis(tribromophenoxy)ethane	No data	
14	4090-51-1	2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	No data	-
15	57583-54-7; 125997-21-9	Resorcinol bis(diphenylphosphate) (RDP)	No data	-
16	5945-33-5; 181028-79-5	Bisphenol-A bis(diphenyl phosphate) (BDP)	-49%	А
17	66034-17-1	Substituted amine phosphate mixture (P/N intumescent systems)	No data	-
18	7723-14-0	Red phosphorous	-28%	Α
19	79-94-7	Tetrabromobisphenol-A	-12%	Α
20	84852-53-9	Ethane-1,2-bis(pentabromophenyl)	+18%	Α
21	88497-56-7; 57137-10-7	Brominated polystyrene	+10%	А

A: price data from Alibaba.com

M: limited price data from <a href="http://www.made-in-china.com/showroom/yadele/product-">http://www.made-in-china.com/showroom/yadele/product-</a>

<u>detailsoCQeASubMtn/China-Flame-Retardant-Ethylenebistetrabromophthalimide-CAS-32588-76-4.html</u> (accessed on 31 January 2014)

It must be noted that some of the above estimates may differ to the information submitted by consultees (see Confidential Annex). Therefore, the above table should only be seen as indicative and not a robust review of market prices.

#### 10.2.3Information on cost of alternatives per kg from literature

Some additional information on the costs of alternatives is available from a range of literature sources. The 2006 Danish EPA report offers some indication of the price difference between DecaBDE-retardant plastics and alternative formulations.

Table 10-4: Cost comparison of alternatives to DecaBDE-based formulations – Danish EPA (2006)								
Comparison	Polymer/compound	European price range (€/kg)	Comments					
	Standard HIPS	0.95 – 1.25	HB fire standard					
	HIPS + DecaBDE	1.50 – 1.80	This HIPS+DecaBDE price reflected the Southeast Asia					
HIPS compounds	HIPS + other BFR: - UL 94 V-0 - UL 94 V-1 HIPS/PPE + halogen- free FR	1.90 - 2.10 1.70 - 1.90 2.30 - 2.90	market. In addition to the basic PS price, the compound price reflects primarily the fire rating (V-2 at the lower end of the price range, and V-0 at the upper end), as well as the volume purchased, the specific FR used, etc.					
Comparison	Polymer/compound	Resin costs (€/kg)	Resin cost for "average" TV-set rear enclosure*	Resin cost for "average" TV-set front & rear enclosure				
	FR HIPS + DecaBDE	1.6 – 1.8	13.0	20.3				
Various V-0 systems for enclosures	FR ABS + TBBPA or brominated epoxy oligomer	1.9 – 2.5	16.8	26.4				
on the	ED 4 DC /D C							
	FR ABS/PC + Halogenated FR	2.5 – 3.0	21.0	33.0				
on the American market in 2004		2.5 – 3.0 3.0 – 3.6	21.0	33.0				

Source: Danish EPA (2006)

A further table, available from a recent HELCOM publication, compares the most commonly used alternatives, their median prices and possible affordability issues for producers.

Table 10-5: Cost comparison of alternatives to DecaBDE-based formulations – HELCOM (2013)								
Material	Possible substitutes	Price of substitutes (€/kg)	Affordability issues for producers					
	RDP - cannot be direct substitute for pure HIPS	<3.5	Minimal or none					
HIPS/PPO; PC/ABS	ТРР	6						
	Bisphenol-A	4.5						
Textiles and	Phosphorous-based FRs, such as Pyromescent	5.5	Minimal, except for					
upholstery for furniture	Mixed phosphorus/halogenated FRs, such as Pyrozoyl 6P	6.5	transportation applications where they can be significant					
Building and construction materials	Different types of phosphorus-based products, such as Reofos and Kronitex	4	Minimal or none					
Source: HELCOM (	2013)							

<sup>\*</sup>Average" TV-set is a 27.5-inch CRT unit with front and rear enclosure weights of 3.5 and 1.95 kg, respectively

HELCOM asserts that the total cost increase for end products is rather insignificant, e.g. 1.5 to 2.5% of total purchase price for a TV set, if PC/ABS and an alternative FR were used rather than DecaBDE-retardant HIPS. However, these costs cover only the cost of raw materials for the production process and do not include the costs for any process or technology changes that may be necessary in a given case.

Due to cases where direct substitution is not possible - for example, the automotive and aviation industry where textiles need to meet considerably stricter fire safety regulations - it is very complicated to assess the final costs of substitution of PBDEs. For replacement of backcoated fabric with a barrier layer or an inherently flame-retardant fibre, the solution can include costs of new materials, fabrics, foams, barrier layers, etc. (HELCOM, 2013).

Finally, the latest (2013) report by the Danish EPA provides a summary of cost differences between BFRs and non-halogenated alternatives for applications in electrical and electronic equipment, based on information from PINFA from the year 2010. Materials with non-halogenated FRs are generally 10-30% more expensive than materials with BFRs, as shown below.

Table 10-6: Indicative cost of phosphorous, inorganic and nitrogen FRs – PINFA (2010)							
Commonwell	Cost differential						
Component categories	on material level	in finished product					
Wire and cable	ca. 20%	Represents 1-5% of the retail price of					
Enclosures	ca. 20%	end products (fridge, TV, etc.)					
Components	10-20%						
Wiring	10-30%						
Source: Danish EPA (2013)							

#### 10.2.4Conclusions

The information available is certainly limited and data from consultation may well contradict what is available from sources such as Alibaba.com. Moreover, there is considerable uncertainty on the parameters of use of each alternative (price per tonne, loading, other changes in formulations and operating costs). Nevertheless, to the extent that this information can be considered in this analysis, we have not conclusively identified any alternative that can be assumed to be too costly, and therefore, unlikely to be used by industry.

Consequently, no exclusion of any alternative can be undertaken and all 21 shortlisted alternatives will be taken to Screening Step 4.

# 10.3 Step 4 – Screening for suitability (hazards)

We have used a number of information sources in our efforts to screen the shortlist of alternatives so that a more manageable list of <u>realistic</u> alternatives can be generated. For the screening of the shortlist for suitability (i.e. environmental and human health effects), the following key sources have been consulted:

- The Authorisation List<sup>62</sup>
- The Candidate List of Substances of Very High Concern for Authorisation<sup>63</sup>
- The C&L Inventory<sup>64</sup>
- Information from the Existing Substances Regulation<sup>65</sup>

#### and

- The CoRAP List of Substances<sup>66</sup>
- The SIN List<sup>67</sup>
- The European chemical Substances Information System PBT List<sup>68</sup>
- The Endocrine Active Substances Information System (EASIS) database<sup>69</sup>
- The US EPA PBT Profiler<sup>70</sup>

The first three sources are considered the most important in screening out demonstrably more hazardous substances. The remaining sources may give indications of current or potential future concern but are only used to highlight those areas rather than issue a judgement on the suitability of the alternatives. Consequently, these screening criteria-tools have been ordered by priority level based on the importance of the relevant information sources, reliability, importance, if peer reviewed or not, etc.

**Table 10-8** provides the master list of the identified potential alternative substances. For each entry in the columns, a different background colour has been given in accordance with the following approach (**Table 10-7**). **Substances that have been allocated at least one 'red' entry have been considered suitable for elimination from further consideration**.

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Available at: <a href="http://echa.europa.eu/addressing-chemicals-of-concern/authorisation/recommendation-for-inclusion-in-the-authorisation-list/authorisation-list (last accessed on 7 November 2013).">http://echa.europa.eu/addressing-chemicals-of-concern/authorisation/recommendation-for-inclusion-in-the-authorisation-list/authorisation-list (last accessed on 7 November 2013).</a>

<sup>&</sup>lt;sup>63</sup> Available at: <a href="http://echa.europa.eu/candidate-list-table">http://echa.europa.eu/candidate-list-table</a> (last accessed on 7 November 2013).

<sup>&</sup>lt;sup>64</sup> Available at: http://echa.europa.eu/regulations/clp/cl-inventory (last assessed on 7 November 2013).

Available at: <a href="http://echa.europa.eu/information-on-chemicals/information-from-existing-substances-regulation">http://echa.europa.eu/information-on-chemicals/information-from-existing-substances-regulation</a> (last accessed on 7 November 2013).

Available at: <a href="http://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-list-of-substances">http://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-list-of-substances</a> (last accessed on 7 November 2013).

Available at: <a href="http://w3.chemsec.org/">http://w3.chemsec.org/</a> (last accessed on 21 November 2013).

<sup>&</sup>lt;sup>68</sup> Available at: <a href="http://esis.jrc.ec.europa.eu/index.php?PGM=pbt">http://esis.jrc.ec.europa.eu/index.php?PGM=pbt</a> (last accessed on 21 November 2013).

Available at: <a href="http://ihcp.jrc.ec.europa.eu/our activities/food-cons-prod/endocrine disrupters/eas database/intro#follow-the-main-steps">http://ihcp.jrc.ec.europa.eu/our activities/food-cons-prod/endocrine disrupters/eas database/intro#follow-the-main-steps</a> (last accessed on 21 November 2013).

Available at: <a href="http://www.pbtprofiler.net/">http://www.pbtprofiler.net/</a> (last accessed on 21 November 2013).

Table 10-7: Criteria used in screening the master list of alternatives for suitability								
Priority	Criterion	Red colour	Orange colour	Yellow colour				
1	Annex XIV	Substance is found on	N/A	N/A				
	List	the Annex XIV List						
2	Candidate	Substance is found on	N/A	N/A				
	List	the Candidate List						
3	Harmonised	Substance is classified	Substance is classified with	N/A				
	C&L	with one of the following	hazard codes other than					
		hazard codes:	those of the 'Red category'					
		H317, H334, H340, H350,						
		H360, H370, H372, H373,						
4	ECD DAD	H400, H410, H413	College of the colleg	N1/A				
4	ESR RAR	Substance has been	Substance has been subject to a Risk Assessment under	N/A				
		subject to a Risk Assessment under the	the ESR and has not been					
		ESR and has been	identified with a Conclusion					
		identified with a	(iii) for any environmental					
		Conclusion (iii) for one or	scenario					
		more environmental	Sections					
		scenarios						
5	ESIS PBT	Substance has been	Substance is being	N/A				
	List	conclusively identified by	evaluated and is yet to be	,				
		a Member State as a PBT	concluded by a Member					
		substance	State as a PBT substance					
6	CoRAP List	N/A	Substance is found on the	N/A				
			CoRAP List (year and					
			Member State provided)					
7	SIN List	N/A	Substance is found on the	N/A				
			SIN List					
8	Notified	N/A	Substance is notified with	Substance is classified				
	C&L		one of the following hazard	with hazard codes other				
			codes <u>in its most common</u>	than those of the 'Red				
			notification:	category'				
			H317, H334, H340, H350,					
			H360, H370, H372, H373,					
0	FACIC	N/A	H400, H410, H413	NI/A				
9	EASIS	N/A	Substance has been	N/A				
	Database		identified as a potential endocrine disruptor					
10	US EPA PBT	N/A	Substance appears to meet	Substance appears to				
10	Profiler*	13/7	all 3 US EPA PBT criteria (all	meet only 1 or 2 of the				
			3 letters appear in red	US EPA PBT criteria (the				
			colour)	respective letters				
			,	appear in red colour)				

<sup>\*</sup> The PBT criteria used by the US EPA PBT profiler are different from the PBT criteria in Annex XIII to the REACH Regulation; thus, a PBT substance according to the US EPA PBT Profiler is not necessarily a PBT substance according to REACH. Furthermore, the US EPA PBT Profiler is based on (Q)SARs information

Table 10-8: Screening of identif	ied potential alt	ernatives f	for DecaBD	E for suitabil	ity						
Potential alternative substance	CAS No	Annex XIV List	Candidate List	Harmonised C&L	ESR RAR	ESIS PBT List	CoRAP List	SIN List	Notified C&L	EASIS Database	US EPA PBT Profiler
Mixtures of esters of phosphoric acid	1003300-73-9	Х	Х	Х	Х	Х	Х	Х	No entry		Х
Triphenyl phosphate (TPP)	115-86-6	Х	Х	Х	Х	Х	2015-UK	Х	H400, H410	Х	PBT
Magnesium hydroxide	1309-42-8	Х	х	Х	Х	Х	х	Х	NC - H315, H319,H335 - H302, H315, H319, H332, H335	х	N/A
Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	Х	х	H351	List 4	Х	х	Х	H302, H315, H331, H411 - H315, H351, H373, H411	Х	РВТ
Ammonium polyphosphate	14728-39-9; 68333-79-9	Х	х	х	Х	Х	Х	Х	NC	Х	N/A
Aluminium trihydroxide	21645-51-2; 8064-00-4	Х	Х	х	Х	Х	х	Х	NC - H315, H319, H335	Х	N/A
Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	21850-44-2	Х	Х	х	Х	х	х	Х	NC	Х	₽BT
Melamine polyphosphate	218768-84-4	Х	Х	Х	Х	Х	Х	Х	No entry	Х	Х
Organic phosphinates	225789-38-8	Х	Х	Х	Х	Х	Х	Х	No entry	Х	Х
Cresyl diphenyl phosphate (CDP)	26444-49-5	Х	Х	Х	Х	Х	Х	Х	H400, H410 - H302	Х	Х
Ethylene bis(tetrabromophthalimide)	32588-76-4	Х	Х	Х	Х	No - FR	Х	Х	NC	Х	PBT
Bis(tribromophenoxy)ethane	37853-59-1	Х	Х	Х	Х	Х	Х	Х	NC	Х	PBT!
2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	4090-51-1	Х	Х	Х	Х	Х	Х	Х	No entry		РВТ
Resorcinol bis(diphenylphosphate) (RDP)	57583-54-7; 125997-21-9	х	Х	х	Х	Х	х	х	H412 - NC - H411 H400, H412 - H319, H412	Х	PBT
Bisphenol-A bis(diphenyl phosphate)	5945-33-5	Х	Х	H413	Х	Х	Х	Х	H413	Х	PBT
(BDP/BAPP)	181028-79-5	Х	Х	Х	Х	Х	Х	Х	H411 - NC	Х	PBT
Substituted amine phosphate mixture (P/N intumescent systems)	66034-17-1	х	Х	х	Х	х	х	х	H319, H412	Х	х
Red phosphorous	7723-14-0	Х	Х	H228, H412	Х	Х	х	Х	H228, H412 - H250, H300, H314, H330, H400	Х	N/A
Tetrabromobisphenol-A (TBBPA)	79-94-7	Х	Х	H400, H410	List 4	Х	Х	YES	H400, H410	Х	PBT
Ethane-1,2-bis(pentabromophenyl)	84852-53-9	Х	Х	Х	Х	Х	2012-UK	Х	H413 - NC	Х	PBT
Brominated polystyrene	88497-56-7	Х	Х	Х	Х	Х	Х	Х	NC - H319	Х	Х

The above screening process would appear to result in the elimination of only two alternative substances, Bisphenol-A bis(diphenyl phosphate) (BDP/BAPP) (CAS No. 5945-33-5; 181028-79-5) and Tetrabromobisphenol-A (TBBPA) (CAS No. 79-94-7). However, there appears to be some uncertainty on the harmonised classification of BDP (CAS No. 5945-33-5). The UK Competent Authority has submitted a proposal for the removal of the H413 classification (Aquatic Chronic 4)<sup>71</sup>. In light of this, it is considered appropriate to maintain the substance in the shortlist and only remove TBBPA. Therefore, a total of 19 potential alternative substances remain. Additionally, a proprietary product has also been eliminated from the shortlist as the information on it is very limited, thus a meaningful assessment cannot be undertaken.

# 10.4 Step 5 – Screening for market availability

The final step of screening is for market availability. The only readily available criterion is the availability of a REACH Registration. It is acknowledged that this cannot be a very strict criterion for a number of reasons:

- The analysis is based on what information could be found on the ECHA Registered Substances online database on 28 January 2014
- The lack of information on the ECHA website cannot be construed to signify the absence of a registration or to imply that a registration will not be submitted in the future
- The tonnage band of substances may change, if demand for them increases, and registrations
  may be updated accordingly allowing for substances to be placed on the market at the
  appropriate tonnage band
- There is still one round of registrations to take place in 2018 for substances places on the market at a tonnage of 10-100 t/y. This tonnage is quite small compared to the historical consumption of DecaBDE, but this does not mean that there may not be several suppliers of any single substance
- Use of this criterion might exclude less hazardous substances because substances that are manufactured or imported below 100 t/y per manufacturer or importer and that are not classified with CMR (Cat 1A or 1B) are not required to be registered until 2018.

Overall, the REACH Registration criterion is not a 'hard and fast' rule and has only been used to provisionally exclude substances for which market presence is uncertain and for which data availability on hazards is likely to be more modest.

With the above caveats in mind, the market availability of the shortlisted alternatives is shown in **Table 10-9**. In orange, substances without a current registration on the ECHA website are shown.

The table provisionally eliminates from further consideration seven substances. This results in a final shortlist of 12 potential alternative substances, which were compared to DecaBDE in Section 5. The final shortlist includes a variety of different substances, such as:

Alternative BFRs

- Phosphorous-based FRs
- P/N intumescent systems
- Inorganic FRs.

<sup>&</sup>lt;sup>71</sup> See document here: <a href="http://echa.europa.eu/documents/10162/9de48032-7e70-426d-9c83-25a004b3999a">http://echa.europa.eu/documents/10162/9de48032-7e70-426d-9c83-25a004b3999a</a>

Table 10-9: Screening of identified potential alternatives for DecaBDE for market availability							
Potential alternative substance	CAS No	REACH Registration (t/y)					
Mixtures of esters of phosphoric acid	1003300-73-9	X					
Triphenyl phosphate (TPP)	115-86-6	1,000-10,000					
Magnesium hydroxide	1309-42-8	100,000-1,000,000					
Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	1,000-10,000					
Ammonium polyphosphate	14728-39-9; 68333-79-9	Х					
Aluminium trihydroxide	21645-51-2; 8064-00-4	1,000,000-10,000,000					
Tetrabromobisphenol-A bis (2,3-dibromopropyl ether)	21850-44-2	1,000-10,000					
Melamine polyphosphate	218768-84-4	Х					
Organic phosphinates	225789-38-8	Х					
Cresyl diphenyl phosphate (CDP)	26444-49-5	Х					
Ethylene bis(tetrabromophthalimide)	32588-76-4	100-1,000					
Bis(tribromophenoxy)ethane	37853-59-1	Х					
2,2'-Oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide	4090-51-1	100-1,000					
Resorcinol bis(diphenylphosphate) (RDP)	57583-54-7; 125997-21-9	1,000-10,000					
Bisphenol-A bis(diphenyl phosphate) (BDP/BAPP)	5945-33-5; 181028-79-5	100-1,000 1,000-10,000					
Substituted amine phosphate mixture (P/N intumescent systems)	66034-17-1	10-100					
Red phosphorous	7723-14-0	1,000-10,000					
Ethane-1,2-bis(pentabromophenyl)	84852-53-9	>1,000					
Brominated polystyrene	88497-56-7	Х					

# 11 Annex 5 – Similarities and differences between DecaBDE and EBP

#### 11.1 EBP and DecaBDE

Information on the similarities and differences between DecaBDE and EBP, the main alternative to DecaBDE, has been provided by Albemarle, a registrant of both substances and is reproduced below by way of background information. All data have been provided by Albemarle (2014b) and are provided for information.

The two substances share similarities, for example, two aromatic rings; 10 bromine atoms; high molecular weight; large molecular size; limited solubility in water and organic solvents; and poor suitability to gas chromatography. Furthermore, their two-dimensional structures appear similar (Figure 11-1).

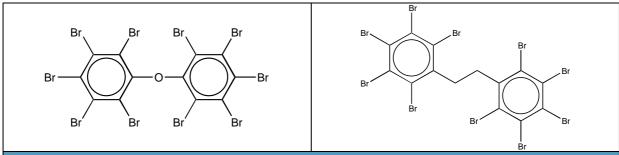


Figure 11-1: Structures of DecaBDE (I) and EBP (r) Source: Albemarle (2014b)

Nevertheless, the two molecules have important differences in their molecular shape, dimensions, and conformations (**Table 11-1**, **Figure 11-2**). Molecular shape and dimensions affect the manner in which molecules interact with their environment. For example, a molecule's ability to traverse membranes, bind to receptors and interact with solvents is influenced by its shape and dimensions (Albemarle, 2014b).

DecaBDE exists as a single 3-dimensional conformer. The 10 bulky bromine atoms on the two aromatic rings constrain the molecule to a single conformation with the aromatic rings orthogonal (approximately perpendicular) to one another and a 120° bend at the oxygen bridge (Albemarle, 2014b).

The rings in EBP also have ten bromine atoms but are separated by an ethane bridge rather than an oxygen bridge. This ethane bridge creates enough separation between the two fully substituted aromatic rings for the molecule to rotate around the bridge and assume several 3-dimensional configurations, each with distinct molecular dimensions. The different conformers vary in energy with the molecule spending more time in the lowest energy configuration. EBP's most stable conformer is folded at an acute angle at the ethane bridge resulting in a shorter molecular length than DecaBDE. Nevertheless, EBP molecular volume, surface area and cross sectional diameter are larger than DecaBDE (Albemarle, 2014b).

The pronounced differences in the molecular shape and size of DecaBDE and EBP can be expected to create differences.

Table 11-1: Molecular dimensions of EBP and DecaBDE								
Burnanta		DeceRDE						
Property	Most stable	Least stable	DecaBDE					
Length (Å)	14.4	16.8	15.1					
Cross Sectional Diameter (Å)	10.3	9.5	10.0					
Surface Area (Å <sup>2</sup> )	408	417	390					
Volume (Å <sup>3</sup> )	400	400	372					

Source: Albemarle (2014b)

Note: Dimensions were calculated as described in Louwen and Stedeford (2011)<sup>72</sup>, and performed September 2012. Surface areas and volumes were calculated in Spartan molecular modelling software using quantum mechanic calculated structures

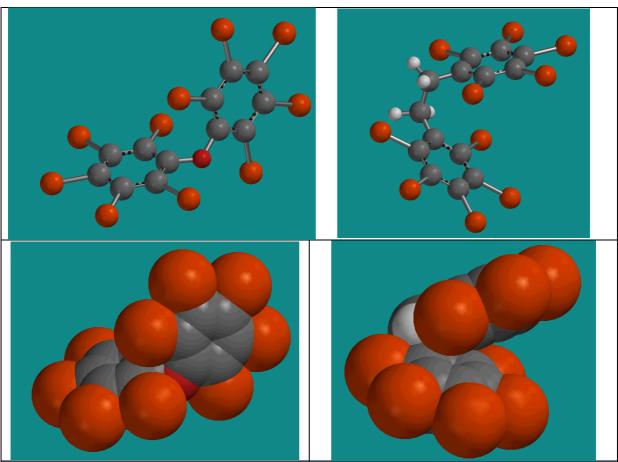


Figure 11-2: Structures of DecaBDE (left) and EBP's (right) most stable conformer 73. Orange = bromine; white = hydrogen; grey = carbon; red = oxygen

Source: Albemarle (2014b)

<sup>&</sup>lt;sup>72</sup> Louwen, J and Stedeford, T. 2011. Toxicology Mechanisms and Methods 21(3):183-192.

Sturctures and energies were computed with the program GAMESS using the M08-HX density functional and the 6-31G(p,d) basis set (Albemarle, 2014b).

# 11.2 Lower brominated diphenyl ethers and ethanes

#### 11.2.1 Introduction

Biodegradation studies conducted to date indicate EBP is persistent with no evidence of environmental breakdown. These studies include:

- A ready biodegradation test
- An enhanced aerobic sludge/soil study using <sup>14</sup>C-EBP
- A prolonged anaerobic sewage sludge test run at elevated temperature with <sup>14</sup>C-EBP.

The studies using <sup>14</sup>C-EBP investigated transformation with both non-specific and specific methods to detect biodegradation (Albemarle, 2014b).

As a first step, Albemarle generated conformation and molecular dimension data for representative hexa-, hepta-, octa- and nonabrominated diphenyl ethers and ethanes using the same method as for DecaBDE and EBP. This information is reported below (Albemarle, 2014b).

#### 11.2.2 Conformation

While the DecaBDE molecule is constrained to one 3-dimensional conformation, individual lower brominated diphenyl ether moieties may exist in more conformers. The conformers of each molecule vary in energy, with some more stable than others. Their aromatic rings may be in- or out-of-plane with each other, and each ring may rotate over 180°. In general, the lower brominated diphenyl ethers are asymmetric with one ring in the C-O-C plane and the other approximately perpendicular to the plane (Albemarle, 2014b).

The ethane bridge profoundly affects the molecular shape of lower brominated diphenyl ethanes. The ethane bridge allows the aromatic rings to adopt a single trans or up to two gauche arrangements around the C-C bridge. The conformers of each molecule vary in energy, with some more stable than others. In general, trans conformers are higher in energy (less stable) than gauche conformers. The dihedral angle around the  $C_{bridge}$ - $C_{ring}$  bond is such that neither of the two  $C_{bridge}$ -H or the  $C_{bridge}$ - $C_{bridge}$  bonds is in the plane of the phenyl ring. This leads to a maximum of six symmetrically unique conformers. Depending on the pattern of substitution, this number can be further reduced to three (154, 206, 207) or five (153, 197). Whereas the aromatic rings of the diphenyl ethers are roughly perpendicular to one another, the lower brominated ethanes are folded with one of the rings typically twisted in its orientation to the other (Albemarle, 2014b).

#### 11.2.3 Molecular dimensions

Molecular dimensions of the six representative hexa-, hepta-, octa- and nonabrominated diphenyl ethers and -ethanes are provided in **Table 11-2**. In general, ethane congeners are capable of existing as a greater number of potential conformers than the corresponding ether congeners. Similar to EBP, the lower brominated diphenyl ethanes generally have lower molecular lengths but higher cross sectional diameters, surface areas and volumes. That is, the hexa-, hepta-, octa- and nonabrominated diphenyl ethanes reported here have larger surface areas and volumes than the corresponding ethers. The ethanes' cross sectional diameters for the modelled octa- and nona-s are also larger than the corresponding ethers. For both the ethanes and ethers, surface area and volume increase with increasing bromination (Albemarle, 2014b).

		Molecular Dimensions									
Congener			Brominated Di	iphenyl Ethe	rs	Brominated Diphenyl Ethanes					
	Conformer*	Length [Å]	Cross- sectional diameter [Å]	Surface area [Ų]	Volume [ų]	Length [Å]	Cross- sectional diameter [Å]	Surface area [Ų]	Volume [ų]		
138	1	14.35	9.63	319	299	14.06	9.33	340	326		
	2	14.75	8.80	319	299	13.24	9.71	343	326		
	3	14.75	8.25	315	298	13.54	9.78	340	326		
	4	-	-	-	-	13.92	9.07	337	326		
	5	-	-	-	-	16.75	9.37	349	327		
	6	-	-	-	-	16.69	9.21	349	327		
154	1	14.90	10.07	322	299	13.05	9.70	340	326		
	2	14.99	8.72	318	299	13.74	9.15	336	326		
	3	-	-	-	-	17.03	9.62	350	327		
183	1	14.53	10.02	338	317	13.60	9.70	356	343		
	2	14.34	10.05	338	317	13.91	9.87	352	343		
	3	14.98	8.76	335	316	13.12	10.14	356	343		
	4	14.88	9.51	335	316	16.70	9.60	367	345		
	5	-	-	-	-	16.70	9.74	367	345		
	6	-	-	-	-	14.00	9.69	358	343		
197	1	14.96	8.78	352	334	14.11	9.31	366	360		
	2	14.77	9.57	352	334	13.72	9.88	367	361		
	3	14.86	9.95	352	334	13.26	10.21	368	361		
	4	-	-	-	-	16.74	9.44	381	362		
	5	-	-	-	-	16.81	9.50	381	362		
206	1	14.70	10.09	371	352	14.05	10.16	388	378		
	2	14.90	9.80	367	351	14.45	9.95	384	378		
	3	-	-	-	-	16.71	9.77	398	380		
207	1	14.75	9.56	368	351	14.14	9.87	382	378		
	2	14.76	9.93	368	351	13.85	10.22	383	378		
	3	-	-	-	-	17.01	9.49	396	380		
209	1	15.06	10.0	390	372	14.41	10.3	408	400		

Source: Albemarle (2014b)

### 11.2.4 Conclusions

Molecular shape and dimension affect the manner in which a molecule interacts with its environment as well as its biological activity. For example, a molecule's ability to traverse membranes, bind to receptors, and interact with solvents is affected by its size and shape. Profound differences exist between DecaBDE and EBP, and the lower brominated diphenyl ethers and ethanes (Albemarle, 2014b).

<sup>\*</sup> Conformers are listed in descending order of stability; the most stable conformer (e.g. lowest energy) is listed first

#### 11.3 Toxicokinetics and bioaccumulation

#### **11.3.1 DecaBDE**

DecaBDE's mammalian kinetics are dominated by diffusion-limited uptake. The major fraction of an oral DecaBDE dose is eliminated in the faeces without prior absorption because of its low/slow diffusion through cells, high binding to faecal matter, and the finite length of the GI tract. DecaBDE's low/slow diffusion through cells is related to its limited aqueous solubility (substances must be in solution prior to passive diffusion). DecaBDE binds extensively to faecal matter, which further limits its solubility. The finite length of the GI tract limits the duration that DecaBDE is available for absorption. Despite these barriers, a small fraction of the dose may be absorbed through the intestine into the bloodstream. All blood exiting the GI tract flows directly to the liver. Substances > 300 daltons are preferentially eliminated in the bile. The liver shuttles the major fraction of the absorbed dose directly to the bile where it is eliminated in the faeces as the parent molecule. A small fraction of the absorbed dose reaching the liver enters the systemic circulation and on subsequent passes is extracted from the blood by the liver, transported to bile and eliminated in the faeces as the parent molecule. Metabolism is insignificant, and does not play an important role in DecaBDE's elimination (Albemarle, 2014b).

DecaBDE's low/slow uptake limits blood concentrations. Blood concentrations do not increase with oral doses  $\geq$  10 mg/kg/d, and steady state concentrations are reached within a matter of a few daily doses.

Certain parts of this information were obtained in work leading up to the GLP/guideline-compliant developmental neurotoxicity study required by the EU. This information has been published  $^{74}$ , and was included in the REACH registration dossier of DecaBDE and is summarised below (Albemarle, 2014b):

- Maximal DecaBDE plasma concentrations were observed in rats at repeated oral doses of 10 mg/kg body weight. Administration of repeated oral doses of 100 or 1000 mg/kg body weight did not result in plasma concentrations higher than those at 10 mg/kg/d. Plasma concentrations were generally indistinguishable over a dose range of 2 orders of magnitude, i.e., 10 to 1000 mg/kg/d in dams, foetal litters and neonatal pups
- The lack of a dose response in maternal plasma concentration is due to a combination of factors, including binding to faecal macromolecules, diffusion-limited uptake from the gut into the portal circulation, and efficient first-pass elimination in the bile, such that only a small fraction of the dose is systemically bioavailable

Biesemeier JA, Beck MJ, Silverberg, H, Myers NR, Ariano JM, Bodie ES, Sved DW, Jacobi S, Stump DG, Hardy M, Stedeford T. 2010. Effects of dose, administration route and/or vehicle on decabromodiphenyl ether (DecaBDE) concentrations in plasma of maternal, fetal and neonatal rats and in milk of maternal rats. Drug

Metab Disposition 38: 1648-1654. Supplemental Information: pg 1-18.

<sup>7</sup> 

Biesemeier JA, Beck MA, Silberberg H, Myers NR, Ariano JM, Radovsky A, Freshwater L, Sved DW, Jacobi S, Stump DG, Hardy ML, Stedeford T. 2011. An Oral Developmental Neurotoxicity Study of Decabromodiphenyl Ether (DecaBDE) in Rats. Birth Defects Research, Part B. 92:17-35. Supplemental Info: pg 1-68.

- Steady-state plasma levels had been reached by the first sampling, that is, after 15 daily doses, and likely occurred much earlier. Therefore, prolonged dosing periods are not required to establish a steady state and it is not expected that the body burden increases with time
- At oral doses ≥ 10 mg/kg/d, DecaBDE's absorption is governed by zero-order kinetics, e.g. a constant amount is absorbed per unit time, whereas first-order absorption kinetics, e.g. a constant fraction of the dose is absorbed, occurs at oral doses below 10 mg/kg/d. The total amount absorbed from doses ≥ 10 mg/kg/d will always be greater than the fractional amount absorbed from doses < 10 mg/kg/d. Thus, studies performed at doses ≥ 10 mg/kg/d represent a worst case
- Maximal maternal plasma concentrations after repeated doses is ca. 1000 ng/mL
- Maternal plasma concentrations dictate those in foetal plasma and maternal milk. Foetal plasma and maternal milk concentrations are below those in maternal plasma.

The above information was derived in laboratory rats and is directly relevant to the environmental risk assessment. Wild rodents play an important role in ecosystems, and serve as a food source for numerous terrestrial predators. Oral DecaBDE exposures ≥10 mg/kg bw/d do not produce corresponding increases in blood concentrations, and maximal plasma concentrations after repeated exposures are ca. 1000 ng/mL. This correlates with the general lack of toxicity observed in multiple repeated dose studies at doses up to and exceeding 1000 mg/kg/d<sup>76 77 78 79</sup>. Thus, 1000 ng/mL plasma represents an internal no effect level. This information indicates terrestrial predators would not be exposed to prey containing levels higher than those associated with blood levels of ca. 1000 ng/mL. Levels reported in biological samples collected in the wild are substantially below this (Albemarle, 2014b).

#### Effect of lower doses and vehicle/solvent

Biesemeir et al. (2010) compared the bioavailability of DecaBDE administered by gavage in one of two vehicles, e.g. corn oil or soyaphospholipone/Lutrol (SPL). SPL was the vehicle used by Morck et al. (2003), who reported higher absorption than that observed after dietary administration. Morck et al. based their absorption estimate on the fraction of a gavage dose recovered in bile, whereas prior estimates were based on blood levels after dietary administration. Morck et al.'s results have subsequently been interpreted to indicate (a) DecaBDE's systemic bioavailability may be up to 10% of an oral dose, and (b) an SPL vehicle provided better availability than corn oil. However, further work demonstrates that the SPL vehicle actually produces lower DecaBDE plasma concentrations compared to corn oil (Biesemeier et al. 2010). This demonstrates the importance of verifying results and assumptions through repetition in different laboratories (Albemarle, 2014b).

As discussed above, DecaBDE blood levels are governed by first-order absorption kinetics at oral doses < 10 mg/kg/d and zero-order absorption at doses ≥ 10 mg/kg/d. The total amount absorbed at doses > 10 mg/kg/d will always be greater than that from lower doses irrespective of a higher

NTP (National Toxicology Program). Toxicology and carcinogenesis studies of decabromodiphenyl oxide [CAS 1163-19-5] in F344 rats and B6C3F1 mice (feed studies). 309, 1-244. 2008. Technical Report Serie.

Hardy ML, Mercieca MD, Rodwell DE, Stedeford T. Prenatal Developmental Toxicity of Decabromodiphenyl Ethane in the Rat and Rabbit. Birth Defects Research (part B) 2010; 89(2):139-146.

Biesemeier et al., 2010. See above.

Biesemeier et al., 2011. See above.

percentage absorption at doses < 10 mg/kg/d. Morck et al. claimed a higher % absorption than previously reported based on the fraction of the gavage dose detected in the bile (ca. 10%) compared to the ca. 0.3% uptake after dietary administration of substantially higher doses (NTP 1986). However, Morck et al.'s estimate of 10% absorption is not representative of systemic bioavailability, which is determined via blood concentrations (substances may be eliminated in the bile without prior systemic circulation.) DecaBDE has a very low systemic bioavailability as demonstrated in multiple studies including that of NTP 1986. Further, the dose administered by Morck et al., 3  $\mu$ mol/kg, is within the range where first order absorption kinetics would apply. That is, at an oral dose of 3  $\mu$ mol/kg a constant fraction of the dose would be absorbed. This, coupled with the fact that higher peak levels are typically associated with gavage versus dietary administration, accounts for the differences in percent of dose absorbed. As shown by Biesemeier et al. (2010), an SPL vehicle results in lower DecaBDE blood levels than the common vehicle, corn oil (Albemarle, 2014b).

DecaBDE is eliminated in the faeces as the parent molecule, largely without prior systemic circulation. Metabolism is minimal. For example, Huwe et al. (2007)<sup>80</sup> estimated 1% of a total BDE 209 dose appeared metabolised to 1 NonaBDE and 2 OctaBDEs (Albemarle, 2014b).

## 11.3.2 EBP kinetics after a single gavage dose

Two rat kinetics study using <sup>14</sup>C-test material have been completed on EBP. The results of the latest PK study confirm the first study<sup>81</sup>, and are summarised as follows.

Blood, tissues, urine and faeces were collected at various time points from rats administered a single oral dose of 14C-labeled and unlabelled EBP. Groups of non-catheterised, bile duct- and jugular vein-catherised rats were included in the study. Nearly all of the <sup>14</sup>C-activity (ca. 90%) was recovered in the faeces and suggests EBP is excreted quantitatively in the faeces. Only background levels of <sup>14</sup>C-activity were detected in bile, blood, urine or plasma at all time points. Compounds with molecular weights >300 are generally eliminated in the bile and faeces, and the absence of <sup>14</sup>Cactivity in the bile indicates EBP was not taken up from the GI tract into the enterohepatic circulation. The lack of radioactivity in blood and plasma indicates EBP has negligible systemic bioavailability. Tissues analysed were spleen, liver, kidney, adipose, stomach plus contents, small intestine plus contents, cecum plus contents, and large intestine plus contents. Only background levels of <sup>14</sup>C-activity were detected in spleen, liver, kidney and adipose tissue. <sup>14</sup>C-activity above background was detected on the analysis of the combined intestinal-contents-plus-intestinal- tractorgans. The <sup>14</sup>C-activity moved distally in the GI tract with time post-doing. Pooled faecal extracts (0-24 h, 24-48 h) were analysed via HPLC-UV/ßRAM. Faeces collected at 0-24 post dosing contained ca. 70% of the administered dose, while that collected 24-48 h post-dosing contained ca. 20% of the dose. The majority of the radioactivity at either collection period eluted at the retention time of the parent molecule. An additional, small peak containing the radiolabel eluted prior to the parent molecule; nonabromodiphenyl ethanes are typical impurities in EBP and would elute prior to the EBP molecule. The data indicate EBP was not absorbed at detectable levels following a single oral dose. This is based on the high recovery in faeces coupled with essentially background radioactivity levels

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Huwe et al. 2007. Accumulation, whole-body depletion, and debromination of decabromodiphenyl ether in male Sprague-Dawley rats following dietary exposure. Environ Sci Technol 41:2371-2377; Additions and Corrections 41:4486.

Black S., 2012 unpublished report, Pharmacokinetic studies of [14]C-decabromodiphenylethane (EBP). Testing laboratory RTI, International Research Triangle Park, NC, USA. Report No. RTI/0212983,001.002. (Owner: Albemarle Corporation).

in urine, bile, blood, plasma and tissues. HPLC-UV/ßRAM analysis of faeces indicated EBP was excreted unchanged in the faeces, without prior absorption, following oral administration (Albemarle, 2014b).

The information from this second study of <sup>14</sup>C-EBP, and performed by a different test laboratory from the first kinetic study. The study addresses both the potential for systemic exposure and metabolism.

## 11.3.3 EBP kinetics in fish

Absorption efficiency of EBP in fish was examined in a recent publication by Xiao et al. (2013)<sup>82</sup>. The authors confirmed negligible absorption efficiency of EBP in juvenile rainbow trout 13 month old and weighing approximately 25 g. Experiments were performed in stainless steel aquaria (50L volume), with aerated, filtered tap water at 13 °C and a water exchange rate of 6 times/day. Hardness, pH, alkalinity and dissolved oxygen were controlled. The day-night cycle was 12 hours each. Test chemicals were dissolved in hot toluene and spread onto 3.5 g of food pellets, shaken as slurry for 16 h and dried for 20 h. 6 fish per aquarium were fed a single meal with the test substance that was consumed within 10 minutes. Controls were fed uncontaminated diets. Fish faeces was siphoned from the aquaria twice daily collected on pre-weighed glass-fibre filters and dried overnight in a fume hood. Faeces was then transferred to centrifuge tubes and kept in the dark until extraction. The fish were killed after 5 days and stored at -18°C until analysis. 5 days was determined in a preexperiment as the time the fish needed to digest one meal. A single exposure was chosen to minimise excretion from the body to the gut and elimination via other routes, such as respiration or biotransformation. The concentrations of the standards including EBP in the diet were verified after extraction. Faeces was extracted with 20 mL dichloromethane in an ultrasonic bath (10 min) followed by re-extraction with 5 mol of n-hexane. Spiked faeces were used to determine recovery. Combined organic phases were reduced to 2 mL of n-hexane and 100 µL of Aldrin in n-hexane was added as internal standard. The analysis was performed with GC/MS. Fish were homogenised and 2g aliquots were added to a test tube. 300  $\mu$ L of the surrogate standard mixture was added. Extraction was performed with 20 mL acetone/hexane 1:5 for 5 min, re-extraction after centrifugation with 2x 10 mL hexane/diethylether 9:1. The combined organic phases were washed with 20 mL 0.9% NaCl solution in 0.1M phosphoric acid and then re-extracted with n-hexane. After evaporation of the organic phase under nitrogen, the fat content was determined in the residue and the residue re-dissolved in hexane, an aliquot of 2 mL was treated with sulphuric acid mono hydrate for lipid removal and then analysed by GC/MS electron ionization, another aliquot of 2 mL was treated with concentrated sulphuric acid for lipid removal and analysed by GV/MS/ electron capture negative ionization. Feed was analysed in triplicate, feces once and fish samples in duplicate. EBP was included as potential benchmark standard in all 4 experiments. The apparent absorption efficiency was calculated as Ed =  $n_{fish}/n_{fish}+n_{faeces}$ , with nfish: measured amount of the substance in fish, nfaeces measured amount of the substance in feces at the end of the test. The apparent recovery was determined as Rapp =  $n_{fish} + n_{faeces} / n_{dose}$  where  $/ n_{dose}$  is the dose of the chemical in the food. For all tests, EBP was only detected in the faeces and not in the fish and the authors qualified this chemical as non-absorbable benchmark. A negligible amount of the substance remained in the gut of the fish when they were homogenised. The dose in the feed was calculated from triplicate analysis and was 2 µg for EBP, the dose in the faeces amounted to 1 µg calculated from the sum of duplicate analysis of 5 samples and the amount in the fish was below the detection limit of 0.003 µg

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Xiao R, Adolfsson-Erici M, Åkerman G, McLachlan MS, MacLeod M, 2013 A benchmarking method to measure dietary absorption efficiency of chemicals by fish, Environmental Toxicology and Chemistry, 32 (12) 2695–2700.

as calculated by duplicate analysis of 4 homogenates containing 6 fish. This study confirmed a negligible uptake of EBP in fish that is in accordance with the results of the toxicokinetic studies in rats (Xiao & al, 2013).

#### 11.3.4 Conclusions on toxicokinetics

Available data on DecaBDE show that, in mammals, uptake after repeated exposure follows a biphasic kinetic, which was first order at low dose levels and zero order at dose levels from 10 mg/kg/bw per day in rats, indicating that higher external dose levels did not lead to higher absorption and blood levels. The saturation blood level was  $1 \mu g/mL$  plasma (Albemarle, 2014b).

The available data on EBP in rats and fish indicate very low absorption efficiency and a negligible uptake from the gastro-intestinal tract at least after single oral exposure. This indicates a very low to negligible potential for bioaccumulation (Albemarle, 2014b).



Risk & Policy Analysts Limited Farthing Green House, 1 Beccles Road Loddon, Norfolk, NR14 6LT, United Kingdom

> Tel: +44 1508 528465 Fax: +44 1508 520758 E-mail: post@rpaltd.co.uk Website: www.rpaltd.co.uk

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