

Australian Government

Department of Health National Industrial Chemicals Notification and Assessment Scheme

Decabromodiphenyl Ether

Priority Existing Chemical Assessment Report Assessment No. 41

May 2019

National Industrial Chemicals Notification and Assessment Scheme

NICNAS

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Priority Existing Chemical Assessment Report Decabromodiphenyl ether - May 2019

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Table of Contents

COPY	RIGHT	i
PREF/	ACE	4
ACRO	DNYMS AND ABBREVIATIONS	6
OVER	VIEW	8
Back Intro Heal Occu Publ Envii Envii RECO	kground oduction and uses Ith effects upational exposure lic exposure ironmental effects ironmental exposure MMENDATION OMMENDATION	
1		
1.1 1.2 1.3 1.4	Declaration Objectives Sources of information Applicants	
2 B	ACKGROUND	17
2.1 2.2 2.3	Overview of flame retardants International perspective Australian perspective	
3 IC	DENTITY, PROPERTIES AND ANALYSIS	28
3.1 3.2	Chemical identity Physical and chemical properties	
4 U		
4.1 4.2 4.3 4.4 4.5 4.6	Manufacture Importation of decaBDE powder and dispersions Uses of decaBDE powder and dispersions DecaBDE in imported articles Human and Environmental Health Effects Release and Fate	
5 El	NVIRONMENTAL EXPOSURE	42
6 H		45
6.1 6.2	Occupational Exposure Public exposure	45 49

7	HAZARD CLASSIFICATION	64
8	DISCUSSION AND CONCLUSIONS	65
E	Environmental hazard and risk	65
H	Human health risk	66
AF	PPENDIX 1 – NOMENCLATURE FOR PBDE CONGENERS	71
AF	PPENDIX 2 – CHEMISTRY OF PBDE BROMINATION AND DEBROMINATION	
RE	ACTIONS	78
I	ntroduction	78
F	Formation reactions	78
[Debromination reactions	80
AF	PPENDIX 3: DETERMINATION OF SOURCES OF PBDE IN AUSTRALIAN HOMES	83
9	REFERENCES	90

Preface

This assessment was carried out under the National Industrial Chemicals Notification and Assessment Scheme (NICNAS). This Scheme was established by the *Industrial Chemicals (Notification and Assessment) Act 1989* (Cwlth) (the Act), which came into operation on 17 July 1990.

The principal aim of NICNAS is to aid in the protection of people at work, the public and the environment from the harmful effects of industrial chemicals.

NICNAS assessments are carried out in conjunction with the Australian Government Department of the Environment and Energy, which carries out the environmental assessment for NICNAS.

NICNAS has two major assessment programs: the assessment of human health and safety and environmental effects of new industrial chemicals prior to importation or manufacture; and the other focussing on the assessment of chemicals already in use in Australia in response to specific concerns about their health and/or environmental effects.

There is an established mechanism within NICNAS for prioritising and assessing the many thousands of existing chemicals in use in Australia. Chemicals selected for assessment under the Act are referred to as Priority Existing Chemicals.

This Priority Existing Chemical report has been prepared by the Director, NICNAS, in accordance with the Act. Under the Act, manufacturers and importers of Priority Existing Chemicals (applicants) are required to apply for assessment. Applicants for assessment are given a copy of the draft report and 28 days to advise the Director of any errors. Following the correction of any errors, the Director provides applicants and other interested parties with a copy of the draft assessment report for consideration. This is a period of public comment lasting for 28 days, during which requests for variation of the draft report may be made. Where variations are requested, the Director's decision concerning each request is made available to each respondent and to other interested parties (for a further period of 28 days). Notices in relation to public comment and decisions made appear in the *Commonwealth Chemical Gazette*.

In accordance with the Act, publication of this report revokes the declaration of this chemical as a Priority Existing Chemical; therefore, manufacturers and importers wishing to introduce this chemical in the future need not apply for assessment. However, manufacturers and importers need to be aware of their duty to provide any new information to NICNAS, as required under Section 64 of the Act.

For the purposes of Section 60F(7) of the Act, copies of assessment reports for Existing Chemical assessments are freely available from the NICNAS website (<u>www.nicnas.gov.au</u>). Summary Reports are published in the Commonwealth Chemical Gazette available on NICNAS website. Copies of this and other Priority Existing Chemical reports are available on the NICNAS website. Hard copies are available free of charge. Please contact us to request a copy.

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More information on NICNAS can be found at the NICNAS website:

http://www.nicnas.gov.au

Other information on the management of workplace chemicals can be found at the website of Safe Work Australia:

http://www.safeworkaustralia.gov.au

Acronyms and abbreviations

Acronym / abbreviation	Meaning
ABS	acrylonitrile butadiene styrene
ADG	Australian Dangerous Goods
AICS	Australian Inventory of Chemical Substances
ATSDR	Agency for Toxic Substances and Disease Registry
BAF	bioaccumulation factor
BCF	bioconcentration factor
BDE	bromodiphenyl ether
BFR	brominated flame retardants
BMF	biomagnification factor
bw	body weight
CAS	Chemical Abstracts Service
CFR	Code of Federal Regulations (US)
CTD	characteristic travel distance
decaBDE	commercial decabromodiphenyl ether
DEE	Australian Government Department of the Environment and Energy
dw	dust weight
EC	European Commission
EC ₅₀	median effective concentration
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECOSAR	Ecological Structure Activity Relationship (US EPA software program)
ESD	emission scenario document(s) (published by OECD)
EU RAR	European Union Risk Assessment Report
FSANZ	Food Standards Australia New Zealand
GC	gas chromatography
GC-MS	gas chromatography – mass spectrometry
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
GM	geometric mean
HIPS	high impact polystyrene

Acronym / abbreviation	Meaning
HPLC	high-performance liquid chromatography
IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
K _{ow}	octanol/water partition coefficient
kg	kilogram
kPa	kilopascal
LDPE	low-density polyethylene
octaBDE	commercial octabromodiphenyl ether
OECD	Organisation for Economic Cooperation and Development
ng	nanogram
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ethers
PBFR	polybrominated flame retardants
PBT	persistent, bioaccumulative and toxic
PCB	polychlorinated biphenyls
PEC	predicted environmental concentrations
pentaBDE	commercial pentabromodiphenyl ether
PET	polyethylene terephthalate
pg	picogram
PNEC	predicted no effect concentration
POP	persistent organic pollutant
QSAR	quantitative-structure-activity relationship
STP	sewage treatment plant
tetraBDE	commercial tetrabromodiphenyl ether
TSCA	Toxic Substances Control Act (US EPA)
TWA	time-weighted average
US EPA	United States Environmental Protection Agency
VECAP	Voluntary Emissions Control Action Programme
wt	weight
WWTP	waste water treatment plant

Overview

Background

Decabromodiphenyl ether (decaBDE; CAS No. 1163-19-5), was declared a priority existing chemical (PEC) for a full risk assessment under the *Industrial Chemicals (Notification and Assessment) Act 1989* (Cwlth) (the Act) by notice in the Commonwealth Chemical Gazette of 7 June 2005. DecaBDE was declared because it represented 42% (180 tonnes) of all polybrominated flame retardants (PBFRs) imported into Australia in 2004 and some animal studies reported that decaBDE caused liver degeneration and fibrosis of spleen in rats, liver hypertrophy and follicular cell hyperplasia and neurobehavioural changes in mice at a critical phase of neonatal brain development. There were also concerns that it cans photodegrade to lower brominated diphenyl ether congeners (breakdown products) that are hazardous to human health and /or the environment.

The declaration also listed the breakdown products of decaBDE. The breakdown products of decaBDE may be various, and dependent on the mechanism of breakdown (photolysis, species-dependent metabolism or pyrolysis). Very little information is available on the identity, concentrations, or the effects of the breakdown products other than lower brominated diphenyl ethers. Some lower brominated diphenyl ether congeners are known to bioaccumulate and cause developmental toxicity in animals. For the purpose of this assessment, toxicity data for the lower brominated diphenyl ethers is represented by data for the commercial mixtures of pentaBDE and octaBDE, and congeners contained in these mixtures, as the majority of hazard information has been generated using these substances. This does not imply that these congeners are necessarily breakdown products of decaBDE.

Polybrominated diphenyl ethers (PBDEs) with three to ten bromine atoms are used as additive flame retarding compounds commercially. Flame retardants are used to retard fire in both natural and synthetic polymeric materials, such as cotton textiles and thermoplastic resins. The only PBDE product in current production is commercial decaBDE. Current formulations of decaBDE contain around 97% or more BDE-209 (BDE-209 is the standard nomenclature of decabrominated PBDE congener), with the major impurities being lower brominated diphenyl ethers, predominantly the three nonabrominated diphenyl ether congeners (UNEP, 2014).

Introduction and uses

DecaBDE is not manufactured in Australia. According to the information gathered between July 2015 to June 2016, decaBDE is imported into Australia mainly as the raw chemical (~200 tonnes in powder form with > 97% purity), as a water-based blend containing 37% decaBDE (~14 tonnes) and in imported articles.

In Australia, decaBDE is used in fire retardant polymers/resins for wire insulation, conveyor belts, plastic boxes housing electronics and in electrical equipment, awnings, carpet backing, tarpauline/canvas, and in textiles such as curtains, rainwear apparel and fabrics for motor vehicles. In the building industry, decaBDE is used in the manufacture of paper foil laminate to use in home insulation (18% to 41% concentration of decaBDE), formulation of hot melt adhesive and architectural foam.

Health effects

DecaBDE has low oral and very low dermal absorption. It has low acute oral, dermal and inhalation toxicity in animals. It is not a skin or eye irritant. DecaBDE does not exhibit any cytogenetic effects in vitro or in vivo. Repeated exposure by oral route indicates low systemic toxicity even at a high dose level.

There are no effects on fertility and development in animal studies. No changes are seen in the reproductive organs in rats and mice treated for 2 years with up to 50,000 ppm of decaBDE. Behavioural disturbances in neonatal mice exposed to decaBDE have been reported. However, a clear interpretation of the significance for human health of the behavioural differences seen in mice has not been established and thus uncertainty as to their significance of these effects remains. It is not classified for carcinogenicity.

Occupational exposure

Exposure during transportation is not expected unless following an accident and/or if due to breached packaging. Occupational exposure may occur during industrial processing in the plastic, textile and rubber industries and during recycling of plastics.

As decaBDE is a solid (powder) with very low vapour pressure, no significant exposure to the vapour at ambient temperature is expected. No measured occupational exposure data were provided by the Australian industry.

Public exposure

Public exposure includes direct consumer exposure through use of materials containing decaBDE and indirect exposure via the environment. Exposure to decaBDE is dominated by indirect exposure via the environment (that is, inhalation or ingestion of decaBDE-containing dust released from articles within a household).

NICNAS commissioned the Commonwealth Scientific and Industrial Research Organisation (CSIRO) to conduct a study to understand the potential sources of human exposure to PBDEs through dust in Australian homes (October 2007). The study was designed to assess the distribution of PBDEs in common household items in South Australian homes using a screening technique based on X-ray fluorescence (XRF) spectroscopy. Dust samples from selected homes were analysed by an accredited independent laboratory for common and important congeners of PBDEs. The dust analysis from homes showed presence of tetra, penta, hexa, hepta and deca brominated –PBDE congeners. In most cases the dominant congeners were BDE-209, 99 and 47, in order of decreasing occurance. BDE-28 and 33 were negligible in most samples; however, several other congeners were detected at varying levels. The levels of decaBDE in samples present in the vicinity of curtains were low and there was no clear gradient away from the source. It is unlikely that the curtains sampled contained decaBDE based on XRF results. The results indicated that all tested televisions (TVs) contained decaBDE. The dust samples targeting TVs as a source gave variable results and did not show any clear pattern; but also no extreme decaBDE concentrations.

The chemical BDE-209 was detected in six out of ten breast milk samples collected from Australian women, with concentrations ranging from 0.5 to 1.4 ng/g lipid weight. Correlations of milk levels and household dust levels of BDE-209 were not found. The mean BDE-209 concentration in overseas breast milk samples ranged from 0.12 to 0.92 ng/g lw. Breast milk is the major route of exposure to decaBDE in infants (<2 years). The highest value of 10.9 ng/g lw BDE-209 reported in a sample was used in estimating the oral exposure to infants from breast milk intake. The worst case exposure from breast milk was calculated to be 85 ng/kg bw/day.

Environmental effects

The available aquatic toxicity data indicate that decaBDE can have adverse effects on survival, growth, fitness, reproduction and thyroid hormone functions of fish and amphibians (UNEP, 2014). Frogs are particularly sensitive to decaBDE. The data indicate the persistence and bioaccumulation potential of decaBDE and debromination of decaBDE in the environment, as they show that accumulation of decaBDE may cause adverse effects in vulnerable life stages of fish and amphibians. These adverse effects can occur at levels that are comparable to those found in heavily polluted sites (UNEP, 2014).

The available data show that decaBDE only has adverse effects on plants and soil microbes and earthworms at concentrations that are above environmentally relevant concentrations.

There are limited data on the avian toxicity of decaBDE, but an LD50 of 44 μ g/egg in chicken embryos has been reported. This corresponds to an LC50 of 2300 μ g/kg lipid weight in chicken eggs.

Environmental exposure

The chemical decaBDE (BDE-209) is a ubiquitous global contaminant that is routinely detected in air, soils, sediments and biota. The main sources of decaBDE in the environment include release from articles during use, from plastics manufacturing facilities, and from metal and electronics recycling facilities. BDE-209 is lipophilic, so it readily adsorbs to the surface of particulate matter. Movement of contaminated particulate matter is the main mechanism for transport of BDE-209 through the environment.

While routinely detected in Australia, concentrations of BDE-209 are generally low compared to levels overseas. BDE-209 was detected in 29 of 30 samples of urban soil in Melbourne, with the highest concentrations being found near electronics recycling facilities and plastic and foam manufacturing facilities. Concentrations in air were found to be high near an automotive shredding and metal recycling facility in Brisbane.

High concentrations of BDE-209 are found in Australian biosolids, and it has been estimated that approximately 100 kg of BDE-209 is applied to Australian agricultural land each year through application of biosolids as soil improver.

The chemical BDE-209 has been detected in Australian sediments, in the Parramatta River, Port Phillip Bay, Port Jackson West and Brisbane River, but at low levels compared to sediments from North America, Europe and Asia. It was dectected in fish in the Parramatta River, but it made up only a small fraction of the total PBDE concentration in these fish. Similarly, BDE-209 has been detected in white-bellied sea eagles from the Homebush Bay area with the concentration of BDE-209 much lower than the total concentration of PBDE contaminants. In both cases, the extent of debromination of BDE-209 to less brominated congeners is not known. Monitoring in white ibis eggs in urban areas of Sydney and Brisbane found values of up to 550 µg/kg lipid weight.

Recommendation

This section provides the recommendation arising from the priority existing chemical assessment of the declared chemical, decaBDE.

Recommendation

Having regard to the human health and environmental effects of decaBDE and fate in the environment, and noting that it is listed on Annex A of the Stockholm Convention on Persistent Organic Pollutants to which Australia is a signatory, it is recommended that the Australian Government explore options for managing the use of decaBDE and its import into Australia, taking into account the information in this report.

Secondary Notification

This risk assessment is based on the information available at the time of notification. The Director may call for the reassessment of the chemical under secondary notification provisions based on changes in certain circumstances. Under Section 64 of the *Industrial Chemicals (Notification and Assessment) Act (1989)* the notifiers, as well as any other importers or manufacturers of the notified chemical, have post-assessment regulatory obligations to notify NICNAS when any of these circumstances change. These obligations apply even when the notified chemical is listed on the Australian Inventory of Chemical Substances (AICS).

Therefore, the Director of NICNAS must be notified in writing within 28 days by the notifiers, other importers or manufacturers:

Under Section 64(1) of the Act; if

- additional toxicological information becomes available on decaBDE, or degradants of decaBDE;
- additional information has become available to the person as to an adverse effect of degradants of decaBDE on occupational health and safety, public health, or the environment.

or

Under Section 64(2) of the Act; if

- the chemical (decaBDE) is to be used for any other purpose than either (a) those purposes disclosed to the Director through the call for information to industry (2017), or (b) for a purpose that is not critical as defined by Annex A of the Stockholm Convention;
- the amount of chemical being introduced by a notifier has increased, or is likely to increase, significantly;
- the chemical has begun to be manufactured in Australia;
- additional information has become available to the person as to an adverse effect of the chemical on occupational health and safety, public health, or the environment.

The Director will then decide whether a reassessment (a secondary notification and assessment) is required.

1 Introduction

1.1 Declaration

Decabromodiphenyl ether (decaBDE; benzene, 1,1'-oxybis-, decabromo derivative; bis(pentabromophenyl) ether, CAS No 1163-19-5), was declared a priority existing chemical (PEC) for a full risk assessment under *the Industrial Chemicals (Notification and Assessment) Act 1989* (Cwlth) (the Act) by notice in the *Commonwealth Chemical Gazette* of 7 June 2005. DecaBDE was declared because it represented 42% (180 tonnes) of all polybrominated flame retardants (PBFRs) imported into Australia in 2004. DecaBDE is used in fire retardant polymers/resins for wire insulation, plastic boxes housing electronics and in electrical equipment such as TVs and set top boxes, and is also used in textiles such as curtains, awnings, and fabrics for motor vehicles.

In animal studies, evidence existed that decaBDE caused liver degeneration and fibrosis of spleen in rats, and liver hypertrophy and follicular cell hyperplasia in mice. There was also evidence that exposure to decaBDE at a critical phase of neonatal brain development caused neurobehavioural changes in mice and effects on sperm oxidative stress and chromatin deoxyribonucleic acid (DNA) damage in mouse offspring. There were concerns that decaBDE can photodegrade to lower brominated diphenyl ether congeners (breakdown products) that are hazardous to human health and/or the environment. Some lower brominated diphenyl ether congeners are known to bioaccumulate and cause developmental toxicity in animals.

1.2 Objectives

The objectives of this assessment are to:

- identify the extent and patterns of use of decaBDE;
- identify the health and environmental hazards of decaBDE and its degradation products;
- determine the potential for environmental, occupational and public exposure; and
- make recommendations for minimising environmental, occupational and public health risks, and appropriate hazard communication measures, where applicable.

1.3 Sources of information

Consistent with these objectives, the report presents a summary and evaluation of relevant information relating to the potential health and environmental hazards and risks from exposure to decaBDE.

Importers of decaBDE facilitated the provision of relevant scientific data, including information on physicochemical properties, human and environmental exposure and toxicity (published and unpublished data) through the Bromine Science and Environmental Forum (BSEF, 2005). Information on uses and quantities imported to Australia both as a chemical and in articles was provided by companies importing decaBDE or articles containing decaBDE. Information was obtained from published papers identified in a comprehensive literature search of several online databases and retrieved from other sources, particularly the 2002 Risk Assessment Report on decaBDE published by the European Union (EU RAR) (EC, 2002a), the 2004 European Union Update on the EU RAR (for environment only) (EC, 2004a), and the 1994 IPCS review of PBDEs (IPCS, 1994) and the IARC assessment for carcinogenicity (IARC, 1999). The EU RAR report focused on the data available up until 2001,

and this covered all of the studies conducted according to OECD Test Guidelines. More recently published papers were generally from academic sources, and focused on endocrine disruption modes of action. The primary data sources for industry reports assessed in the EU RAR were not reviewed by NICNAS. More recent data have been summarised in Annex to UNEP/POPS/POPRC.10/10/Add.2 (Decabromodiphenyl ether - Risk profile) document accepted by the Stockholm Convention Conference of the Parties (UNEP, 2016). Summaries of the relevant health and environmental effects are taken from this document.

Data provided to NICNAS by industry for an assessment of polybrominated flame retardants (PBFRs) in 1999 (NICNAS, 1999) and following a call for information for PBFRs conducted in 2017 indicated no manufacture of decaBDE in Australia, but importation of decaBDE as a pure chemical or in chemical products for formulation into articles in Australia was continuing. However, information provided by the applicants in the 2017 survey indicated that some companies that were previously importing DecaBDE, in pure form or contained in articles, had ceased to import DecaBDE or articles containing the chemical.

The characterisation of human exposure to decaBDE in Australia was partly based upon monitoring information from a group of monitoring studies commissioned by the Environmental Protection and Heritage Council (EPHC) and Australian Government Department of the Environment and Energy (DEE), for which the final reports were published in January 2005 (breast milk) (Harden et al. 2005) and March 2007 (human serum, indoor environments, sediment) (Toms et al. 2006a, 2006b, 2006c). In addition, assessment included consideration of overseas use patterns and occupational exposure models.

Additionally, NICNAS commissioned one project for this assessment.

• Determination of Sources of PBDEs in Australian Homes, which was undertaken by the Centre for Environmental Contaminants Research, CSIRO, Adelaide. (Appendix 3)

1.4 Applicants

CHT Australia Pty Ltd

7th Floor, 390 St Kilda Road MELBOURNE, VIC 3004 **Textor Pty Ltd**

41 Tullamarine Park Rd

TULLAMARINE, VIC 3043

Electrolux Home Products Pty Ltd

Edward Street

ORANGE, NSW 2800

RCA International Pty Ltd

3 Pilgrim Court

RINGWOOD, VIC 3134

Motherson Elastomers Pty Ltd (formerly Empire Rubber Pty Ltd)

PO Box 515

BENDIGO VIC 3550

Marchem Australasia Pty Ltd

558-562 Geelong Road

BROOKLYN, VICTORIA 3012

Epson Australia Pty Ltd

3 Talavera Road

NORTH RYDE, NSW 2113

LG Electronics

2 Wonderland Drive

EASTERN CREEK, NSW 2766

Huntsman Advanced Materials (Australia) Pty Ltd

Gate 3, Ballarat Road

DEER PARK, VIC 3023

Martogg Group (trading as) Kantfield Pty Ltd

185 - 195 Frankston-Dandenong Road

DANDENONG, VIC 3175

IMCD Australia Limited

1st Floor, 372 Wellington Road

MULGRAVE, VIC 3170

Exel Composites Pty Ltd

PO Box 72

BAYSWATER, VIC 3153

Brenntag Australia Pty Ltd

260 - 262 Highett Road

HIGHETT, VIC 3190

Plastral Pty Ltd

130 Denison St

HILLSDALE, NSW 2036

Samsung Electronics Aust. Pty Ltd

3 Murray Rose Avenue

SYDNEY OLYMPIC PARK, NSW 2127

Redox Pty Ltd 2 Swettenham Road MINTO, NSW 2566 Specialty Coatings (Aust) Pty Ltd 124-130 Cochranes Road MOORABBIN, VIC 3189

2 Background

2.1 Overview of flame retardants

A flame (or fire) retardant chemical is a compound or a mixture of compounds that reduces or impedes the ignition or growth of fire when added to or incorporated chemically into a combustible material. Flame retardants do not "fire-proof" a material and the retardant action do not necessarily apply to all aspects of combustion or fire conditions. Flame retardant effectiveness depends on the material into which it is incorporated; unsuitable flame retardants may increase the rate of combustion in some materials. It is not possible to assess a flame retardant by itself. Its effectiveness needs to be related to its incorporation into particular materials or products, to a specified incorporation/application method and a specified loading/application rate/retention, as well as to the particular fire hazard characteristic assessed and the assessment conditions.

There are accepted test methods for measuring fire performance of materials and products, and generally the tests used to assess materials and products that have been treated with flame retardants are the same as those used to assess the non-retarded materials and products. The tests are used for fire hazard assessments, quality control and setting of specifications for a product, and may be incorporated in fire safety standards and regulations. They encompass various types of tests relevant to assessing ignition resistance and flame spread, as well as tests of heat release, smoke release and toxicity of combustion products. The procedure for evaluating the effectiveness of a flame-retarded material includes identifying appropriate fire test methods for the material or product through consultation of the Standards Australia catalogue, testing laboratories or research organisations. Findings of fire tests are usually presented as graded numerical results (Standards Australia, 1990, 1993).

Flame retardants are used to retard fire in both natural and synthetic polymeric materials, such as cotton textiles and thermoplastic resins. Classes of materials commonly subject to flame retarding treatment include:

- electrical components such as printed circuit boards, insulation for wires and cables, connectors, plugs, cabinets and housings for electrical appliances;
- furniture, cushioning and thermal insulation used in buildings;
- fabrics and apparel such as carpets, drapes, furniture upholstery, workwear, children's wear, military fabrics; and
- polymer components inside mass transit vehicles (airplanes, boats, buses, trains) and private vehicles.

Flame retardants can be additive or reactive. Additive flame retardants are added to a polymer without bonding or reacting with the polymer. For instance, they could be mixed into plastics prior to, during, or after polymerisation and dispersed evenly throughout the product, but not chemically bound to it. An additive flame retardant mix may also be applied as a coating or surface finish such as in a back-coating applied to a textile, or in paints. Immersion of a polymeric material in a solution of flame retardant, with or without application of external pressure, is another method of application.

Additive flame retardants are sometimes volatile and may tend to bleed out of a product and vaporise or collect at the surface, a process known as "blooming", resulting in the gradual loss of flame retardancy. The degree (rate) to which blooming may occur is dependent on a number of factors, which include: size and shape of the flame retarding molecule/polymer;

geometric structure of the plastic matrix; stability of the flame retarding molecule/compound in the 'melt', that is compatibility of the flame retarding molecule/compound with the plastic polymer; volatility (vapour pressure) of the flame retardant; temperature (generally increased temperature will increase blooming potential); and stability of the polymer matrix in contact with solvents, such as tendency to swell. The specific combination of these properties for a particular flame retardant and polymer matrix will determine whether or not, or to what extent, blooming is likely to occur.

Laundering of materials treated with additive flame retardants can result in gradual leaching or physical breakdown of retardant coatings, and flame retardants applied as surface coatings can also be displaced through physical wear and tear of coatings over time.

In contrast to additive flame retardants, reactive flame retardants undergo reactions that chemically bind them to the raw materials that are used in the final product. This prevents them from bleeding out of the polymer resulting in the retention of the product's flame retardant property.

The choice of a given flame retardant depends on the type of application; one flame retardant cannot necessarily be substituted with another for any particular application. Their suitability is subject to variables such as the material to be flame-retarded, the fire safety standards with which the product must comply, cost considerations and recyclability. For base chemicals that are being flame retarded, the effects on the physical properties of the end product, such as tensile strength, flexibility and elongation properties, as well as the effects on the product during mixing and transformation, such as properties of the polymer melt, need to be considered. For additive flame retardants, compatibility with the polymer or the textile being treated avoids their migration to the surface, increasing the permanency of the flame retardant property of the product. Exposure considerations at each life cycle stage of the flame retardant chemical including during production and transport of raw materials, manufacturing, assembling of semi-finished products, use of end products and service life and waste disposal, recycling or incineration, need to be taken into account (OECD, 1994).

Classes of flame retardants

Chemicals used as flame retardants can be classified into four main classes - inorganic (including antimony, aluminium, boron, magnesium and tin compounds), halogenated, organophosphorous (primarily phosphate esters, chlorinated phosphate esters), and nitrogen-based products. Bromine and chlorine are the only halogens used in flame retardant compounds with commercial significance, the former being more important due to its greater flame retarding efficiency.

The graph below was produced by one of the major producers of flame retardants, and provides an indication of the relative global market proportions of the main classes of flame retardants.

Major families of flame retardants (ICL Industrial Products, 2005)



Key: Br=bromine-based; Cl=chlorine-based; P=Phosphorous-based

Halogenated flame retardants can be further divided into three classes based on chemical structure: aromatic, aliphatic, and cycloaliphatic. They can also be subdivided based on whether they are chlorine- or bromine-containing (brominated flame retardants, or BFRs). In general, among the BFRs, those in the aromatic group tend to be the most thermally stable and may be processed in thermoplastics at fairly high temperatures without the use of stabilisers and at very high temperatures with stabilisers. Aliphatic compounds tend to break down more easily and are more effective at lower temperatures, but usually require thermal stabilisers for processing as they are less temperature-resistant (IPCS, 1997).

Polybrominated diphenyl ethers

Polybrominated diphenyl ethers (PBDEs) are a group of aromatic brominated compounds in which one to ten hydrogen atoms in the diphenyl ether structure are replaced by bromine atoms. There are 209 possible PBDE congeners containing between one and ten bromine atoms, although most of these are unlikely to be commercially available. This group of PBDEs with three to ten bromine atoms are used as additive flame retarding compounds commercially. The only PBDE product in current production is commercial decabromodiphenyl ether (decaBDE). While tetrabromodiphenyl ether (tetraBDE), pentabromodiphenyl ether (pentaBDE) and octabromodiphenyl ether (octaBDE) are commercial formulations containing a mix of 3-6, 4-6 and 6-10 bromine atoms, respectively, the manufacture of all these has been discontinued. Current formulations of commercial decaBDE contain \geq 97% BDE-209, with the major impurities being lower brominated diphenyl ethers, predominantly the three nonabrominated diphenyl ether congeners (IPCS, 1994). The other commercial PBDE products, particularly pentaBDE and octaBDE have also been used as flame retardants, although the only manufacturer of these chemicals in the USA ceased the production of these two flame retardants in 2005 due to concerns over health effects, and their production in Europe is now prohibited. However, due to the production and use of these chemicals in the recent past, many articles incorporating these flame retardants are still in use. Another commercial PBDE product, known as tetraBDE, is reported to have been used in Japan but was reported to no longer be in production in 1994 (IPCS, 1994). The reported characteristics indicate that its composition was similar to that of commercial pentaBDE but with higher relative proportions of lower brominated species. See Appendix 1 for discussion of the congener distribution in these older products.

As the commercial PBDE products are mixtures of individual congeners, and analytical techniques are specific to each individual congener, references to 'decaBDE' relate to use as a commercial chemical, whereas analytical results are reported for 'BDE-209', and the analyte indicative of decaBDE.

2.2 International perspective

The growth of international interest in PBDEs

Three technical mixtures of PBDEs (pentaBDE, octaBDE and decaBDE) had been in commercial production since the 1960s. This group of BFRs began to be the subject of concerns in the 1980s and 1990s when several environmental monitoring programs conducted primarily in Europe, Japan and North America indicated that increasing levels of some congeners were detected in outdoor and indoor air, dust, sewage sludge, sediment, fish, aquatic birds, marine mammals and other wildlife. In air samples, BDE-209 was first identified near plants manufacturing fire retardants in Sweden (Zweidinger et al. 1979). BDE-209 was first measured in soil and sludge samples in 1979 around manufacturing plant areas in the USA (de Carlo, 1979) and along the Visken River in Sweden where a number of textile manufacturing plants were located (Anderson & Blomkist 1981). PBDEs in general were found in marine life as well as in fish-eating birds and marine mammals (Jansson et al 1987; Watanabe et al 1987) and in birds (Chen and Hale 2010). Human monitoring also showed the same trends; PBDE congeners were found in adipose tissue, serum and breast milk. Hexa- to octabrominated PBDE congeners were found in the pooled adipose tissue samples of 865 Americans in a study initiated by the US EPA in 1987 (Cramer et al 1990). In Germany, PBDEs in general were found in the breast milk samples of 26 women (Kruger, 2001a).

In response to these earliest findings, initial international engagements included:

- an International Programme on Chemical Safety (IPCS, 1994) report on the effects of PBDEs on human health and environmental quality;
- the voluntary agreement to not produce PBDE mixtures apart from pentaBDE, octaBDE, and decaBDE by international flame retardant producers; and
- the joint assignment of UK and France to conduct decaBDE, octaBDE and pentaBDE risk assessment under EC Council Regulation 793/93, building upon the IPCS report.

Apart from the issues regarding persistence and bioaccumulation, PBDEs potentially produce brominated dioxins and furans at some stage of their life cycle (IPCS, 1994). In the USA, eight brominated flame retardants including pentaBDE, octaBDE and decaBDE were subject to a Toxic Substances Control Act (TSCA) test rule (published 5 June 1987), which requires that they be analysed for the presence of brominated dioxins and furans [US Federal Register 52: 21412] (US EPA, 1987).

Assessments by national and international bodies

The increasing interest in the PBDEs resulted in a number of international and national studies on the PBDEs, including decaBDE. Major assessments included:

- The International Programme on Chemical Safety (IPCS) published an Environmental Health Criteria (EHC 162) monograph on Brominated Diphenyl Ethers in 1993 (IPCS, 1994);
- The European Chemicals Bureau published the European Union Risk Assessment Report (EU RAR): Bis(pentabromophenyl) ether. 1st Priority List, Volume 17 (EC, 2002a); with an update of the environmental part of the report in 2004 (EC, 2004a);
- The International Agency for Research on Cancer (IARC) Monographs on the Evaluation of Carcinogenic Risks to Humans: Some Flame Retardants and Textile Chemicals, and Exposures in the Textile Manufacturing Industry, volume 48 (IARC, 1990); and

• Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers (PBBs and PBDEs) (ATSDR, 2004).

The US EPA has also produced an assessment of decaBDE as part of its Voluntary Children's Chemical Evaluation Program (VCCEP), US EPA's Right to Know initiative. The assessment was sponsored by the American Chemistry Council's Brominated Flame Retardant Industry Panel (BFRIP) (2002). The US EPA has also produced an assessment of BDE-209 under its Integrated Risk Information System (IRIS) program that was released in December 2008 (US EPA, 2008), an exposure assessment of polybrominated diphenyl ethers in May 2010 (US EPA 2010) and a draft report released in July 2012 for public comment on *An Alternatives Assessment for the Flame Retardants Decabromodiphenyl ether (DecaBDE)*.

Assessment and risk management activities in Europe

Risk Assessment under Commission Regulation No. 793/93

DecaBDE was the subject of a risk assessment carried out in accordance with Council Regulation (EEC) No 793/93 of 23 March 1993, on the evaluation and control of the risks of existing substances. A risk assessment under the chemical name bis(pentabromophenyl)ether was subsequently conducted, with the results published in 2002 (EC, 2002a).

The report raised concerns about long-term effects in the environment, finding a high level of uncertainty associated with the risk assessment for "secondary poisoning" and inconclusive data concerning the possibility of degradation of decaBDE in the environment to more toxic lower brominated diphenyl ethers and brominated dibenzofurans.

The 2004 addendum to the report noted widespread exposure to decaBDE in the biota, including in the eggs of predatory birds, and raised concerns about long-range transport of the substance and possible impacts on organisms remote from sources of release. There were also concerns about the neurotoxic potential of the substance. It noted the need for more data in these areas, and also the technical difficulties in acquiring such data. The report recommended continued environmental exposure monitoring for decaBDE and its degradation products and a formal review of the monitoring data at regular time periods, such as every three years.

Policy discussions in May 2004 about the report resulted in an agreement by the European Competent Authorities that a voluntary emission reduction program proposed by the brominated flame retardant industry in response to the reports should be implemented in parallel with the collection of further data.

In May 2008, the EC released a communication on the results of the risk evaluation of decaBDE based on current practices in relation to the life-cycle of all imported and manufactured decaBDE. The conclusions for the human health aspect were: there is a need for better information to characterise developmental neurotoxic effects that may occur from occupational exposure; and further animal studies for this endpoint are needed in mice or rats. As the consumer exposure was deemed negligible, it was considered that no further information or testing is required. However, the EC stated that further evidence is needed that humans exposed through the environment are not at risk of acquiring developmental neurotoxic effects; apart from mice/rat studies, suitable biomonitoring, reported annually, is required in the next ten years. For environment considerations, the conclusions were that no further information is needed to reduce risk in atmospheric contamination, nor in the

contamination of microorganisms in the sewage treatment plant. However, persistent, bioaccumulative and toxic properties of decaBDE in aquatic and terrestrial ecosystems are not adequately characterised and further information and environmental monitoring are required over the next ten years (EC, 2008).

Restriction of Hazardous Substances and Waste Electrical and Electronic Equipment Directives

In February 2003, the European Commission adopted the directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment, called the Restriction of Hazardous Substances Directive, (RoHS) (Directive 2002/95/EC). This directive restricts (with exceptions) the use of ten hazardous materials, including polybromodiphenyl ethers, in the manufacture of various types of electronic and electrical equipment. The RoHS directive took effect on 1 July 2006, and was required to be enforced. This directive became a law in each member state.

The European Commission decided to exempt decaBDE from the list of hazardous substances banned in the RoHS directive, based on the outcome of the EU RAR assessment. This decision was challenged in the European Court of Justice (ECJ) by the European Parliament and Denmark, supported by Finland, Norway, Portugal and Sweden. The plaintiffs lodged their legal case on the basis that the European Commission had been selective in the studies used to come to its decision to continue allowing the use of decaBDE even though alternatives were 'practicable', as the RoHS Directive stipulates. The decision to exempt decaBDE, it was argued, was also against the opinion of the Commission's own Scientific Committee on Health and Environmental Risks, which strongly recommended 'further risk reduction' on the basis of a risk assessment undertaken to help decide whether decaBDE should be included in the RoHS Directive list of banned substances.

On April 1 2008, the ECJ annulled the Commission's Decision on the basis that procedural errors were made when establishing the exemption. As of July 2008; therefore, deca-BDE was no longer allowed to be used in electronics and electrical applications as decided by the European Court of Justice.

The RoHS is closely linked with the Waste Electrical and Electronic Equipment Directive (WEEE) 2002/96/EC which sets collection, recycling and recovery targets for all types of electrical goods and is part of a legislative initiative to solve the problem of huge amounts of toxic electronic waste. The WEEE Directive has set a minimum rate of four kilograms per head of population per annum recovered for recycling. The directive has undergone a number of minor revisions since its inception in 2002. The changes affect the method for calculating collection rates, which were previously four kg per inhabitant per year. The collection rates were revised to 45% of the weight of electrical and electronic products entering the market.

Restrictions on decaBDE in Sweden and Norway

Despite the restrictions legally set in place by the European Commission, Sweden and Norway (a non-EU state) legislated further restrictions by banning the use of decaBDE. In Sweden, decaBDE was banned in textiles, furniture and cables in January 2007; this was lifted in May 2008 after a legal challenge by the EU (EBFRIP, 2008). Norway has restricted all decaBDE applications, with some exemptions in the transport sector in April 1, 2008 (Norwegian Pollution Control Authority [SFT] 2008).

Assessment and risk management activities in the United States of America

The United States of America (USA) Congress has not passed any legislation pertaining to the restriction of pentaBDE, octaBDE or decaBDE use. Complementing the phase-out of pentaBDE and octaBDE in many states, and the voluntary phaseout by Great Lakes Corporation in the USA which took effect on 31 December 2004, the United States Environmental Protection Agency (USEPA) promulgated a Significant New Use Rule (SNUR) under the Toxic Substances Control Act in June 2006 covering six groups of PBDEs (tetra-, penta-, hexa-, hepta-, octa- and nonabrominated diphenyl ethers). The action was taken on the grounds that these substances may be hazardous to human health and the environment and to ensure the management and evaluation of these chemicals, should production and importation be reinstated in the future (71 Fed. Reg 34,015, 13 June 2006). The US EPA conducted a review of available decaBDE toxicology data in 2008.

PentaBDE and octaBDE formulations were voluntarily withdrawn from the US marketplace by their manufacturers at the end of 2004, leaving only the decaBDE formulation being marketed for use in commercial products in the USA. Based on screening-level review of hazard and exposure information, the US EPA, in 2009, secured commitments from the principal manufacturers and importers of decaBDE to initiate reductions in the manufacture, import and sales of decaBDE starting in 2010, with all sales to cease by 31 December 2013 (https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/polybrominated-diphenyl-ethers-pbdes.) In April 2012, the USEPA issued a proposed rule that would amend the Toxic Substances Control Act (TSCA) section 5(a) Significant New Use Rule (SNUR) for certain polybrominated diphenylethers (PBDEs), and that would require persons who manufacture, import, or process any of three commercial PBDEs, including in articles, for any use after 31 December 2013, to conduct testing under TSCA section 4(a).

In 2014, the US EPA, through its Design for the Environment and Green Chemistry, developed "An Alternatives Assessment for c-decaBDE" to aid users in selecting suitable alternatives (<u>https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/polybrominated-diphenyl-ethers-pbdes</u>).

Assessment and risk management activities in Canada

In 2006, Canada's ecological screening assessment report (Environment Canada 2006a, Government of Canada, 2006) concluded that PBDEs were entering the environment in a quantity or concentration or under conditions that have or may have an immediate or longterm harmful effect on the environment or its biological diversity. Based on the assessment, PBDE congeners (tetra to decabrominated BDE) were added in December 2006 to the List of Toxic Substances in Schedule 1 of the Canadian Environmental Protection Act 1999 (CEPA 1999).

As a first step in the risk management process, regulations prohibiting the manufacture and prohibiting the use, sale, offer for sale, and import of tetra-, penta- and hexabrominated diphenyl ethers or any resin, polymer or other mixture containing these PBDEs were published in the Canada Gazette (Vol. 142, No. 14 – 9 July 2008). Other proposed actions set out in a risk management strategy included plans to minimise emissions of decaBDE in textile and plastics processing through an Environmental Performance Agreement with stakeholders (Environment Canada, 2006b).

In August 2010, Environment Canada published its Ecological State of the Science Report on the Bioaccumulation and Transformation of Decabromodiphenyl Ether (Environment Canada,

2010). This report, based on the scientific literature published up to 25 August 2009, concluded that decaBDE does not meet bioaccumulation criteria as defined under the *Persistence and Bioaccumulation Regulations* under CEPA 1999 (Environment Canada, 2010).

In February 2012, Health Canada published the "Human Health State of the Science Report" on decabromodiphenyl ether, and concluded that decaBDE was not harmful to human health at current levels of exposure. Health Canada addressed uncertainties in the health and exposure databases on decaBDE due to the limited data on the levels of decaBDE in environmental media and food and the absence of significant potential for genotoxicity and limited carcinogenicity potential in experimental animals. Further reduction of human exposure to decaBDE in Canada is expected as a result of implementing regulations that prohibit the manufacture of decaBDE congeners and the additional regulatory actions that are under development by the Government of Canada.

Based on the Human Health State of the Science Report and the Ecology State of the Science Report on decaBDE, Canada revised its risk management strategy, which further broadened the control measures for decaBDE to include restriction of both the substance and all products that contain it (not limited to electrical and electronic equipment as indicated in the March 2009 risk management strategy). The final revised strategy consisted of the following main elements:

- 1. Expand prohibitions on the manufacture, use, sale and import currently in force for tetra- to hexabrominated congeners (as prescribed by the PBDEs regulations, see link below) to all PBDEs assessed under the Canadian Environmental Protection Act, 1999 (CEPA 1999). As such, prohibitions on the use, sale, offer for sale and import would be extended to hepta-, octa-, nona- and decabrominated congeners, and any resin or polymer containing these substances.
- 2. Development of control measures under CEPA 1999 to restrict PBDEs in manufactured and imported products. While further information needs to be gathered, the intention is to prohibit the manufacture, use, sale, offer for sale and import of all new products containing tetra- to decabrominated congeners at concentrations greater than 0.1% by weight.
- 3. Development of Federal Environmental Quality Guidelines for PBDEs.
- 4. Development of a risk management strategy for the waste sector (for example, landfills, incinerators and recycling facilities) that will include PBDE-containing products at end-of-life.
- 5. Monitoring Canadians' exposure to PBDEs and concentrations in the environment.

(https://www.canada.ca/en/health-canada/services/chemical-substances/other-chemical-substances-interest/polybrominated-diphenyl-ethers-risk-assessment.html).

Status of decaBDE under International Conventions and Councils

The Stockholm Convention

On 13 May 2013, Norway as a party to the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention), submitted a proposal to list decabromodiphenyl ether (commercial mixture, decaBDE) in Annexes A, B and/or C to the Convention. The proposal was submitted in accordance with Article 8 of the Convention and was reviewed by the Persistent Organic Pollutants Review Committee (POPRC) at its ninth meeting in October 2013. At its tenth meeting in October 2014, the Committee evaluated the draft risk profile for

decaBDE in accordance with Annex E of the Convention and at its eleventh meeting adopted the risk management evaluation and concluded that decaBDE with its main constituent BDE-209 is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted. The Committee decided to recommend to the Conference of the Parties (COP) that it consider listing decabromodiphenyl ether (BDE-209) in Annex A to the Convention, with specific exemptions for some critical spare parts, to be defined, for the automotive and aerospace industries. By the same decision (POPRC-11/1), it was noted that alternatives to decaBDE that were not persistent organic pollutants were available (UNEP, 2016).

An intersessional working group, established to assess the information and strengthen the recommendation on the listing of decaBDE, confirmed that substitution of decaBDE was possible and that phase-out of decaBDE was ongoing in both the automotive and aerospace industries. It further suggested that the production and use of decaBDE in vehicles could be further defined and limited to spare parts for use in legacy vehicles – defined by European Automobile Manufacturers Association (ACEA) as vehicles that have ceased mass production prior to July 2018 (UNEP, 2016).

For the automotive industry, the production and use of decaBDE would be limited to parts for use in legacy vehicles (UNEP, 2016). No additional information indicating any use of decaBDE in textiles produced by small and medium-size enterprises in developing countries was submitted.

The eighth meeting of the Parties to the Stockholm Convention on Persistent Organic Pollutants (POPs) (COP 8) convened from 24 April - 5 May 2017 in Geneva, Switzerland. The Parties agreed to adopt the decision to list decaBDE in Annex A to the Convention with some specific time-limited exemptions for production and use. The Parties based their decision on the risk profile for decaBDE, adopted by the POP Review Committee (POPRC) at its tenth meeting and the risk management evaluation prepared in accordance with Article 8 of the Stockholm Convention.

In their decision (UNEP/POPS/ COP.8/CRP.14), the Parties decided to list decaBDE, with specific exemptions for the production and use of commercial decaBDE for:

- parts for use in legacy vehicles defined as vehicles that have ceased mass production, and with such parts falling into one or more of the following categories: powertrain and under-hood applications such as battery mass wires, battery interconnection wires, mobile air-conditioning pipes, powertrains, exhaust manifold bushings, underhood insulation, wiring and harness under hood (engine wiring, etc.), speed sensors, hoses, fan modules and knock sensors; fuel system applications such as fuel hoses, fuel tanks and fuel tanks under body; pyrotechnical devices and applications affected by pyrotechnical devices such as air bag ignition cables, seat covers/fabrics (only if airbag relevant) and airbags (front and side); suspension and interior applications such as trim components, acoustic material, and seat belts;
- parts in vehicles falling into one or more of the following categories: reinforced plastics (instrument panels and interior trim); under the hood or dash (terminal/fuse blocks, higher-amperage wires and cable jacketing (spark plug wires)); electric and electronic equipment (battery cases and battery trays, engine control electrical connectors, components of radio disks, navigation satellite systems, global positioning systems and computer systems); fabric such as rear decks, upholstery, headliners, automobile seats, head rests, sun visors, trim panels, and carpets;

- aircraft and their spare parts for which 'type' approval has been applied for before December 2018 and has been received before December 2022; textile products that require anti-flammable characteristics, excluding clothing and toys; additives in plastic housings and parts used for heating home appliances, irons, fans, immersion heaters that contain or are in direct contact with electrical parts or are required to comply with fire retardancy standards, at concentrations lower than 10% by weight of the part; and
- polyurethane foam for building insulation.

It was also decided that the specific exemptions for parts in vehicles shall expire at the end of the service life of legacy vehicles or in 2036, whichever comes earlier, and that the specific exemptions for spare parts for aircraft for which type approval has been applied for before December 2018 and will be received before December 2022 shall expire at the end of the service life of those aircraft.

The Parties considered a proposed exemption for recycling of materials that contain decaBDE (mostly waste plastics and e-waste). Ultimately, the Parties did not agree to an exemption for recycling. The consideration was centred on the challenge of separating waste that contains decaBDE from waste that does not contain the chemical. Some Parties indicated that doing this is impractical and; therefore, recycling should be exempted. Other Parties were opposed to this exemption because it would allow decaBDE from waste materials to remain in circulation for many years. These Parties indicated that the technology is available to separate these wastes.

The Parties decided on a process for reviewing decaBDE exemptions. Parties listed in the register of specific exemptions had to submit justifications for the exemption to the Secretariat by December 2019. The Persistent Organic Pollutants Review Committee (POPRC) will review this information in 2020 and will make recommendations to the COP on finalisation of the exemptions (ENB 15/252, 2017).

Rotterdam Convention

DecaBDE is not included under the Rotterdam Convention, the 1992 Convention for the Protection of the Marine Environment of the North-East Atlantic ("OSPAR Convention"; OSPAR, 2004) or the Arctic Monitoring and Assessment Programme (AMAP, 1998).

2.3 Australian perspective

As previously discussed, polybrominated flame retardants including PBDEs were declared Priority Existing Chemicals (PECs) for preliminary assessment as a group on 7 March 2000 under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), primarily due to concerns regarding the potential bioaccumulation and persistence of some of the PBFRs that may impact adversely on the environment and human health. The report focused on use patterns and potential exposure to PBFRs in Australia. Recommendations included a full (risk) assessment when hazard data become available from international assessments; depending on the outcomes of the assessments and the chemicals in use in Australia, to balance consideration of any adverse effects of these chemicals against the need for fire retardancy for certain articles and use situations to protect human health and property; for industry to carefully consider the selection of PBFR compounds for use and ensure that those known to be hazardous are avoided and those with unknown hazards are not introduced. It was further recommended that labels, material safety data sheets and other hazard communication materials be revised to reflect the information on hazards already available for these chemicals (NICNAS, 2007).

Subsequently, decaBDE, along with HBCD and TBBPA, were declared on 7 June 2005 as PECs for full risk assessment. Reasons for declaration of decaBDE included evidence of liver, spleen, and neurobehavioural effects in animal studies and concerns over photodegradation of decaBDE to lower brominated diphenyl ether congeners. The declaration notice for decaBDE covered its degradation products including penta- and octabrominated diphenyl ethers. PentaBDE and octaBDE were themselves declared on 3 January 2006 as PECs for full risk assessment under the Act (Chemical Gazette, January 2006).

In 2007, studies commissioned by the Australian Government Department of the Environment and Energy (DEE) (formerly the Department of the Environment, Water, Heritage and the Arts), indicated that the highest levels of polybrominated diphenyl ethers (PBDEs) in Australia were detected in the blood of young children and lower levels in women of child bearing age (Toms et al. 2007). NICNAS completed an interim public health risk assessment on PBDE congeners, focusing on the most toxic and bioaccumulative tetrabrominated to hexabrominated congeners (all found in commercial pentaBDE), (NICNAS, 2007). As a result of these new studies, it was considered that, although there was no current evidence of any adverse health effects in newborns or in children from exposure to PBDEs, because the chemicals have the potential to cause developmental effects in the offspring of treated laboratory rats at levels not greatly higher than those observed in humans, the potential for these effects to occur in humans could not be ruled out. Therefore, a precautionary approach was adopted by immediately prohibiting the import and/or manufacture of some of the PBDEs into Australia.

3 Identity, Properties and Analysis

3.1 Chemical identity

Chemical identit	Chemical identity information						
IUPAC name	bis(pentabromophenyl)ether						
Chemical name	benzene, 1,1'-oxybis[2,3,4,5,6-pentabromo-decabromodiphenyl ether						
CAS no:	1163-19-5						
EINECS No:	214-604-9						
SMILES representation	O(c(c(c(c1Br)Br)Br)c1Br)c(c(c(c(c2Br)Br)Br)Br)c2Br						
Synonyms	DBDPE; DBBE; DBBO; DBDPO; decabromobiphenyl oxide; decabromodiphenyl oxide; decabromophenoxybenzene; benzene 1,1' oxybis-, decabromo derivative; BDE-209; decaBDE; bis(pentabromophenyl) ether; 1,1'-oxybis(2,3,4,5,6- pentabromobenzene); 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether; decabromobiphenyl ether; decabromophenyl ether; ether, bis(pentabromophenyl); pentabromophenyl ether						
Trade name	FR 300BA; DE 83RTM; Saytex 102; Saytex 102E; FR 1210; Adine 505; AFR 1021; Berkflam B 10E; BR 55N; Bromkal 81; Bromkal 82-ODE; Bromkal 83-10DE; Caliban F/R-P 39P; Caliban F/R-P 44; Chemflam 011; DE 83; DP 10F; EBR 700; Flame Cut BR 100; FR 300BA; FR-P39; FRP 53; FR-PE; FR-PE(H); Planelon DB 100; Tardex 100; NC- 1085, HFO-102; Hexcel PF1; Phoscon Br-250; NCI-C55287; Caliban-F/RP-44; 102(E); DB 10; DB 101; DB 102; DE 83R; Decabrom; Fire Cut 83D; Flame Cut 110R; FR 10; FRD 004; Myflam 11861; Nonnen DP 10; Nonnen DP 10(F); NSC 82553; Planelon DB; Planelon DB 101; Plasafety EB 10; Plasafety EBR 700; Pyroguard SR 250; Duroquard SP 270						
Molecular formula	C ₁₂ Br ₁₀ O						
Molecular weight	959.2						
Structural formula	$Br \\ Br \\$						

DecaBDE is a member of a class of chemicals known as PBDEs. This class includes all chemicals with the diphenyl ether structure where one or more of the hydrogens have been substituted by bromine, and the members range from monobrominated to decabrominated. In all, there are 209 different chemicals (congeners) in the category of PBDEs once the positional isomerism is taken into account. Of these, a much smaller group is in industrial use (Appendix 1). These derive from the commercial products tetraBDE (stated to be no longer in production in 1994 (IPCS, 1994), pentaBDE, octaBDE and decaBDE. While pentaBDE and

octaBDE consist of a range of congeners of different bromination levels, decaBDE is close to a pure single congener as currently produced.

Polybrominated diphenyl ethers (PBDE) are also referred to in literature as polybrominated diphenyl oxides (PBDPOs) or polybrominated biphenyl oxides (PBPOs).

Breakdown products

As well as decabromodiphenyl ether, the decalaration also list its "breakdown products". The breakdown products of decaBDE may be various, and dependent on the mechanism of breakdown of decaBDE (ie photolytic, metabolic by species, or pyrolytic). Both metabolism and photolysis in aqueous systems have shown major breakdown pathways that include reductive debromination, or formation of oxygenated species. However, for the purposes of this report, the breakdown products of most concern are taken to be lower brominated diphenyl ethers. It is noted that very little information is available on the identity, concentrations, or the effects of the breakdown products other than lower brominated diphenyl ethers.

The risk profile for decaBDE, prepared by the Persistent Organic Pollutants Review Committee (POPRC), states that in spite of the persistence and long environmental half-life of decaBDE in sediment, soil and air, there is considerable evidence that decaBDE is debrominated to lower brominated PBDEs under abiotic conditions, as well as in biota. Observed debromination products detected range from mono- to nonaBDEs, and include listed POPs such as tetra-to heptabrominated PBDE congeners and bromophenols. The biotransformation of decaBDE in biota, in particular, is considered to be of concern.

3.2 Physical and chemical properties

3.2.1 Physical properties

Commercial decaBDE is a fine white to off-white crystalline powder. The individual congener, BDE-209, is a white crystalline solid.

Information on vapour pressure, water solubility and environmental partitioning are discussed further below. DecaBDE does not contain any functional groups that are able to dissociate under normal environmental conditions. Due to its application as a flame retardant, it is assumed to not have flammability properties (ATSDR, 2004).

Physical	properties	of decaBDE
	P. 0 P 0. 0.00	

Property	Value	Reference
Melting point	300-310°C	EC (2002a)
Decomposition temperature	> 320°C	EC (2002a)
Specific gravity	3.0	EC (2002a)
Water Solubility	0.1 μg/L at 25°C	Stenzel and Markley (1997)
Dissociation constant (pKa)	Not expected to dissociate under normal environmental conditions.	
Vapour pressure (Pa)	4.63×10 ⁻⁶ @ 21°C	Stenzel and Nixon (1997)

Property	Value	Reference
Partition coefficient (<i>Log K_{ow}</i>)	6.27 - 9.97	*See comments and ref. below
Henry's Law Constant	0.04 Pa.m ³ /mol	Cetin and Odabasi (2005)
Log Koc	5.61	EPIWin v3.11

*6.27 (measured – generator column method (MacGregor and Nixon (1997)) and 9.97 (estimated using an HPLC method (Watanabe and Tatsukawa (1990)) .

3.2.2 Chemical properties

DecaBDE is produced by treatment of diphenyl ether with an excess of bromine in the presence of a Lewis acid (Friedel-Crafts) catalyst such as aluminium tribromide (AlBr₃) under a variety of conditions. Control of stoichiometry and reaction time is used to produce a final product with the required percentage of bromine incorporated (ATSDR, 2004).

DecaBDE is unstable at high temperatures, and formation of polybrominated dibenzofurans and dibenzodioxins during incineration may occur. It also decomposes photolytically.

4 Use, Manufacture and Importation

4.1 Manufacture

The data collected through the call for information to industry (2017) indicated that the manufacture of decaBDE has never occurred in Australia.

4.2 Importation of decaBDE powder and dispersions

Commercial grade decaBDE

Information on the quantities and uses of raw decaBDE powder and decaBDE dispersions imported into Australia from March 2016 to February 2017 was obtained from importers and companies who have used decaBDE in their productions. In addition, some importers of manufactured articles in Australia provided data of decaBDE imported in their electric and electronic products.

Approximately 246 tonnes of decaBDE are imported annually under the brand names Great Lakes DE-83R, FR-1210, and Saytex 102E, in the form of powder, at purities \geq 97% BDE-209.

The raw decaBDE powder is transported to Australia by sea and then from wharves to importers' warehouses by road freight. It is packaged in 25 kg polylined paper bags that are packed in 6 metre shipping containers, usually on pallets wrapped in shrink-wrap plastic. The bags are unpacked and stored in the warehouses on pallets. The pallets are delivered from importers to customers by road freight.

There is no repacking of the product by importers and bags are not opened prior to use.

Dispersions of decaBDE

Approximately 5 tonnes of decaBDE was imported annually in a water-based blend containing 37 % decaBDE. This is imported in 227 kg plastic drums and stored in bunded raking in the importer's warehouse. The majority is sold unopened, while some are opened by the importer and used in the formulation of a water-based acrylic emulsion system.

A drop in the import volume of decaBDE occurred in 2007 and 2008; however, the import volume increased to its normal pattern from 2010. Data collected in 2017 showed a further increase in the import and use of decaBDE in Australia. Although there has been an increase in the import volume in powder form, there has been a reduction in the amount contained in water-based blends and the concentrations of decaBDE contained in epoxy resin has remained constant (refer to table below).

DecaBDE	·			Qua	antity (tor	nnes)			
FOILI	2004	2005	2006	2007	2008	2009	2010	2011	2017
Powder ((≥97% purity)	219	194	208	170	58	104	208	223	245.6

Table	1. Amount	of decaBDE	imported	into	Australia	2004-2017
TUNIC	I. Amount		mportea		Austiana	

Decabromodiphenyl Ether									
DecaBDE		Quantity (tonnes)							
Form	2004	2005	2006	2007	2008	2009	2010	2011	2017
Contained in water- based blends @ 37 -46%	15*	15*	15*	15* (pro- jected)	15* (pro- jected)	15* (pro- jected)	15* (pro- jected)	15* (pro- jected)	5.2
Contained in epoxy resin @ 10%-30%	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	-
Totals	234.0	208.3	222.5	185.0	73.0	119.0	223.0	238.0	250.8

* This figure represents the amount of decaBDE in the formulation calculated as 100% decaBDE.

4.3 Uses of decaBDE powder and dispersions

Plastics industry

Information obtained from industry indicates that decaBDE is used by plastics compounders as an additive flame retardant in a variety of resins. The main resins are acrylonitrilebutadiene-styrene (ABS), low density polyethylene (LDPE) and high impact polystyrene (HIPS). DecaBDE is also used in combination with an antimony oxide (antimony trioxide, antimony pentoxide), which acts as a synergist. In the plastics industry, decaBDE powder is supplied to plastics compounders, and the compounded flame-retardant resins are sold to companies who convert the resins into finished parts. These parts are usually commissioned custom-made parts, sometimes for export. According to 2017 data, about 123 tonnes decaBDE are used in plastic products.

Typical usage in LDPE is in a masterbatch that is foamed with cross-linked polyethylene and extruded to create insulation used in transport vehicles such as trains and planes; and in extruded film that surrounds the flexible duct work of heating/cooling systems in house construction. Examples of usage in HIPS are electrical appliances such as refrigerators, climate control housing, and certain ducting junction boxes for heating and cooling in housing applications. The major use of decaBDE in HIPS for housing of cathode ray tube (CRT) televisions (EC, 2002) is not known to have been conducted in the Australian industry. Examples of polyethylene copolymers use are in electrical and industrial fan shroud housing, fabricated using extrusion.

Glass reinforced nylons are used in housing applications for pumps, mounts and brackets etc. Occasionally "under the bonnet" applications in engine assembly may contain the flame retardant glass-filled nylons, including filter casings and electrical wiring boxes and/or fuses.

Commonly used articles such as electrical connections, light switches, power points and power packs also contain ABS resins. Control housing covers for appliances are sometimes made from ABS. Some fittings in the automotive industry are produced using ABS resin. ABS/polycarbonate resins are used in injection moulding of parts for medical devices, some domestic electrical appliances, and automotive casings. Electrical boxes, electrical connections and capacitor covers made from polypropylene contain decaBDE as a flame retardant.

In Australia, the resins are used to produce articles predominantly for the electrical, automotive and building industries. These articles usually require flame retardant chemicals as part of the design, for safety reasons, and to comply with various Australian or international standards related to flame retardancy. Examples of such end articles are:

- fan housings;
- brackets;
- electrical housings;
- building panels;
- traffic lighting surrounds;
- ducting;

•

- scuff protectors;
- cable wiring;
- heat-shrink tubing for joining electrical cables;
 - casings for electrical equipment, such as
 - o in hot water units;
 - o in automotive backcasing behind instrumentation;
 - in hopper bowls of poker machines;
 - \circ in mounts and brackets of casings;
- electrical boxes;
- capacitor covers;
- air conditioning ducting;
- foam insulation in transport vehicles;
- insulating foam in building walls.

Rubber industry

In the Australian rubber industry, decaBDE powder is used in the manufacture of flame retardant rubber conveyor belts for use in mines, including underground coalmines, and in the manufacture of ventilation bands used as seals around air ducts in mine ventilation systems. Nearly 18 tonnes are used annually for this purpose. Concentrations of decaBDE in these rubber compounds range from 1% to 5.1%.

Textiles industry

Data collected in 2017 indicated that approximately 56 tonnes of decaBDE were used in the formulation of textile coatings in Australia. This comprises approximately 5.2 tonnes of decaBDE imported as aqueous dispersions, and approximately 51 tonnes of raw decaBDE imported in powder form. There are a number of Australian Standards that specify the use of flame-retarded textiles in various circumstances.

The chemical decaBDE is blended into soft acrylic or polyurethane coatings by coating formulators, who either coat fabric themselves or sell to fabric coaters. Coated fabric may be exported or sold on to companies that cut and sew the fabric into articles.

Curtains/upholstery

In curtain and upholstery fabric manufacture, decaBDE is added into aqueous acrylic resin polymer dispersion at concentrations between 9 % and 14 %. The polymer is blade coated onto the fabric, and dried and cured, becoming fused to the fabric. The coating is applied to www.nicnas.gov.au 2800 638 528 or +61 02 8577 8800 Control info@nicnas.gov.au

the back side of the fabric. Reported uses for the curtains and upholstery fabrics include hotel curtains, public seating (including aircraft seating), and hospital chairs. Other possible uses include automotive and public transport upholstery; and curtains and seating fabrics in hospitals, nursing homes and theatres.

Carpet backing

The chemical decaBDE is used to formulate mixtures used for carpet backing, including automotive carpets. It is used in one formulation at a concentration of 8.5%. DecaBDE is pre-mixed with other ingredients into a paste that is added into a liquid formulation used to coat the back of carpets. It is flow coated onto the carpet back during manufacture of the carpet and heat cured.

Rainwear apparel

A solvent-borne system of polyurethane resin is used for blade coating and is used for rainwear apparel on one side of the fabric only (the inside of the garment). DecaBDE constitutes approximately 12.5% by weight of the final product. The rainwear apparel is worn over clothes as outerwear. Several worksites in Australia manufacture this type of garment.

Construction industry

Paper foil laminate in home insulation

The chemical decaBDE is used in the manufacture of paper foil laminate used in home insulation. Concentration of decaBDE in these products ranges from 18% to 41%. At least 20 tonnes a year (approximately) is used for this purpose.

Adhesives

A minor amount of raw decaBDE powder is used in the formulation of hot melt adhesives. Hot melt adhesives are solvent-free adhesives that are heated to a characteristically low viscosity, molten liquid state for application to substrates, applied hot, and then cooled, setting and bonding rapidly. DecaBDE is used to make a hot melt pressure-sensitive adhesive tape used in air conditioning ducting, and a hot melt adhesive for carpet backing materials. In the case of the adhesive tape, the decaBDE is added to the resin at 5% in the hot melt process and the resin is then extruded onto the backing of silicone-based paper which is then cut to shape.

Architectural foam

The chemical decaBDE is also used to flame retard a polyol mixture, which is subsequently mixed with a polyurethane prepolymer for use as a coating on house architectural decorations. Nearly 54 tonnes of decaBDE is used in the construction industry.

Summary

An estimation of the proportions of decaBDE imported as raw chemical or in dispersions that are used by the various industry sectors is provided in Table 2. The estimates are based on information on annual usages of decaBDE provided to NICNAS by customers of importers.

Industry Sector	Estimate of average annual usage (tonne)	Percentage of the total (%)
Plastics	123	49.0
Rubber	18	7.2
Textiles	56	22.3
Building	54	21.5

Table 2: Use of decaBDE imported as raw chemical or in dispersions (2017 data)

4.4 DecaBDE in imported articles

DecaBDE has also been imported into Australia in articles. In the imported articles, decaBDE is incorporated in plastic components, in textile parts or other products. Historically, the main use of decaBDE worldwide (estimated up to 95%) was in HIPS back housing of CRT televisions and the combined flame retardant and tensile strength properties of decaBDE-treated HIPS were difficult to substitute. Technological changes, moving away from CRT televisions, are expected to have reduced total importation volumes.

DecaBDE in plastic components

Printed circuit boards

Printed circuit boards are assemblies consisting of a copper-foiled laminate on which small electric and electronic components, encapsulated in plastic and metal, are mounted. Both laminates and plastic for encapsulation are flame retarded, usually with brominated flame-retardants. Printed circuit boards are widely used in electric and electronic equipment.

Housing of electric and electronic equipment

Housing of electric and electronic equipment, like television sets and computer monitors, commonly contains decaBDE as the fire retardant component. DecaBDE can be incorporated in a base polymer, consumer electronics, office machines, medical and laboratory equipment and domestic appliances. Use of decaBDE in electronic equipment housing, with the vast majority in TV set CRT housing, was found to comprise roughly 80% of USA consumption of decaBDE in 2005, and this was confirmed by a calculation based on numbers to TV sets sold, loadings of decaBDE and weights of flame retarded parts (Lowell Center for Sustainable Production, 2005).

Other components of electric and electronic appliances and machines

DecaBDE may also be present in a number of other components of electric and electronic appliances and machines such as light fittings, switches and relay parts, motor and pump parts, cables, moulding fillers, and other plastic insulation parts.

Toys

DecaBDE content in a number of toys purchased in China has been measured (Chen et al. 2009). The paper refers to an estimate that China manufactures more than 70% of the world's toys; therefore, the measurements in China reflect the likely composition of toys on
the Australian market. Of 69 toys, only one had a total PBDE content greater than 0.1%, and the median PBDE content was 53 ppm. The toy with maximum PBDE content included 0.42% decaBDE and had a total PBDE content of 0.53%. These analyses indicated that PBDEs are not included in toys at concentrations at which they would be effective as flame retardants, and their presence is likely to be incidental, possibly from inclusion of recycled plastics.

DecaBDE in textile products

DecaBDE may also be present in the imported textile components of a variety of products, such as protective clothing, carpets, curtains, upholstered furniture including foam and stuffing, tents, and interiors for transportation, offices, and public premises. However, the concentrations of decaBDE in these textile components and the total volume of decaBDE imported each year are unknown.

Other articles

Imported articles that may contain decaBDE include synthetic insulation materials, polyolefin based foils, and translucent and glass fibre reinforced panels.

Australian data

DecaBDE enters Australia in various imported articles. In some articles like cars, trains and aircrafts, decaBDE is present in very small amounts in plastics, textiles and electrical/electronic parts.

4.5 Human Health and Environmental Effects

4.5.1 Human Health Effects

In this section, the human health effects which were agreed by the Parties to the Stockholm Convention are described. Toxicity data for health end-points not discussed by the Parties are taken from the EU Risk Assessment Report (EC, 2002a). Further, the expert opinion on the carcinogenicity data on decaBDE published by IARC is summarised. The EU and IARC reports include full critical appraisal of reported studies, while the information in the Stockholm Convention documents is reported without full critical appraisal.

Toxicity of decaBDE has been investigated mainly in rodents. Several effects of decaBDE are reported, including developmental toxicity and effects on the thyroid hormone system.

Available scientific evidence suggests that decaBDE could act as a developmental neurotoxicant. Several studies have shown developmental neurotoxicity in rodents. Consistent and persistent alterations in behaviour, habituation and memory were observed in mice and rats administered a single dose of decaBDE during the "brain growth spurt" period. Reduced ability to habituate to a new environment and reduced activity (locomotion, rearing and total activity) were noted in rats treated at 20 mg/kg bw decaBDE. Effects on the cholinergic system in both mouse and rat brains which could lead to disturbed cognition (learning and memory), and reduction in neural connections between the left and right brain hemispheres were also reported. The neurodevelopmental effects of decaBDE in mice were reported at dose levels relevant for pregnant women and appeared to get worse with age. Exposure to decaBDE was reported to exert direct toxic effects on neuronal cells and interfere with neuronal signalling. It also induced oxidative stress, apoptosis and irreversible white matter hypoplasia targeting oligodendrocytes in rats. However, a clear interpretation

of the significance for human health of the behavioural differences seen in mice has not been established and thus uncertainty as to their significance remains.

The exact mechanism of PBDE developmental neurotoxicity is not known, although two general and not mutually exclusive modes of actions are emerging: one indirect, related to effects of PBDEs on thyroid hormones, and the other involving possible direct effects of PBDEs on the developing brain. Animal studies have reported decreased T3 and T4 levels following exposure to high levels of decaBDE; increased thyroid stimulating hormone (TSH) levels at the high BDE-209 exposures and no effects at lower doses. Studies on rodent offspring indicated that low doses of BDE-209 may adversely affect the developing thyroid.

Some studies have suggested that in utero exposure to BDE-209 at high parental doses may cause reproductive toxicity and lead to developmental abnormalities such as testicular histopathological changes, sperm-head abnormality and sperm chromatin DNA damage. However, other studies did not observe any effects on the reproductive system in either Sprague Dawley (SD) pregnant female rats exposed to BDE-209 from gestational day 0-19 or in male rats exposed to a mixture composed of three commercial BDEs (52.1% DE-71, 0.4% DE-79, and 44.2% decaBDE-209). The mixture affected liver and thyroid physiology but not male reproductive parameters in exposed rats.

Recent studies have indicated that BDE-209 may cause DNA damage through the induction of oxidative stress. Reduced qualitative and quantitative CD8 T-cell response was observed in mice after long-term BDE-209 exposure indicating immunotoxic effects of BDE-209. However, other studies did not observe any immunotoxic effects on the T cells in rats (UNEP, 2016).

DecaBDE has low oral and very low dermal absorption. After a single oral dose of radiolabelled decaBDE, less than 10% of the dose was absorbed. The highest concentrations on a lipid weight basis were found in plasma and blood-rich tissues, and the adipose tissue had the lowest concentration of decaBDE. No data on bioaccumulation or rate of elimination of decaBDE were available. Following intravenous administration, decaBDE undergoes hepatic metabolism resulting in the production of three main metabolites. Some decaBDE is absorbed intact from the intestine and excreted intact or in the form of metabolites (such as debrominated hydroxylated diphenyl oxides) (EC, 2002a).

DecaBDE exhibited low acute oral, dermal and inhalation toxicity in animal studies. It was not a skin or eye irritant. Repeated exposure by the oral route indicated low systemic toxicity even at high doses. No dermal or inhalation toxicological data were available. DecaBDE did not exhibit any cytogenetic effects in vitro or in vivo. Absence of alert-structure for genotoxicity further strengthened this conclusion (EC, 2002a).

The International Agency for Research and Cancer (IARC, 1990) concluded that no data were available from studies in humans on carcinogenicity of decaBDE and there was limited evidence for its carcinogenicity in experimental animals. The IARC members' finding for the overall evaluation was that decaBDE was not classifiable as to its carcinogenicity to humans and classified it in Group 3: "Not classifiable as to its carcinogenicity to humans".

4.5.2 Environmental Effects

In this section, the environmental effects of decaBDE, as agreed by the Parties, are summarised. This section should be read in conjunction with the Stockholm Convention *Risk profile on decabromodiphenyl ether* (UNEP/POPS/POPRC.10/10/Add.2) for a comprehensive description of these effects.

Aquatic Toxicity

DecaBDE has been shown to result in delayed development metamorphosis in amphibians (UNEP 2014). In one study, delayed metamorphosis in African clawed frog tadpoles was associated with effects to the thyroid system (Qin 2010). An aquatic no observed effect concentration (NOEC) for amphibians of below 1 μ g/L derived from this study was noted in the POPRC Risk Profile of commercial decaBDE (c-decaBDE) (UNEP 2014).

In fish, in some studies, significantly altered thyroid system function has been observed at environmentally relevant concentrations (UNEP, 2014), while other studies reported negative results. Significantly increased mortality in zebrafish larvae was also reported, with a low observed effective concentration (LOEC) of 1.92 mg/L; no such significant increase was observed for exposures of 0, 0.08 or 0.38 mg/L. A no observed effect level (NOEL) for decaBDE of approximately 3 ng/g bw/day or 0.41 ng/g food for thyroid hormone disruptive effects and mortality in fish was also derived (UNEP 2014).

Trans-generational effects have also been observed, and were attributed to transfer of decaBDE from mother to offspring (UNEP 2014, He 2011).

In vivo debromination has been observed in fish studies, with nona-, octa-, hepta-, hexa- and penta-brominated congeners being reported as degradants (Noyes 2011, 2013; Chen, 2012; Kuo, 2010; He, 2011). These less brominated congeners may; therefore, be contributing to the observed effects in fish.

Soil organisms and plants

Various studies on the effects of decaBDE on soil organisms and plants show a lack of acute toxicity, with adverse effects observed only at high doses (UNEP 2014). No observed effect concentrations (NOECs) of 5349 mg/kg dry weight and 4910 mg/kg were derived for plants and earthworms respectively (UNEP 2014). Effects on nitrifying bacteria, red clover seedling emergence or survival, or reproduction of soil invertebrates were not observed when exposed to 1000 mg/kg decaBDE (UNEP 2014). Ryegrass seedlings have been shown to reduce growth, as well as reducing the chlorophyll b and carotenoid content in leaves on exposure to 100 mg/kg decaBDE in soil.

Avian toxicity

Limited data on avian toxicity are available. It was reported that when chicken eggs were injected with a single dose of 80 µg/egg, with an LD50 of 44 µg/egg, 98% mortality rate for embryos was observed (UNEP 2014). The study found the average lipid weight in the eggs under consideration to be 19.3 g, giving an LD50 of 2300 µg/kg lipid weight. Since birds have been reported to metabolise decaBDE to less brominated congeners, avian toxicity is also relevant. BDE-209 has been associated with immunomodulatory changes, developmental toxicity, altered reproductive behaviour, and reduced fertility and reproductive success (UNEP 2014).

4.6 Release and Fate

4.6.1 Release

DecaBDE is a general purpose additive flame retardant, used predominantly in plastics (especially in electronic housing items), rubber and textiles. It is not chemically bound to these materials, but is physically incorporated in them. As a consequence, it is released

slowly to the surrounding environment from articles in which it is incorporated (Sun et al., 2016). Emissions during decaBDE production, from sites where it is incorporated into the material, from articles during their service lives, and upon disposal or recycling are all considered to be significant in a global context (UNEP, 2014).

Since all of the decaBDE used in Australia is imported into the country, there is no release to the environment as a result of decaBDE manufacture in Australia.

The amount of decaBDE that is released when decaBDE powder is mixed into plastic or rubber, or when decaBDE suspension is applied to textiles, is not known. Some release at this lifecycle stage is to be expected; however, little is known about the extent of releases to the environment at this lifecycle stage (UNEP, 2014). Industrial processing in Australia is subject to strict regulation and processing takes place in appropriately engineered facilities. Therefore, significant release of decaBDE to the environment is not expected at this stage.

Release from articles to soil and sediment during their service lives can be significant. DecaBDE is primarily adsorbed to particulate matter in the atmosphere, and the primary pathway for removal is via wet and dry deposition, with the final environmental sinks being soil and sediment (ECHA, 2014). It is noted that the atmosphere is the principal source of persistent organic pollutants (POPs) in vegetation via deposition of particulates directly onto the plants, rather than absorption from soil (Bartrons et al., 2016).

DecaBDE is routinely detected in domestic wastewater streams. Research suggests that decaBDE is released from articles transferred to clothing via household dust or air, and released to the sewage system on laundering (Saini et al., 2016 and references therein.). DecaBDE is highly lipophilic, and as a result is predominantly adsorbed to dissolved carbon in influent, and partitions almost entirely to biosolids in waste water treatment plants (WWTPs). Based on extensive monitoring data from Australian WWTPs, the authors of a study estimated 167 kg decaBDE is accumulated in biosolids in Australia per year (Gallen et al., 2016). Since 59% of biosolids in Australia are applied to agricultural land, approximately 99 kg decaBDE is predicted to be released in this manner every year. This estimate (based on measured data) of the amount of decaBDE accumulated in biosolids in Australia per year is consistent with an estimate of 110 kg per year based on modelling by Clarke and co-workers (Clarke et al., 2010).

Photolytic degradation of decaBDE can also result in the release of less brominated PBDEs from articles, as well as release of brominated phenols, dioxins and furans (UNEP, 2014; ECHA, 2014).

Release from synthetic vulcanised rubber products containing decaBDE has been shown to be low, and so low emissions from synthetic rubber products used in the mining industry in Australia are expected during use or on disposal (UNEP, 2014).

Emissions of decaBDE from articles that have been disposed of are considered to be of significant magnitude internationally (UNEP, 2014). Articles that are no longer servicable are often disposed of to landfill, and contaminants, such as decaBDE, can be emitted via the leachate that forms as rain seeps through the waste. The leachate is either evaporated in ponds, or discharged to the sewage system, where it contributes to WWTP influent. DecaBDE has been detected in landfill leachates in Canada and the UK. A study by the UK Environment Agency indicated that landfill leachates were a significant source of emissions in the UK. However, an extensive study of landfill leachates in Australia found that landfill leachate contributes an insignificant amount of decaBDE to WWTP influent compared to other sources (Gallen et al., 2016). It seems likely that Australia's relatively low population

density and low rainfall may account for the lower emissions of decaBDE from landfills in Australia.

4.6.2 Fate

As decaBDE is a highly lipophilic chemical that partitions strongly to sediment and soil and has high octanol-water and organic carbon-water partition coefficients (log Kow = 6.27 - 12.11, Koc = $150\ 900 - 149\ 000\ 000\ L/kg$); 96% is predicted to partition to soil and sediment and less than 3.4% is predicted to partition to water or air (UNEP, 2014). In the air compartment, decaBDE is almost entirely adsorbed to particulates (UNEP, 2014).

DecaBDE is generally persistent in the environment, but does degrade under some conditions; it photodegrades in sunlight and undergoes metabolic degradation in some organisms (UNEP, 2014, Mizukawa et al., 2017). It is not susceptible to hydrolysis (UNEP, 2014). An experiment run under dark anoxic conditions for 3.5 years in a biomimetic system found the half-life of decaBDE to be between 6 and 50 years (Tokarz, 2008). This is supported by sediment monitoring, which found no evidence of degradation over 30 years (Kohler, 2008). Similar results were found by Orihel et al., (2016).

DecaBDE is also persistent in soil. Studies have shown that in soils amended with biosolids containing decaBDE, the concentration of decaBDE remains high, even many years after the last biosolids application (Eljarrat, 2008, Sellstrom, 2005)

DecaBDE concentrations remained high four years after application of sewage sludge containing PBDEs (Eljarrat 2008). While laboratory studies have shown that decaBDE can photodegrade in soil or sediment matrices on exposure to sunlight (UNEP, 2014), its extent of photodebromination in soil appears to be low in the field (Sellstrom, 2005).

A significant route of decaBDE to soil is via application of biosolids as a soil improver. The biosolids are mixed into the surface soil through tilling and only a small amount of the decaBDE in these solids is sufficiently exposed to sunlight to photodegrade. This may not be the case for the decaBDE that is deposited on the surface of the soil through wet/dry deposition of particulates from the atmosphere. In this case, the deposited decaBDE would be exposed to sunlight to a far greater extent, although the amounts of decaBDE would presumably be much lower, except near point sources such as e-waste recycling plants.

DecaBDE has also been shown to photodegrade in house dust (Stapleton and Dodder, 2008) and on textiles (Kajiwara et al., 2008; 2013a, 2013b). The potential for photodegradation on textiles is of particular concern; decaBDE is commonly applied to the backs of curtains in Australia, where exposure to light is high. This could be a significant source of less brominated PBDE congeners and brominated dioxins and furans, which are known photodegradation products (UNEP, 2014). However, it is noted that window glass will protect the decaBDE on curtains to some extent by absorbing some ultraviolet (UV) light.

DecaBDE is also metabolised in some organisms. Studies have shown that decaBDE is biodegraded in sewage sludge (Kim 2013, Zenneg, 2013). The strongest evidence for biotransformation of PBDEs comes from the fact that BDE congeners that are not present in commercial mixtures are detected in organisms (UNEP, 2014). It appears that most vertebrates are able to metabolise decaBDE to less brominated PBDE congeners; however, the extent of degradation varies among species, and depends on the amount absorbed and the organism's metabolic capacity (UNEP, 2014). Mono- to octa-BDEs have been reported as degradants in fish (UNEP, 2014) and their relative amounts and identities vary between species of fish (UNEP 2014). Hydroxy- and methoxy-BDEs have also been reported as

degradation products (UNEP, 2014). Debromination of decaBDE has also been reported in birds and eggs.

The bioavailability of decaBDE is generally low. It does not pass through biological membranes easily, and its propensity to bind to particulate matter further reduces its bioavailability. Despite this, it is bioavailable enough to be detected in a wide variety of tissues, species, food webs and top predators (UNEP, 2014).

Given its lipophilicity, decaBDE partitions to blood-rich tissue in organisms, for example the liver, intestine and gills, rather than adipose tissue (UNEP, 2014). This contrasts with the behaviour of less brominated PBDE congeners, which partition primarily to adipose tissue (UNEP, 2014).

5 Environmental Exposure

The chemical BDE-209 is a ubiquitous global contaminant. It is routinely detected in air, soil, sediment and biota, particularly in urban and industrialised areas, and is often among the dominant PBDE congeners detected. When compared with other countries, concentrations of BDE-209 in the Australian aquatic environment are generally low, with the highest measured concentrations in estuaries in industrial centres. Agricultural soil amended with biosolids is expected to contain significant concentrations of BDE-209, even many years after application. Urban soils in Australia have been shown to be contaminated with congeners formed in BDE-209, with electronics recycling facilities identified as a point source (McGrath et al, 2016).

Detection of BDE-209 has occurred in air in urban, regional and remote regions worldwide (UNEP 2014). In a study commissioned by the then Department of the Environment and Heritage (now Department of the Environment and Energy) (Toms et al. 2006c) BDE-209 was detected in all of the indoor air samples collected, including both home and office environments, but at comparatively low levels when compared with values from overseas. BDE-209 is not manufactured in Australia, so there is no release from manufacturing facilities, but the process of blending it into plastics has been identified as a significant source of BDE-209 in the atmosphere (UNEP 2014). Electronic waste recycling facilities (Hearn et al, 2012) have also shown to be significant atmospheric point sources of BDE-209, with concentrations in air of up to 510 pg/m³ BDE-209 at an outdoor automotive shredding and metal recycling facility in Brisbane (Hearn et al., 2012). BDE-209 was the dominant PBDE congener detected in this study. Any BDE-209 released to the atmosphere is expected to partition to atmospheric particulates and partition to soil via wet/dry deposition.

BDE-209 is routinely detected in urban soils. It was detected in 29 of 30 soil samples from the greater Melbourne area in a recent study, and was found to be the dominant PBDE congener (McGrath et al., 2016). Electronics recycling facilities were found to be significant sources of PBDEs with the highest concentration measured to be 13100 ng/g, but the study also showed widespread contamination of urban areas, even in locations where the source of the PBDEs is not obvious. The median BDE-209 concentration was 34.08 ng/g soil, and several industrial sites had concentrations of greater than 1000 ng/g; the three largest concentrations were near electronics recycling facilities (13100 ng/g, 1060 ng/g) and a site classified as a 'Plastics and Foams' manufacturing facility (McGrath et al., 2016). These results are comparable with soil studies from overseas (McGrath et al., 2016, 2017).

BDE-209 was detected in landfill soil, with the highest measured concentration being 774 ng/g soil (McGrath et al., 2016). Testing of soils in Adelaide found similar results, confirming that PBDE contamination is widespread (Shanmuganathan 2010).

A recent monitoring study of 16 Australian WWTPs found BDE-209 in every sample of biosolids (Gallen et al, 2016). Mean concentrations were between 67 and 1340 ng/g biosolids, with an average of approximately 500 ng/g. Assuming 1.3 million tonnes of dewatered biosolids are produced each year (based on 2013 values), and that 59 % of the biosolids are applied to agricultural land as soil improver, the authors estimated that biosolids application results in 99 ± 98 kg decaBDE being applied to Australian agricultural land each year. These values are very similar to the estimates by Clarke et al. (2008) that approximately 110 kg of decaBDE is released to agricultural soils each year through application of biosolids.

Based on the recent data from Gallen et al. (2016) on the concentration of BDE-209 in Australia biosolids, it is estimated that a single application would result in a soil concentration of $3.3 \mu g/kg$. This estimate assumes an application rate of $1 kg/m^2/year$, a mixing depth of 0.1 m and a soil density of $1500 kg/m^3$ (EPHC 2009), together with the average measured biosolids concentration from the most recent Australian study of 500 ng/g biosolids (EPHC 2009, Gallen et al, 2016). Values could be considerably higher at sites which have received multiple applications of biosolids, given that decaBDE is both immobile and persistent in soil. Sellstrom et al. (2005) have shown that higher concentrations of decaBDE are found in earthworms than in soil amended with biosolids contaminated with decaBDE, and so concentrations of BDE-209 in earthworms could exceed $3.3 \mu g/kg$ if the soil were amended with an average sample of the biosolids found in the study (Gallen 2016). Earthworms living in soil contaminated with decaBDE have been identified as a source of decaBDE in terrestrial food webs (Sellstrom et al. 2005).

A study of brominated flame retardant concentrations in Australian sediments found generally low levels of PBDEs compared to sediments from North America, Europe and Asia, with decaBDE being the dominant congener at 86% of the sampling locations (Toms et al. 2006c). Aggregate concentrations of the 26 PBDE congeners tested were below 10 ng/g sediment in all cases, with the exception of sediment from the Parramatta River, Port Phillip Bay, and Port Jackson West, which had concentrations of decaBDE of up to 35 ng/g. A complementary study by Roach et al. (2008) found similarly high levels in the Parramatta River, with a median concentration of 25.3 ng/g. The maximum concentration measured in this study was 45 ng/g, and decaBDE represented between 89% and 96% of the detected BDE congeners. Sediment from 22 sampling locations on the Brisbane River had an average decaBDE concentration of 4.4 ng/g (Anim et al., 2017).

In the monitoring study of the Parramatta River, PBDEs were detected at low levels in bream (*Acanthopagrus australis*) and flounder (*Pseudorhombus jenynsi*) (total PBDE concentrations of 26 and 36.3 ng/g lipid weight respectively), and decaBDE made up only a small fraction of the total, 2% in bream and 5% in flounder (Roach et al., 2008). The extent to which this is due to debromination resulting from metabolism in the fish is not known. PBDE concentrations were extremely high in white-bellied sea eagles from the Homebush Bay area, with aggregate concentrations of up to 45900 µg/kg lipid weight in adipose tissue (Manning et al., 2008). A small fraction of the total PBDE load was made up of decaBDE, with a maximum concentration of 60 µg/kg measured in adipose tissue (Manning et al., 2008). The extent of debromination due to metabolism in the birds is not known.

An Australian monitoring study of organohalogenated pollutants in white ibis (*Threskornis molucca*) eggs found decaBDE at high levels (Ridoutt and Kingsford, 2011). Eggs from urban areas had significantly higher levels than eggs from peri-urban or rural areas. The mean concentration from urban areas in Sydney and Brisbane was approximately 270 μ g/kg lipid weight, with values of up to 550 μ g/kg lipid weight detected. The mean concentration in peri-urban areas was approximately 100 μ g/kg lipid weight, with values of up to 180 μ g/kg lipid weight detected, and values in inland areas were approximately 30 μ g/kg lipid weight, with values of up to 80 μ g/kg lipid weight detected (Ridoutt and Kingsford, 2011).

The available measurements of μ g/kg concentrations in the Australian environment are summarised in Table 3 below.

Table 3. Summary of measured environmental concentrations of BDE-209 in Australia.

Location	Matrix	Value	Reference
Brisbane (automotive shredding and recycling facility)	air	510 pg/m ³	Hearn et al., 2012
Melbourne (electronics recycling facility)	soil	13.1 mg/kg	McGrath et al., 2016
Melbourne (landfill)	soil	0.77 mg/kg	McGrath et al., 2016
Australia-wide	biosolids	0.07 – 1.34 mg/kg	Gallen et al., 2016
Parramatta river, Sydney	sediment	32.5 µg/kg	Toms et al. 2006c
Port Phillip Bay, Melbourne	sediment	35.6 µg/kg	Toms et al. 2006c
Port Jackson West, Sydney	sediment	22.5 µg/kg	Toms et al. 2006c
Parramatta river, Sydney	sediment	45 μg/kg	Roach et al., 2008
Homebush bay, Sydney	<i>Haliaeetus leucogaster</i> (white-bellied sea eagle)	60 µg/kg	Manning et al., 2008
Urban Sydney and Brisbane	<i>Threskornis molucca</i> (white ibis) eggs	270 μg/kg lipid weight (mean) 550 μg/kg lipid weight (max)	Riddout and Kingsford, 2011
Peri-urban Sydney and Brisbane	<i>Threskornis molucca</i> (white ibis) eggs	100 μg/kg lipid weight (mean)	Riddout and Kingsford, 2011
Inland Australia	Threskornis molucca (white ibis) eggs	30 μg/kg lipid weight (mean) 80 μg/kg lipid weight (max)	Riddout and Kingsford, 2011

6 Human Exposure

6.1 Occupational Exposure

DecaBDE is not manufactured in Australia. As mentioned previously, occupational exposure may occur during industrial processing in the plastic industry, textile industry, rubber industry and plastic recycling industry.

There are direct and indirect sources of decaBDE exposure at workplaces. Direct occupational exposure arises from industrial processes where decaBDE is processed or handled and eventually released into the workplace environment, such as through manual addition to blends.

As described under 'Manufacture, Importation and Use' (Section 4), decaBDE is mostly used as an additive flame retardant in plastic, textile and rubber products, and can be released in dust from the manufactured articles. These products are the main sources of indirect exposure in the workplace. For example, the chemical has been detected in dusts collected in workplaces.

The possible routes of occupational exposure include inhalation, skin contact, ingestion and ocular contact.

In practice, ocular exposure is expected to be very low because practically all industrial process operators in Australia wear eye protection when at work. Occupational exposure via ingestion is expected to be insignificant unless poor personal hygiene practices exist in the workplace. Inhalation of dust and skin contact are the major routes of exposure.

DecaBDE is a solid with very low vapour pressure ($4.6 \cdot 10^{-6}$ Pa at 21°C). Therefore significant exposure to the vapour will not occur at ambient temperature.

Dermal exposure through handling of decaBDE powder, or decaBDE-containing materials, may occur at workplaces. The degree of dermal absorption is considered to be low for decaBDE based on its high molecular weight and high log Kow.

Occupational exposure is assessed on the basis of "similar exposure groups". A total of four industry scenarios have been determined, each of which involves a unique pattern of use, quantity handled, and frequency and duration of exposure. It is expected that workers in each industry scenario will have similar exposure. These "similar exposure groups" are:

- polymer industry workers;
- textile industry workers;
- rubber industry workers; and
- plastic recycling industry workers.

In addition, workers can be exposed to decaBDE during transportation and warehousing of the chemical if a container is broken accidentally.

Occupational exposure studies

A number of exposure studies were conducted in electronic equipment recycling plants in Sweden (Sjodin et al. 2001; Pettersson et al. 2001; Thuresson, 2004; Pettersson-Julander et al. 2004; Julander et al. 2005). These studies have been reviewed and summarised in Table 4. As indicated in the table, most of these studies used high volume sampling (that is, sampling

flow rate greater than 4 L/min). While this flow rate is suitable for environmental sampling of "total suspended particulate matter", it will; however, result in the collection of a disproportionate number of large particles and thus will overestimate worker exposure.

Two studies (Thuresson, 2004; Pettersson-Julander et al. 2004) used sampling methodologies that were appropriate for exposure assessment. Thuresson (2004) found that workers operating the shredding machine from a control room had a mean TWA personal total dust BDE-209 exposure of 0.032 μ g/m³ (n=2, range = 0.031-0.033 μ g/m³); however, sampling duration was not reported. Pettersson-Julander et al. (2004) reported a geometric mean full-shift personal total dust BDE-209 exposure of 0.025 μ g/m³ (mean = 0.03 μ g/m³, n=12, range = 0.035-0.061 μ g/m³) among workers who dismantled waste electronic equipment. These sampling results should be considered to be representative of typical worker exposure in their respective work environments.

Julander et al. (2005) indicated that previous studies of exposure using total dust sampling methodology might have under-estimated exposure to BDE-209 by a factor of 10, as compared to inhalable dust sampling. However, the sample size was too small for a valid conclusion to be drawn. More research is needed in this area.

The apparent half-life of BDE-209 in human serum is 15 days (95% confidence interval, 11-18 days), according to the mathematical model of Thuresson et al. (2006), in a study examining the rate of decrease of PBDE serum levels during non-exposed periods (such as annual leave) in recycling workers.

A number of biological monitoring studies were conducted in electronic equipment recycling plants in Sweden (Sjodin et al. 1999; Hagmar & Bergman, 2001; Thuresson, 2004). These studies have been reviewed and summarised in Table 5. In this table, air sampling results, if available, are also provided along with the biological monitoring results.

As indicated in Table 5, Sjodin et al. (1999) reported a median serum BDE-209 concentration of 5.0 pmol/g lipid wt (range = <0.29-9.5 ng/g lipid wt) in 19 workers who worked in a dismantling and shredding section of an electronic equipment recycling plant. These 19 workers wore dust respirators at work; however, the extent of engineering dust control measures was not described. Hagmar & Bergman (2001) gave a very brief summary of their findings in smelting workers (mean serum BDE-209 level of 2.3 ng/g lipid wt, range = 1.4-5.6 ng/g lipid wt, n=9). There were no comments on personal respiratory protection or engineering dust control measures. Thuresson (2004) reported a mean serum level of 3.8 ng/g lipid wt (range = 2.4-5.2 ng/g lipid wt) based on two readings from two workers. There was also no indication of personal respiratory protection or dust control measures used.

Study reference	Job description / Work	Sampling strategy	Flow rate (L/min)	Sampling duration (min)	Conc of I (mg	BDE-209 /m³)
	area			(
Sjodin et al.	a)	Static (total	3.0 and	500, and	36	12-70 (12)
2001	Dismantling of electronic equipment in Sweden	dust) + Static (env. dust)	9.0	400		

Table 4. A summary of exposure studies at electronic equipment recycling plants inSweden

Study reference	Job description	Sampling strategy	Flow rate (L/min)	Sampling duration	Conc of (mg	BDE-209 /m³)
	b) Shredding of electronic equipment in Sweden	Static (total dust) + Static (env. dust)	3.0 and 9.0	500, and 400	175	150-200 (2)
Pettersson et al. 2001	Dismantling of electronic equipment in Sweden	Static (environ. Dust)	10-20	Not reported	12	Not reported
Thuresson 2004	a) Shredding of electronic equipment in Sweden	Personal	3.0	Not reported	32	31-33 (2)
	b) Testing laboratory	Personal (total dust, N=5) + Static (env dust, N=7)	3.0 and 9.0	Not reported	13 (median)	<0.4-72 (12)
	c) Outdoor air	Static (environ. dust)	9.0	Not reported	22 (median)	8-240 (6)
	d) Smelting area	Personal (total dust, N=2) + Static (env dust, N=4)	3.0 and 9.0	Not reported	0.7 (median)	<0.4-13 (6)
	e) Inside cabin of trucks	Static (env. dust)	9.0	Not reported	4.8 (median)	< 0.4-6 (4)
Pettersson- Julander et al. 2004	a) Dismantling of electronic equipment in Sweden	Personal (total dust)	2.0	480	30 (15); 25 (Geometric mean, GM)	3.5-61 (12)
	b) Other process workers	Personal (total dust)	2.0	480	8.1 (6.7) 6.6 (GM)	3.4-13 (2)
	c) Control (unexposed) group (not defined)	Personal (total dust)	2.0	480	1.7 (0.5) 1.6 (GM)	1.2-2.2 (3)

Study reference	Job description	Sampling strategy	Flow rate (L/min)	Sampling duration	Conc of (mg	BDE-209 /m³)
Julander et al. 2005	Dismantling in an	Static (respirable	1.9	960	3.1 (0.2)	2.9-3.3 (3)
al. 2005	electronics recycling facility in Sweden	dust); Static (total dust); Static (inhalable dust)	2.0 2.0	(2 shifts)	15 (1.4) 192 (24)	14-17 (4) 158-209 (4)

Table 5. A summary of serum concentrations of decaBDE at electronic equipment	ent
recycling plants in Sweden	

Study reference	Job description/Work		Air concentration of BDE-209 (ng/m ³)			concentra 19	ation of
	area				(ng/g li	ipid wt)	
		Ν	Mean	Range	N	Mean	Range
Sjodin et al. 1999	a) Dismantling and shredding of electronic equipment (Sweden)	Air monitoring was not reported.		19 4.8	(medi an)	<0.29- 9.5	
	b) Control group (hospital cleaners)				20	< 0.67	<0.29- 3.7
Hagmar & Bergman 2001	Smelting of electronic waste metals (Sweden)	Air monitoring was not reported.			9	2.3	1.4-5.6
Thuresson 2004	a) Shredding of electronic equipment in Sweden	2	32	31-33	2	0.38	2.4-5.2
	b) Testing laboratory	12 13 <0.4- (median 72*)*		<0.4- 72*	5	2.9 (medi an)	1.4-5.6
	c) Smelters	6	0.7*	<0.4- 13*	2	<1	<1

*High sampling flow rate was used.

Sjodin et al. (2001) measured airborne BDE-209 levels in various offices and computer repair workshops in Sweden, where a large number of computers were running, being used or repaired. The levels were: 0.083 ng/m^3 (mean) in an office (range = $<0.04 - 0.087 \text{ ng/m}^3$, n=4), $<0.04 - 0.093 \text{ ng/m}^3$ (n=2) in a computer repair workshop, and $<0.04 - 0.17 \text{ ng/m}^3$ (n=2) in a computing teaching hall.

Wolf et al. (2000) conducted an emission test for individual parts of a television set. Release of brominated substances from an epoxy resin printed circuit board into the carrier gas at 100°C was not detected using gas chromatography–mass spectrometry (GC-MS).

6.2 Public exposure

Public exposure to decaBDE includes direct exposure through products containing decaBDE and indirect exposure due to the presence of decaBDE in the environment. Direct exposure is assessed based on the typical scenarios that a consumer may encounter. Indirect exposure is assessed based on measured or predicted data on the levels of decaBDE in the different environmental compartments and in food and drinking water. Exposure via the inhalation of dust released by articles containing decaBDE within a household will be considered under indirect exposure in this assessment.

Public exposure to a chemical is not uniform across a population. Some groups or individuals may have higher potential exposures because, for example, they live in the vicinity of the industrial sources, or they have dietary habits or age-specific behaviours that may increase their exposure, such as inadvertent soil ingestion among young children.

Direct consumer Exposure

In Australia, about 43% of imported decaBDE (technical grade) is used in plastics, particularly in low-density polyethylene, high-impact polystyrene (HIPS) and polyethylene copolymers (data collected in 2007). The imported chemical is also used in textile coatings (about 27%) for curtain and upholstery fabric. About 12% is used in paper foil laminates in home insulation. Overseas data also suggest that decaBDE is used mainly in plastics (particularly in the television industry, and in electrical and electronic equipment), and in textiles.

DecaBDE is designed to be an additive flame-retardant in consumer articles. Additive flameretardants are physically incorporated into consumer products and are not chemically bound within the article matrix. Therefore, it is possible for decaBDE to be released from the treated articles to some extent, and consumers who use these treated products may be exposed.

It is unlikely that materials detached from treated articles will be directly ingested. The types of decaBDE-containing consumer articles are not considered likely to be mouthed by young children, with the exception of toys which contain very low levels of decaBDE (Chen et al., 2009).

Exposure of infants by mouthing toys was estimated by Chen et al. (2009) using migration rate data from a study of mouthing of two example toys with decaBDE concentration near the 75th percentile for the measured toys. The toys tested are likely to be representative of those available in Australia. The exposure from toys by dermal, inhalation and hand-mouth behaviour were all negligible. Estimates for mouthing exposure were 5.0 ng/kg bw/day for infants aged 3 to 18 months, and 0.44 ng/kg bw/day for infants aged 19 to 36 months.

Occasional or infrequent skin contact with decaBDE-treated products (for example, electronic devices, home electrical appliances) should result in very low dermal exposure.

However, direct and frequent skin contact with treated textile articles (such as treated automotive textiles, textiles for public seating and child seats, and specialised protective clothing) may result in higher dermal exposure. The dust may also be ingested due to hand and/or mouth behaviour.

Toms et al. (2006a) conducted a study to determine the concentration of BFRs in indoor environments in Australia. Ten surface wipes were obtained from two homes in South East Queensland. The aim of the surface wipe samples was to give an indication of the concentrations of PBDEs on the surface of various products in general use in households. The surfaces sampled represented televisions, refrigerators, stereos and DVD players. BDE-206, -207 and -209 were detected in 9 of the 10 samples collected. The mean concentration was 297 pg/cm² (SD = 797 pg/cm², n=10, range = <4.3 - 2,564 pg/cm²). The surface with the highest concentration was that of a televisions set.

Kemmlein et al. (2003) reported an emission study of a range of flame-retarded articles conducted by the German Federal Environmental Agency. Among those articles tested were rubber insulation board, an upholstered stool and part of a television housing which was manufactured before 1979. The rubber insulation board contained 6% decaBDE, whereas the other two articles were known to contain decaBDE, although the exact quantity was unknown. In this study, the articles to be tested were placed separately in emission chambers for 105-277 days under standard climatic conditions (temperature = 23°C, relative humidity = 50%). For the rubber insulation board, no decaBDE was detected in the chamber's atmosphere or on the interior surfaces of the chamber after 277 days of testing (detection limit: 6 ng/m³). For the TV housing, trace amount of decaBDE was found adsorbed on the interior surfaces of the chamber following 105 days of testing; however, the chemical was not detected in the chamber's atmosphere. A very low emission rate of 0.3 ng/m²/hr was calculated for this TV casing. For the upholstery fabric, no emissions were detected for up to 168 days of testing.

In summary, the above studies indicated that, at most, only trace amounts of decaBDE vapour are emitted from decaBDE-containing products. In Australia, decaBDE-treated paper foil laminates are used in home insulation but are typically used within wall cavities. Given the low vapour pressure of decaBDE, it's very low emission from treated articles, and as it is used mainly in enclosed and non-accessible locations, consumer exposure through inhalation is considered to be negligible. Since computers and home electrical appliances are widely used in indoor environments, there is no distinction between exposure of users of the equipment and others in indoor environments.

Indirect consumer Exposure

Indirect exposure of humans through the environment may occur by consumption of food and drinking water, inhalation of air, and ingestion of soil and dust (particularly in children). Indirect exposure through dermal contact, for example, with soil or dust can occur, but the amount absorbed following dermal contact is considered to be negligible.

DecaBDE can be released and distributed in the environment through many channels:

- release into the atmosphere or waste water from its industrial uses and disposal;
- emission from decaBDE-treated articles, including breakdown of the article matrix; and
- leaching and emission from landfill

Exposure from indoor/outdoor air

Limited studies are available that measured the concentration of decaBDE in indoor air.

Due to its low vapour pressure $(4.6 \times 10^{-6} \text{ kPa at } 21^{\circ}\text{C})$, significant emission of decaBDE vapours from treated articles is not expected. Low emissions from treated articles are demonstrated by many recent overseas studies (Wolf et al. 2000; Sjodin et al. 2001; Kemmlein et al. 2003). De Boer et al. (1998) did not detect decaBDE in the air inside or surrounding a TV set, but a wipe test found a level of <10-40 ug/m² on its surfaces.

In the Australian study by Toms et al. (2006a), nine indoor air samples were collected from five homes and three offices in South East Queensland, while two outdoor air samples were obtained from outside one home site and one office site. Congeners BDE-206, -207 and –

209 were detected in 6 of the 9 indoor samples collected, while they were all detected in all the two outdoor air samples. For indoor air, the mean concentration of the three congeners was 21 pg/m³ (SD = 41 pg/m³, n=9, range = <4.5 - 129 pg/m³). An attempt was made to correlate results with some household parameters and the lowest concentration was found in a house with no carpet and no air-conditioning, while the highest concentration of the three congeners was 1.5 pg/m³ in the backyard of a home and 6.3 pg/m³ at ground level outside an office. Analysis of indoor air for PBDEs was also undertaken by Toms et al. (2009), but contamination of the field blank resulted in no analyses being reported for decaBDE in air.

The highest reported figures for outdoor air were measured in China (Chen et al. 2006, Chen et al., 2008). Two different industrial sites in Guangzhou registered mean concentrations of 4200 pg/m³ (230 –11464 pg/m³) and 13192 pg/m³ (1082-49,937 pg/m³), respectively. An urban site registered a mean concentration of 264 pg/m³ (100 – 444 pg/m³) while samples taken from a city background registered a mean concentration of 478 pg/m³ (145 - 889 pg/m³). Very low concentrations (<0.1 pg/m³) were found in the Great Lakes air in the US after sampling for three consecutive years (n = 4). However, the authors surmised that this may be due to analytical procedures (Strandberg et al. 2001).

Besis and Samara (2012) have collected information on indoor and outdoor air and dust concentrations of PBDEs congeners, including decaBDE, in various countries in Europe, North America, Asia and Australia. A summary of their data confirms earlier observations that PBDE levels are higher in the indoor environment than outdoors. Concentrations in indoor air were higher in workplaces (offices) than in homes. Similarly, concentrations of PBDE in indoor dust were highest in workplaces, particularly in e-waste storage and recycling facilities (Table 6). The concentrations vary largely among different locations depending on differences in emissions strength, the atmospheric phase (particle, vapor, or both) where PBDEs were measured and the sampling season and are generally higher in the warm months (Cetin and Odabasi, 2005).

The most elevated values in the Besis and Samara study were found in the UK, implying that UK is a regional source area for PBDEs to the European atmosphere. In general, very high levels of indoor dust PBDE were found in the UK and USA; most likely due to high use of PBDE-based flame retardants, owing to particularly stringent fire regulations. Significantly high PBDE concentrations were also reported for various industrial sites in China (Chen et al., 2006). In contrast, concentrations of PBDEs in the vicinity of e-waste storage facilities in Thailand did not exceed 150 pgm⁻³. Lower levels were detected in samples from France and Germany, while non-detectable or very low values occurred in the remote/background sites, especially in Iceland, Ireland, Norway, and Sweden. Very low outdoor PBDE levels, in the range 1.7-6.8 pgm-³, have been found in Australia (Toms et al., 2009). Low concentrations were also found in remote locations with negligible local emissions, such as the Arctic (Xiao et al., 2012).

Although there are difficulties in comparing data on PBDEs from studies in which different suites of congeners have been determined, it appears that in most cases BDE-209 is the prevalent congener in outdoor air. However, in the USA, the most abundant congeners in air are BDE-47 and -99, even in studies including decaBDE, which are indicative of PBDE emissions from materials treated with pentaBDE technical formulations (Sjödin et al., 1999; La Guardia et al., 2006). The fact that BDE-209 is not among PBDEs with high concentrations in the USA samples is indicative of lower use of the decaBDE mixture in comparison to the use of the pentaBDE.

Table 6. Concentrations of PBDEs in indoor and outdoor air, and indoor dust in different countries (Adopted from Besis and Samara, 2012)

Country			Conce	entration (range)		
USA	Urban	52 (33-77)	Home	760 (210-3980)	Home	4200 (520-29000)
	Rural	(5.5-15)	Office	1260 (21- 17,200)		Office
Canada	Urban	(38.8-48)	Home	100 (2-3600)	Home	950 (750-3500)
	rural	3.8 (1.2-55)	Office	140 (25-350)	Office	-
UK	Urban	18 (10-33)	Home	128 (60-1622)	Home	2900 (360-520000)
			Office	1082 (82- 15509)	Office	7400 (790-280000)
Sweden	Urban	6.3 (2.2-21)	Home	330 (72-1400)	Home	1400 (13-100000)
			Office	4000 (140- 7300)	Office	1200 (800-13000)
Kuwait	Urban	(158-230)	Home	8.2 (2.5-139)	Home	90 (1-393)
			Office	8.6 (2-385)	Office	-
Greece	Urban	26 (21-30)	Home	11 (3-15)	Home	-
	Rural	3 (2-11)	Office	115 (19-10848)	Office	-
Japan	Urban	19 and 25	Home	17-55	Home	700 (140-3000)
	(2 samples)		Office	-	Office	1800 (260-20000
Thailand	Suburban	45 (8-150)	Home	23 (23-72)	Home	10 (0.6-257)
			Office	52 (46-350)	Office	28000 (320-290000)
China	Urban (Guangzho u)	88-1941	Home	628 (125-2877)	Home	696 (132-3887)
	Rural (Shunde)	195-1450	Office	518 (181-8315)	Office	30700 (6300-82200)
Australia	Urban	1.7 and 6.8	Home	19 (0.5-179)	Home,	1200 (500-13000);
	(2 samples)				2 studies	294 (87-733)
			Office	18 (15-487)	Office	1268 (583-3070)

Values refer to bulk air that is to gas- and particle-phases acquired through active sampling.

Exposure from Dust

Dust, indoor air and, to a lesser extent, food are considered to be the most important sources and pathways for human exposure to PBDEs (US EPA 2010). In this assessment, household consumer products were identified as the main source for the PBDEs in house dust. A Canadian assessment identified food and dust as main sources for exposure in adults (HCA, 2012). Detected decaBDE concentrations in the indoor air range from <LOQ to 651 pg/m³ (Harrad 2010) and from 63 to 10,000 ng/g in dust from Germany, Sweden and the UK (Fromme 2009). Several studies measuring PBDE in dust showed that the decaBDE concentrations in dust exceeded by far the sum of the lower brominated PBDEs (Besis and Samara 2012). The concentrations of decaBDE in North American house dust were comparable to the levels of house dust found in European houses (<500-2000 ng/g) (Fromme 2009). Dust in cars and airplanes may be a significant source of PBDE exposure as reviewed by Besis and Samara (2012). The median levels of decaBDE in dust from cars were about 20 times higher than in house dust, although the levels varied substantially between the studies. This is in line with a recent German study where the mean decaBDE concentration in car, house, and office dust samples were 940, 45 and 120 ng/g, respectively (Brommer et al., 2012). A correlation between decaBDE in house dust and mother's milk is also reported, suggesting that decaBDE levels in indoor environments have an impact on the exposure of breastfeeding children (Coakley et al., 2013).

Toms et al. (2006a) conducted a study to determine the concentration of BFRs in indoor environments in Australia. Nine settled dust samples were collected from five homes and three offices in South East Queensland. Congeners BDE-206, BDE-207 and BDE-209 (decaBDE) were detected in all nine samples collected. The mean concentration of the three congeners was 677 ng/g dust (range = 45 – 2386 ng/g). A study of ten residences in South East Queensland was undertaken as part of a matched study of PBDEs breast milk, dust and air (Toms et al. 2009). DecaBDE was found in all samples, with mean concentration 377 ng/g dust (range 95 – 1585 ng/g).

NICNAS commissioned a study of the distribution of PBDEs in household dust (details in Appendix 3). In this study, four major scenarios were targeted based on their correspondence to major uses of the flame retardants, the variety of possible release mechanisms, and volatilisation:

- a) DecaBDE used in back casing of television sets;
- b) DecaBDE used in flame retarded textiles;
- c) DecaBDE in monitor back casings; and
- d) PentaBDE in circuit boards in homes offices and in furniture foams.

The aim of the study was to determine the major sources of PBDE levels in household dust. The highest values for total PBDEs found in this study were comparable with the highest value seen in a study in the USA (Stapleton et al, 2005); although decaBDE concentrations were not a major contribution to this high level sample.

The findings of the study indicated that furniture foam was a major factor in contributing to the lower brominated PBDEs in household dust. The release of pentaBDE-related congeners from the foam is unlikely to differ greatly internationally, except for the impact of climatic factors such as temperature and sunlight exposure causing embrittlement, and this is likely to be high in the Australian climate.

While some variability of dust concentrations of decaBDE was seen within the study, no "hot spots" of the same magnitude as those seen for the pentaBDE-related congeners were identified. The X-ray fluorescence (XRF) analysis indicated that TVs contained decaBDE; however, the dust samples targeting TVs as a source gave very low levels of decaBDE. Spatial gradient samples did not show any clear pattern.

Given that the scenarios examined in the Australian homes (TVs and monitors) do not account for the high levels of decaBDE observed in the UK homes, coupled with the fact that UK has the strictest textile flame retardancy requirements among major countries, it is plausible to attribute these extreme levels of decaBDE in dust in UK homes to the use of decaBDE in textiles. No textile articles which were likely decaBDE sources were found in the NICNAS study.

The frequency of detection of bromine in chairs and sofas by X-ray fluorescence (XRF) differs very little between Australia (71% of chairs and 72% of sofas) and the USA (67% of chairs and 81% of sofas). In comparison with the results from the international studies, the analysis of the predicted "hot spots" in Australian homes gave low levels of PBDEs. The maximum international dust levels have generally been seen in the UK (Harrad et al. 2008; Sjodin et al. 2006). The highest level recorded by Harrad et al was 520000 ng/g dust; of the order of 100x the highest level seen in a "hot spot" in Australian homes. It is reported that 95% of all upholstery materials in the UK are flame retarded to comply with fire safety regulations (Sjodin et al., 2006), and that this is the only country within the EU that has regulation specifying the level of flame retardancy for domestic upholstery.

Wilford et al (2005) have also suggested that flame-retarded textiles may be a more likely source of particles/fibres than hard plastics (TV sets); however, the release mechanisms have not been well characterised. Textile backcoatings are reported to be composed of a latex material, with a high content of around 30% decaBDE. Specifications for performance of the backcoatings refer to the number of washes of the textile where the flame retardant performance is maintained. The release rate for the flame retardant from the backcoating has not been characterised. It is possible to speculate that constant exposure to UV radiation in the case of curtain materials may cause significant crosslinking of the latex material, leading to embrittlement and flaking off as the textile flexes. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the particles associated with high levels of decaBDE in a USA study (Webster, 2005). The particles were found to be acrylic, consistent with shedding from textile back coatings but not related to other known uses of decaBDE.

In the more general surveys of PBDE concentrations in household dust, Australia was found to have much lower overall levels of the pentaBDE-related congeners BDE-47 and BDE-99 than those seen in the USA or Canada. This may be attributable to more limited use of pentaBDE in Australian furniture foam, although this cannot be independently confirmed. The annual demand worldwide for penta-BDE was estimated as 7,500 tonnes in 2001, of which the Americas accounted for 7,100 tonnes, Europe 150 tonnes, and Asia 150 tonnes.

Comparable indoor dust datasets are available for the USA (43 homes) (Stapleton et al. 2005; Schecter et al. 2005) and Canada (68 homes) (Wilford et al. 2005), with individual home data being available from several studies in the USA. Two studies with individual home data are also available from Kuwait (Geveo et al. 2006), and Singapore (Tan et al. 2007). A number of European studies have been restricted to pooled dust samples (Santillo et al. 2003a & 2003b; Sjodin et al. 2004, Sjodin et al. 2006; Al Bitar, 2004; Knoth et al. 2002), allowing comparison only of mean values between these studies and the Australian data. Table 7 shows the comparison between the Australian data for BDE-47 and 99, as markers of pentaBDE, and

BDE-209, the major constituent of decaBDE, with a number of international studies. These were the only congeners which were both analysed for and detected in all the studies included in this table. Results are given in ng/g dust dry weight (ng/g dw).

High levels of BDE-209 are reported in UK and USA. These countries have very strict textile flame retardancy requirements, and the high levels of BDE-209 could be attributed to its use in textile backcoatings.

One study conducted in the US (Allen et al. 2007) involving single- and multi-family residences in the Greater Boston area, sampled ambient air in bedrooms (mean = 95 pg/m³; range = <51.0 - 269 pg/m³) and main living areas (mean = 94 pg/m³; range = <48 - 651 pg/m³). These figures, when compared to personal air cloud (mean = 174 pg/m³; range = <53 - 1636 pg/m³), indicated that the dust containing BDE-209 is greater in the personal air cloud than in the ambient air.

Similar concentrations (mean = 84 pg/m^3 ; range = $<40 - 87 \text{ pg/m}^3$; n = 4) were found in an office with computers in Sweden (Sjodin, 2001); other areas included in this study were the internal environments of a dismantling plant and are more appropriate for an occupational exposure study.

Allen et al. (2008) measured the levels of PBDE in household dust and air in 20 USA homes. Different PBDE levels in dust from different rooms were reported. Penta- and decaBDE concentrations were significantly higher in the main living area than the bedroom, while there was no significant difference in octaBDE concentrations. This suggests that penta and decaBDE have room-specific sources (such as from televisions, couches) and that microenvironments play an important role in their distribution in household dust. Correlations between air and dust levels existed for the congeners found in pentaBDE, but not for BDE-209.

Two studies which used XRF analysis to characterise the distribution of bromine within household dust from Japan, the UK and USA (Webster et al. 2009) showed that high bromine levels are largely present in scattered particles, rather than being uniformly distributed in the dust. This is consistent with the source of the PBDEs being fragmentation of PBDE-containing matrices, rather than via volatilisation and uniform distribution on dust. Webster et al. (2009) further characterised a clear, elastic material with high bromine content which was found in two dust samples from a single home in Boston. These samples had very high BDE-209 concentrations of 530000 and 260000 ng/g, much higher than any levels measured in Australia. The bromine was associated with calcium, for example from calcium carbonate or kaolin fillers, and the material was examined by Micro-Fourier Transform Infrared Spectroscopy and found to be consistent with an acrylic plastic. This further suggests that the use in textile backcoating is associated with high levels of BDE-209 in dust, as textile backcoating is the only major application of decaBDE that uses an acrylic matrix.

Table 7. International comparison of indoor dust concentrations of BDE-47, BDE-99 and BDE-209 (ng/g dw)

Country	BDE	-47	BDE	-99	BDE-209		
	Median	Max	Median	Max	Median	Max	
UKª	27.2	-	79.8	-	10290	-	
(100 pooled)							
UK ^b	13	160	23	320	2800	520000	
(28 individual)							
(16 individual) Other Europe ^c (259	21.6		32.8		125	_	
pooled)	(mean)		(mean)		(mean)		
Kuwait ^d	2.7	65	3.4	36	83	338	
(17 individual)							
Singapore ^e	20	1500	24	6300	1000	13000	
(31 individual)							
New Zealand ^b	24	150	51	380	ND	ND	
(20 individual)							
Canada ^f	300	33000	430	60000	630	10000	
(64 individual)							
Canada ^b	140	720	330	1800	560	1100	
(10 individual)							
(7 individual)							
USA ^g	674	10538	626	13841	1680	65777	
(43 individual)	110	2222		6000	1200	2222	
USA	410	3300	820	6000	1300	3300	
(20 individual)							
(17 individual)							
USA ^h	230	-	880	-	2000	-	
	(mean)		(mean)		(mean)		
(10 pooled)	(0 (100		722		
Australia	ьо (mean)	-	IU6 (mean)	-	/32 (mean)	-	
(10 pooled)			(mean)		(mean)		
Australia ^j	34.3	210	48.8	294	401	2230	
(9 individual)							

Country	BDE	BDE-47		BDE-99		-209
Australia ^k	56.5	434	87	862	291	1585
(10 individual)						

a. data from Santillo et al. (2003a) and Sjodin et al. (2006).

b. data from Harrad et al. (2008); different sample numbers were used for lower and higher brominated BDEs.

c. Scotland data, from Santillo et al. (2003b), Sjodin et al. (2004), Al Bitar (2004), Knoth et al. (2002)

- d. data from Gevao et al. (2006)
- e. data from Tan et al. (2007)
- f. data from Wilford et al. (2005)
- g. data from Stapleton et al. (2005), Schecter et al. (2005) and Costner et al. (2005)
- h. data from Sjodin et al. (2004)
- i. data from Sjodin et al. (2006)
- j. data from Toms et al. (2006c)
- k. data from Toms et al. (2009)

McPherson et al. (2004) found that decaBDE was present in dust swiped from surfaces of computers in public buildings in eight states in the USA. DecaBDE concentrations ranged from 2 to 213 pg/cm².

Exposure from soil

Most available data reporting BDE-209 levels in soil are from affected areas. Reported levels in soil worldwide range from non-detectible up to 8600 pg/g dw soil in polluted areas. Compared to remote sites, BDE-levels in urban and rural areas are significantly higher.

No Australian monitoring data are available for BDE-209 in soil in residential areas. A recent monitoring study of 16 Australian WWTPs found BDE-209 in every sample of biosolids (Gallen et al, 2016). BDE-209 was detected in landfill soil, with the highest measured concentration being 774 ng/g soil (McGrath et al., 2016) and the soil contamination appears to be widespread (Shanmuganathan 2010).

Biological monitoring studies

Measured data from biological monitoring (such as blood, urine) reflects actual exposure to the substance being detected. It indicates the occurrence of past exposure and the subsequent absorption into the body. It seldom specifies the actual route(s) of exposure, much less the primary route or the contribution of other routes.

In Australia, Toms et al. (2006b) conducted a study to determine the concentration of PBFRs using pooled blood sera samples collected in 2002-03 as part of the (then) Department of the Environment and Heritage's National Dioxins Program (NDP). Additional blood sera samples were collected and pooled in 2004-05. The pooled samples encompass four urban regions and one rural region in Australia.

The mean concentrations of BDE-209, -207, -203 and -197, known decaBDE constituents (Thuresson et al. 2005), tested in this Australian study pooled blood sera samples are presented in Table 8. The difference in sampling sizes (pooled samples) was due to the presence of non-detectable samples that were excluded. BDE-203 and -209 had high incidence of non-detection. BDE-209 has a half-life of 15 days in humans (Thuresson et al., 2006), which may explain the higher number of non-detect samples; however, BDE-203 has a half-life comparable to BDE-207 (37 and 39 days), respectively. Since the results were from pooled sampling, median values were not determined. BDE-207, -203 and -197 were included in this summary because they are possible decomposition products of decaBDE.

Table 8. Levels of BDE-209, in Australian pooled blood sera from different regions and two age groups (ng/g lipid wt)

Regions	Males		Females		
	0 to < 16 yrs	16 to >60 yrs	0 to < 16 yrs	16 to >60 yrs	
Northeast	n.d. – 12	n.d.–6.5	n.d. – 4.3	n.d. – 2.3	
South	n.d.	n.d. – 2.0	-	n.d. – 3.6	
Southeast	2.2	1.1 – 2.7	n.d.	1.4 – 3.3	
West	3.0	n.d. – 3.7	n.d.	n.d.	
Rural	1.4	n.d. – 2.0	1.7	1.1 – 3.1	

[derived from Toms et al. 2006b]

Determination of BDE-209 in human blood was reported in various international studies. Mean concentrations of samples from Mexico, Japan and Sweden were higher than Australian figures (Table 9) by a factor of 3 (for 0 to < 16 yo) and 5 (for 16 to >60 yo). Concentrations from the UK and the USA may be even higher. However, mean concentrations of BDE-209 are of limited value because of the high percentage of nondetects in individual samples. This may be due to the high limit of detection required for this congener, its short half-life, or both.

Individual congener concentrations of decaBDE (BDE-209, -207, -203 and -197) from the biomonitoring in Australia showed that BDE-207 levels were slightly higher than BDE-209 concentrations. While studies involving individuals occupationally exposed to decaBDE show predominantly BDE-209-dominated serum samples (Qu et al. 2007; Bi et al. 2007), a study examining whole blood samples of 3 adults (Environmental Working Group, 2005) and 37 men (Jakobsson et al. 2005) showed BDE-207 levels greater than BDE-209 concentrations by a factor of two. The decreased concentration of BDE-209 observed in blood sera in the latter

case may be due to its shorter half-life or lower degree of bioavailability; the same phenomenon may explain the lower levels seen in these pooled samples. Therussen et al. (2006) have reported that the apparent half-lives of deca- to heptaBDEs in serum increased with decreasing number of bromine substituents. For the fully brominated BDE-209, the apparent half-life was as short as 15 days. It seems likely that nona- and octabrominated PBDEs are formed in humans after exposure to BDE-209, as also indicated in a crosssectional study of rubber workers, using a technical deca-BDE product containing only trace levels of octa- and nona brominated PBDEs (Thuresson et al. 2005).

Liu et al. (2012), found, for the first time, PBDEs in human semen. The authors found that the level of Σ PBDE in semen was about half that in human blood but the levels of BDE-209 and BDE-153 were much higher in the blood than in the semen samples. The range of concentration of total PBDEs in 101 samples (collected from the Fertility Clinic of Reproductive Health Center of Taizhou Hospital, Taizhou China) varied from 15.8 to 86.8 pg/g with a median of 31.3 pg/g in semen and 53.2 to 121 pg/g with a median of 72.3 pg/g in blood samples while BDE-209 level varied from 11.9 to 61.3 pg/g in blood samples and from limit of detection (LOD) to 33.9 pg/g in semen samples. Liu et al. (2012) suggested that lower brominated congeners could be more easily transferred to semen than higher brominated congeners.

In a recent study by Kim et al. (2012), 720 serum samples were collected from nonoccupationally exposed participants (general population with different sex, age, occupation and dietary habits) at four different locations in Korea and monitored for the presence of 27 PBDEs including BDE-209 and related congeners. The congeners mainly present were BDE-153, BDE-47 and BDE-99, with median concentration of 2.07, 1.69 and 0.71 ng/g lipid, respectively. The mean concentration of BDE-209 was 0.91 ng/g lipid and it was detected in fewer than 10% of the samples. The authors found that the major exposure route to PBDEs was due to dust ingestion rather than food consumption, which was supported by Johnson-Restrepo and Kannan (2009) findings and BDE-209 was found to be the predominant congener detected in Korean dust (Wu et al., 2010). Kim et al. also found no significant association between PBDE concentrations and individual and dietary habits, such as consumption of fish, meat, dairy products, etc. which was supported by the findings of Lee et al. (2007). The authors noted the different opinions in regards to the sources of human exposure to PBDEs; one was attributed to the consumption of contaminated food (except in the case of BDE-209), and the other attributed more significantly to the ingestion of dust (Lorber (2008) and Roosens et al. (2009).

Study Ref.	Study Subject	Sample No.	BDE-209 Levels (ng/g lipid wt unless otherwise specified*)		% non-detect
			Mean	Range	
Thomas et al. 2006	Healthy volunteers from 13 locations in the UK, in 2003.	154	<15	<15 - 49	93
Karlsson et al. 2007	Five people in 5 households (1x5) tested in Sweden.	5	10	n.d – 17.4	20

Table 9. Levels of PBDE congener BDE-209 found in human blood.

Study Ref.	Study Subject	Sample No.	BDE-209 Levels		% non-detect
			(ng/g li unless ot specifi	pid wt herwise ied*)	
Kim et al. 2012	720 serum samples collected in 2009 and 2010 from 4 locations in Korea.	720	0.91	n.d- 39.8	91
Jakobsson et al. 2005	Men, sampled 1991 (age: 23-69).	37	1.3 (median)	0.01-21	0
	Same men sampled 2001.	37	1.4 (median)	0.47- 5.2	0
	Volunteers -	5 (Set A)	Not det	ected	100
	umbilical cord -	3 (Set B)	Not det	ected	100
	Volunteers 2002-	5 (Set A)	23		0
Fukata et al. 2005	04 - umbilical cord serum - Japan	3 (Set B)	10		0
	Volunteers 2002- 04 - maternal serum - Japan	5 (Set A)	10		0
Inoue et al. 2006	Lactating mothers aged 20-43 in maternity hospitals from 4 regions of Japan in 2005 - serum	89	1.20 (GM)		20
Lopez, 2004	Women from San Luis Potosi City, Mexico - plasma	5	9.5	4.8-14- 6	-
Environmental Working Group, 2005	Umbilical cord blood from babies born in US hospitals in 2004 – whole blood	10		0.43 – 9.63	70
	Adults – whole blood	3		2.48 – 5.00	-
WWF Detox Campaign,.2004	Adults (from 17 European countries), 2003 - serum	47	No data	1.84 (max)	66
Fischer et al. 2006, BDE-209	Father – 35yr - USA	1	23 (max)	2 and 23	0
measured in a single family in	Mother – 36 yr	1	14 (max)	4 and 14	0

Study Ref.	Study Subject	Sample No.	BDE-209 (ng/g lij unless otl specifi	Levels bid wt herwise ed*)	% non-detect
Sep and Dec 2004	Child – 5 yr girl	1	143 (max)	9 and 143	0
	Toddler – 18 mo boy	1	223 (max)	19 and 233	0

GM= Geometric mean

*The lipid content in blood is about 0.65%; therefore results for lipophilic compounds in pg/g serum may be converted into pg/g lipid by multiplying the former with a factor 150 (taken from Peters, 2004).

The Korean Food and Drug Administration reported average intakes of Σ 3-7 PBDEs (sum of PBDEs ranging between 3 and 7 bromines) and BDE-209 from dietary sources as 6.9 and 4.8 ng/day, respectively (KFDA, 2010), which were much lower than that in Europe and North America. However, the average intakes of Σ 3-7 PBDEs and BDE-209 from dust ingestion were found to be 8.0 and 193.9 ng/day respectively, which were similar to those in Europe. Kim et al. (2012) also observed different concentrations of PBDEs in males and females, and this could be attributed to the fact that three quarters of female participants were mothers who breastfed their children prior to this study. Kim et al. (2012) reported that the median value of Σ 3-7 PBDEs was similar to the median values observed in Asia and Europe, but much lower than those observed in North America.

Exposure from food

Food Standards Australia New Zealand (FSANZ) conducted an analysis of the PBDE content of Australian food (FSANZ, 2007). Thirty-five foods in table-ready form were analysed. As foods were prepared, the possible inclusion of adventitious dust during the preparation process was possible. Foods were selected for analysis if they were thought to potentially contain higher concentrations of PBDEs, based on overseas studies, or if they could contribute significantly in the diet due to higher consumption. Composite samples collected for the 22nd Australian Total Diet Survey (ATDS) were analysed for 26 PBDE congeners ranging from tribrominated to decabrominated.

Results were reported for the concentration of each analysed congener in each foodstuff. An overall PBDE intake was determined for each of a range of age groups using the FSANZ DIAMOND (Dietary Modelling of Nutritional Data) model, using food intake data from the 1995 National Nutrition Survey (NNS), and median and 95th percentile intakes were reported. Individual congener intakes were not reported.

Table 10 presents the 95th percentile intakes of individual congeners for different age groups, calculated from the percentage of each congener in each food and the percentage contribution of each food to the PBDE intake for each age group.

Intake PBDEs from food (ng/kg bw/day)								
	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	Σ ₅ PBDE ¹	BDE 209	Total
Male 2-5	2.33	2.02	0.39	0.31	0.18	5.24	1.21	7.18
Female 2-5	2.40	2.17	0.43	0.34	0.21	5.55	1.23	7.53
Male 6- 12	1.96	1.80	0.35	0.28	0.17	4.56	0.91	6.06
Female 6-12	1.66	1.46	0.28	0.23	0.14	3.76	0.82	5.14
Male 13- 18	1.32	1.23	0.23	0.19	0.12	3.09	0.66	4.18
Female 13-18	1.00	0.87	0.17	0.14	0.08	2.25	0.53	3.14
Male 19+	1.13	1.00	0.20	0.16	0.10	2.58	0.49	3.47
Female 19+	0.86	0.75	0.15	0.12	0.07	1.97	0.42	2.71

Table 10. Estimated daily food intakes of PBDEs using FSANZ data

1. Sum of pentaBDE-related congeners BDE-47, -99, -100, -153, -154

Exposure of infants to decaBDE from breast milk

One published Australian study reported the levels of decaBDE in breast milk (Toms et al. 2009). Dust and air sampling was also conducted in the homes of the milk donors in an attempt to determine the factors which influenced the concentrations of PBDEs in the milk. PBDEs were detected in all matrices and the median concentrations of BDE-209 in human milk, air and dust were: 0.3 ng/g lipid; 7.8 pg/m³ air and 291 ng/g dust, respectively. No correlations between milk levels and household dust levels were found. The study also found a slight decrease in PBDE concentrations from 2002-2003 to 2007-2008 but this may be due to sampling and analytical differences (Toms, 2009). Overall, average PBDE concentrations from these individual samples were similar to results from pooled human milk collected in Brisbane in 2002-2003 (Harden et al. 2005), indicating that this may be an efficient, cost-effective strategy of assessing PBDE concentrations on a population basis.

BDE-209 was not included as an analyte in the previous study on PBDEs in Australian breast milk samples (Harden et al. 2005). Table 10 summarises data from a number of international studies that measured PBDEs in human breast milk. The mean BDE-209 concentration in breast milk ranged from 0.12 to 0.92 ng/g lipid wt., and this was generally found to be a minor contribution to Σ PBDEs.

Study Ref.	Study Subject	Sample	BDE-209 (ng/g lipid wt)		∑ PBDEs measured	
			Mean	Range		
Lopez et al. 2004	Women; Mexico	7	0.3	0.1 – 0.6	4.4	
Lopez et al. 2004	Women, Sweden	5	0.4	0.3 – 0.4	5.2	

Table	11.	Levels	of PBDE	congener	BDE-209	in	human	milk
	-		-					

Study Ref.	Study Subject	Sample	BDE-209		Σ PBDEs measured	
			(19/9 11	na wt)		
Env. Working	Mothers from 14	20	0.24	0.08 –		
Group, 2005	states of the USA			1.23		
Schecter et al.	Milk bank and	47	0.92	n.d–	73.9	
2003	clinic samples			8.25		
	collected; USA					
She et al. 2005	First-time	40	0.80	0.048 –	95.6	
	breastfeeding			4.26		
	mothers Pacific					
	Northwest; USA					
Inoue et al. 2006	Lactating mothers	89	0.12	2.61	1.47 (GM)	
	aged 20-43, Japan					
Chao et al. 2006	Healthy women	20	0.27		3.93	
	aged 24-36;					
	Taiwan					
Wu et al. 2007	First-time mothers	46	<dl< td=""><td><dl-< td=""><td>30.2 (median)</td></dl-<></td></dl<>	<dl-< td=""><td>30.2 (median)</td></dl-<>	30.2 (median)	
	>18 yrs, Boston,			10.9		
	USA.					
Vieth et al. 2004	Women 18-41 yrs;	62	0.17	Max	2.23 (mean)	
	Germany			1.00	1.8 (mean)	

7 Hazard Classification

Based on the available evidence decaBDE does not meet the criteria for classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (UNECE, 2009) for the following endpoints:

- Acute Toxicity
- Irritation
- Sensitisation
- Repeat dose
- Genotoxicity
- Carcinogenicity
- Reproductive and developmental effects
- Lactation effects

8 Discussion and Conclusions

Environmental hazard and risk

DecaBDE is persistent in soil, air and sediment, bioaccumulative in some organisms, and it is not acutely toxic to aquatic species or mammals. Chronic developmental neurotoxicity in mammals has been reported. DecaBDE is of significant international concern, and has been listed on Annex A of the Stockholm Convention on Persistent Organic Pollutants, for global elimination.

Despite its persistence, there is considerable evidence that decaBDE is debrominated to lower brominated PBDEs in the abiotic environment, as well as in biota [p12 UNEP/POPS/POPRC.10/10/Add.2]. The less brominated congeners are generally more bioavailable than the parent chemical and are also persistent, bioaccumulative and toxic in the environment. Some of the less brominated PBDE congeners are also listed or are components of mixtures that are listed on Annex A of the Stockholm Convention on Persistent Organic Pollutants.

High levels of decaBDE are found near industrial sites such as plastic and foam manufacturing facilities, e-waste recycling facilities and car dismantling and metal recycling facilities. It has also been detected in a range of biota in Australia, such as bream, flounder, white-bellied sea eagles, and ibis eggs.

DecaBDE is routinely detected in biosolids in Australia. A single application of biosolids is estimated to result in a concentration of $3.3 \mu g/kg$ in soil based on concentrations obtained from a recent WWTP monitoring study (Gallen et al., 2016). While this is below levels expected to cause adverse effects to terrestrial organisms, decaBDE has been shown to be available to worms, and worms living in agricultural soils which have received biosolids applications may act as a source of decaBDE in food webs.

There may be an unacceptable risk to frogs. Frogs are particularly sensitive to decaBDE, with a NOEC of below 1 μ g/L for delayed metamorphosis in African clawed frog tadpoles (UNEP, 2014). Monitoring data from frog habitats in Australia are not available; however, exposure at levels above those which cause adverse effects may occur in areas near point sources of decaBDE where significant emissions are likely, such as plastic and foam manufacturing facilities, e-waste recycling facilities and car dismantling and metal recycling facilities.

Laboratory studies have shown that decaBDE can cause lethal effects in bird embryos, with an LD50 of 2300 µg/kg lipid weight in chicken eggs (UNEP, 2014; Sifleet, 2009). These levels have not been detected in Australian birds but decaBDE has been measured at up to 550 µg/kg lipid weight with a mean value of approximately 270 µg/kg lipid weight in white ibis eggs from urban areas in Brisbane and Sydney (Ridoutt and Kingsford, 2011). The average level of decaBDE levels in white ibis eggs in the field is only 8.5 times lower than the LC50 for chicken eggs, and the maximum value is only 4.2 times less. Though the measured concentrations are lower than the LC50 values, given the demonstrated developmental neurotoxicity and effects on the thyroid system of decaBDE in other organisms, it is possible there is a risk that decaBDE is causing sub-lethal effects to white ibis embryos in the areas where the eggs were collected.

It is noted that extremely high PBDE levels (aggregate concentrations of up to 45900 μ g/kg) have been reported in white-bellied sea eagles in the Homebush Bay area in Sydney (Manning et al, 2008).

Human health risk

Health effects

Based on the available information, human health risks associated with exposure to decaBDE are low. The bioavailability of decaBDE is low by all routes of exposure. The available studies indicated that decaBDE has low acute toxicity, does not produce skin or eye irritation, and is not a skin sensitiser. It also has low systemic and reproductive toxicity following repeated dosing. DecaBDE was determined by IARC to be not classifiable regarding human carcinogenicity.

However, several studies have reported effects in animal modelling data at lower doses than those used in the classical toxicity studies. These include effects on neurodevelopment and sexual development and are similar to effects reported across a much wider range of studies for lower brominated PBDEs, tetra- to hexabrominated PBDEs. For these congeners, the reported effect levels are lower than for BDE-209. For the lower brominated congeners, there are a wide range of studies on enzyme induction and thyroid hormone levels, which suggest that the neurodevelopment and sexual development effects are likely to be related to hypothyroidism following enzyme induction occurring at critical development periods. The doses at which these effects are reported for decaBDE are much higher than the doses of tetra- to hexabrominated PBDEs. In addition, the supporting information on related effects, such as enzyme induction or thyroid hormone concentration effects indicates a much lower potency for decaBDE.

The effects seen in these endpoints for the lower brominated PBDEs are difficult to relate to human risk, because of differences in the composition of the thyroid hormone system between rodents and humans, and due to the different timings in developmental processes. It is noted that the effects on the cholinergic parameters reported in mouse pups following exposure to tetra- to hexabrominated PBDE congeners were not seen in the non-rodent species, mink, treated either during gestation or a 6 week old pups (Bull, 2008). Based on the comparatively high doses at which equivalent effects are seen for decaBDE, the short half-life and low bioavailability of decaBDE, together with the inconsistency of reports on effects and the uncertainties about human applicability of these studies, the risk to humans from exposure to decaBDE at existing levels is very low.

Routes of exposure

An aspect of international biomonitoring studies which has been the subject of specific interest is the variability of concentrations of the PBDEs among members of a single population, with up to two orders of magnitude difference between individuals in some cases (Schecter et al 2003).

For a number of persistent and bioaccumulative chemicals, such as PCBs, food intake has been shown to be the major exposure route, particularly as these chemicals are more widespread in the outdoor environment compared with the indoor environment. PBDEs, on the other hand, are widespread within indoor environments, as shown by a number of dust monitoring studies in Australia and elsewhere. Variability in house dust concentrations, with results spanning several orders of magnitude, has been seen (Wilford et al. 2005). Exposure calculations in Canada based on dust and food levels of PBDEs (Jones-Otazo et al. 2005) indicated that the indoor dust route is the dominant contributor to PBDE intake by a very large factor when the highest indoor PBDE levels were used, but when the lowest indoor PBDE levels were used, but when the lowest indoor PBDE levels were used, food was the main source of human intake.

Recent work has indicated that there are large differences in exposure, particularly to pentaBDE related congeners in household dust (Sjodin et al. 2004; 2006; Jones-Otazo et al. 2005). There is also evidence that human serum and breast milk levels of PBDEs, particularly the lower brominated congeners, are greatly affected by levels of PBDEs in indoor dust (Wu, 2007). North America has much higher levels of the lower brominated PBDE congeners in household dust compared with elsewhere in the world; and higher levels of these congeners were also found in human serum and breast milk in Americans. However, a link between dietary habits and PBDE levels in humans has not been clearly established, and the age variation of PBDE levels in humans (NICNAS 2007) is unlike that for PCBs, which are largely taken in through food, and reach higher levels in older individuals.

Studies that have examined the relationship between household dust levels of PBDEs and the individual biomonitoring results have been restricted to North America (Wu, 2007; Sharp & Lunder 2004), where comparatively high levels of the lower brominated congeners are found in the household dust. Similar results from the UK would be of high value, because this market has regularly shown comparatively low levels of tetra- to hexabrominated congeners but high levels of BDE-209 relative to other countries in dust sampling. Accordingly, such results from the UK would give information as to the contribution of BDE-209 to the human body burden of lower brominated PBDEs, which cannot be obtained when the intake of the lower brominated PBDEs is high. Comparison of body burden information across a number of countries indicates that the levels found in the UK are consistent with the domestic dust concentration of tetra- to hexabrominated congeners (Sjodin, 2006), suggesting little effect of the high intake of BDE-209. Huwe at al. (2008) indicated that blood may be the most reliable matrix for PBDE biomonitoring and found that lower brominated PBDEs tended to distribute equally into lipids, whereas for higher brominated congeners, especially BDE-209, plasma was found to be the best matrix for their detection.

The EU risk assessment of decaBDE (EC, 2002a) attributed the major exposure route to decaBDE for the general public to be via the environment, and stated that direct exposure was likely to be negligible. While the impact on the conclusions of this human health assessment is minor, the recent work on the significance of indoor dust exposure implies that the indoor environment can be considered as a direct source of exposure to decaBDE. Thus, knowledge of which articles are major contributors to this exposure can be used, if necessary, to develop appropriate risk management measures.

Articles as sources of PBDEs

The literature about release of PBDEs from articles is sparse. A study indicated that polyurethane foams containing PBDEs may embrittle with age, physically break down, and release PBDE-containing foam particles into the environment (Hale et al. 2002). Few chamber studies have been undertaken, and the focus is on release via volatilisation rather than breakdown of the matrix or dust formation through blooming (Kemmlein et al., 2003). A study of wipe samples from computers and monitors is difficult to interpret because it does not include control dust wipes to examine whether the measured PBDEs are from the presumed source, or from more remote sources (Toms et al, 2006a). Cars may also act as sources of exposure to PBDEs, and some very high levels of BDE-209 have been reported inside used cars for sale in the USA (Lagalante et al. 2009). The highest levels were above 1000000 ng/g, in 4 of 60 cars sampled; the maximum level of 3570000 ng/g dust (0.36% BDE-209) was found in a car manufactured in the UK.

A large number of studies on PBDEs in household dust, covering a variety of countries, have been published. While a number of the studies have reported household parameters, such as number of pieces of foam furniture, number of computers and type of floor covering, no success was achieved in correlating the household dust levels of the PBDEs with any of the household parameters. Household dust levels were generally interpreted as being representative of the whole house, although the actual area vacuumed to collect the dust and the position of the dust collection point within the house has not always been reported.

The lack of correlation may be due to inhomogeneous distribution of the PBDE contamination within the dust through the house, variability in the actual PBDE content of the selected article; for example, certain polyurethane foams may contain pentaBDE while other foams may not be flame retarded or contain alternative flame retardants, or the presence of other more major determinants which were not taken into account in the analyses. The study reported in Appendix 3 demonstrates this spatial inhomogeneity. Allen et al. (2008) showed that there was inter-room variability, although not large temporal variability, and that the contents of the household vacuum bag did not correlate well with researcher-collected dust.

Human risks associated with decaBDE debromination

The major area of uncertainty is associated with the possibility that release of decaBDE to the environment may be followed by formation of different PBDE congeners by a debromination process, and exposure of humans to these potentially more bioaccumulative and toxic congeners. The production of lower brominated PBDEs by the reductive debromination of BDE-209 has been widely discussed, and commonly postulated as a source of lower brominated PBDEs seen in environmental and biomonitoring studies. Assessment of human health hazard data for commercial octaBDE as a surrogate for the hexa- to nonabrominated congeners, and individual congeners in this range, and the assessment of the tetra- to hexabrominated congener range (NICNAS, 2007) indicate that the common congeners in these bromination ranges are all likely to be more bioavailable, bioaccumulative and toxic than decaBDE. A similar conclusion may be drawn from the differences identified between the results of equivalent toxicity studies for high purity decaBDE and older lower purity grades of decaBDE reported in the EU RAR (EC 2002a).

Debromination has been seen in laboratory studies of photolytic and metabolic decomposition of BDE-209; however, the applicability of these results to real environmental systems is unclear (Stapleton, 2006). The chemical principles associated with the debromination of decaBDE are discussed in Appendix 2. While debromination of decaBDE can be observed in the laboratory under a range of conditions (such as thermal, photolytic, electrochemical or biological), new literature indicates that there is a growing evidence that reductive debromination occurs in the environment through several processes including through light, anaerobic sediments and in biota (Environment Canada, 2010). Determination of the biological relevance requires confirmation from environmental monitoring studies.

A limitation of almost all of the wide range of existing environmental and biomonitoring studies is that the study design does not allow for distinction between congeners produced by debromination of decaBDE and congeners directly released into the environment by use of lower brominated commercial PBDE products. This is because a fixed list of PBDE analytes is normally examined, and this is dominated by the congeners which are expected to be observed, such as BDE-47 and BDE-99, which are major components of commercial pentaBDE.

Based on consideration of the chemistry of debromination (Appendix 1), it is in theory possible to distinguish the source of such congeners if the ratio of the congeners in the environment is very different to that in the commercial product. In practice, in the case of BDE-47 and BDE-99, this cannot be used as a measure because it is well documented that biomonitoring shows a large change in ratio compared with abiotic monitoring, and this can be related to differential bioaccumulation of the two congeners. In addition, to clearly see a significant change in ratios of commonly found congeners above a background arising from the other lower brominated commercial products, a very large difference would be required.

It is clear from the chemistry information provided in Appendix 2 that the distribution of congeners in any mixture arising from a debromination process is likely to be much more complex than the commercial mixtures themselves, and the mixture will include contributions from congeners which are minor or absent in the commercial mixtures, described as "oddball congeners" by La Guardia (Betts, 2008). A clear example is the observation of the octabrominated BDE-202, which may be considered to be derived from p,p'-debromination of BDE-209, in studies in carp and rainbow trout (Stapleton, 2006). BDE-202 has not been detected in commercial octaBDE products (La Guardia, 2006) and; therefore its observation, regardless of quantitative considerations, is evidence that a debromination process, starting from either BDE-209 or BDE-208 (the only higher brominated congeners structurally able to produce BDE-202) has occurred in this system.

While there is some evidence that certain nona- and octabrominated congeners may be produced under realistic conditions from debromination of BDE-209, the evidence for production of lower brominated congeners in the tetra- to hexabrominated range is lacking. La Guardia (2006) reported at least trace amounts of 21 different congeners with four to six bromines across four different commercial pentaBDE and octaBDE formulations. However, structural considerations indicate that 130 congeners are possible across these ranges of bromination. This leaves wide potential for marker congeners, not found at above trace levels in the commercial products, to be identified to indicate the outcome of possible debromination processes of decaBDE.

At the time these studies were conducted, there was a lack of analytical standards for the majority of these congeners. In the absence of an analytical standard for an individual congener, it is not possible to unambiguously identify a congener. In simpler mixtures, such as the commercial mixtures, it is possible to infer the presence of additional congeners of a particular bromination range. However, in complex environmental monitoring samples, there is uncertainty about unidentified peaks definitely arising from the presence of a PBDE congener without these standards.

Evidence in the form of marker congeners detected in abiotic monitoring or biomonitoring studies could form compelling evidence that a debromination process has occurred, and identification of debromination products in the tetra- to hexabrominated range, while not unambiguously implicating decaBDE as the source, would indicate the possibility of a debromination cascade which could lead from decaBDE to congeners in the most toxic and bioaccumulative bromination range.

Comments in literature suggesting that observations of common congeners such as BDE-47 and BDE-99 may arise as a result of debromination processes must be considered speculative in the absence of firm evidence that the entire spectrum of possible products of a debromination process is found. As an example, Bezares-Cruz et al (2004) identified BDE-47 and BDE-99 among photolytic breakdown products of BDE-209 in organic solvents. However, inspection of the GC chromatograms indicated that these two congeners were not

the dominant tetra- and pentabrominated congeners present. For example, BDE-47 was present in approximately the same concentration as BDE-49 in the photolysis mixture. If the other components of the complex mixture cannot be found (in equivalent proportions to those in the laboratory study) in a sample containing BDE-47, the likelihood is that the source of the BDE-47 is the commercial pentaBDE product, where BDE-47 highly dominates all other tetrabrominated congeners.

In laboratory studies using BDE-209, it may be possible on some occasions to determine from mass balances of specific congeners, even those which are more commonly found as impurities, such as nonabrominated congeners, that debromination is likely to have occurred. However in less controlled situations, for example in biomonitoring studies, the lack of knowledge of trace impurity levels, relative bioavailability of different congeners and relative retention times for different congeners in tissues makes it impossible to unambiguously show that congeners have arisen due to debromination of BDE-209. An exception occurs when congeners which would not be expected on any other basis are found as part of the study, for example BDE-202.

There is currently insufficient evidence that reductive debromination of decaBDE in the environment or in the human body actually results in human exposure to octa- and nonabrominated congeners. Humans are exposed to congeners in these bromination ranges due to use of decaBDE through preferential absorption and retention of impurities in decaBDE, as well as potentially through debromination. No evidence is available to clarify whether debromination of decaBDE to form congeners with less than eight bromine atoms leads to exposure of humans to congeners in these lower bromination ranges. It is worth noting that the high BDE-209 levels in indoor dust in the UK were not reflected in elevated levels of the lower PBDE congeners in human serum and breast milk in the UK compared with the remainder of Europe (Sjodin, 2006). This suggests that internal debromination of decaBDE is not a significant risk factor for levels of lower brominated congeners compared with direct exposure to them.

Appendix 1 – Nomenclature for PBDE congeners

Standard nomenclature system for PBDEs as used in this document. Specific congeners mentioned in text are highlighted in bold.

Monobrominated	
BDE-1	2-bromodiphenyl ether
BDE-2	3-bromodiphenyl ether
BDE-3	4-bromodiphenyl ether

Dibrominated	
BDE-4	2,2'-dibromodiphenyl ether
BDE-5	2,3-dibromodiphenyl ether
BDE-6	2,3'-dibromodiphenyl ether
BDE-7	2,4-dibromodiphenyl ether
BDE-8	2,4'-dibromodiphenyl ether
BDE-9	2,5-dibromodiphenyl ether
BDE-10	2,6-dibromodiphenyl ether
BDE-11	3,3'-dibromodiphenyl ether
BDE-12	3,4-dibromodiphenyl ether
BDE-13	3,4'-dibromodiphenyl ether
BDE-14	3,5-dibromodiphenyl ether
BDE-15	4,4'-dibromodiphenyl ether

Tribrominated	
BDE-16	2,2',3-tribromodiphenyl ether
BDE-17	2,2',4-tribromodiphenyl ether
BDE-18	2,2',5-tribromodiphenyl ether
BDE-19	2,2',6-tribromodiphenyl ether
BDE-20	2,3,3'-tribromodiphenyl ether
BDE-21	2,3,4-tribromodiphenyl ether
BDE-22	2,3,4'-tribromodiphenyl ether
BDE-23	2,3,5-tribromodiphenyl ether
BDE-24	2,3,6-tribromodiphenyl ether
BDE-25	2,3',4-tribromodiphenyl ether
BDE-26	2,3',5-tribromodiphenyl ether
BDE-27	2,3',6-tribromodiphenyl ether

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Tribrominated	
BDE-28	2,4,4'-tribromodiphenyl ether
BDE-29	2,4,5-tribromodiphenyl ether
BDE-30	2,4,6-tribromodiphenyl ether
BDE-31	2,4',5-tribromodiphenyl ether
BDE-32	2,4',6-tribromodiphenyl ether
BDE-33	2',3,4-tribromodiphenyl ether
BDE-34	2',3,5-tribromodiphenyl ether
BDE-35	3,3',4-tribromodiphenyl ether
BDE-36	3,3',5-tribromodiphenyl ether
BDE-37	3,4,4'-tribromodiphenyl ether
BDE-38	3,4,5-tribromodiphenyl ether
BDE-39	3,4',5-tribromodiphenyl ether

Tetrabrominated	
BDE-40	2,2',3,3'-tetrabromodiphenyl ether
BDE-41	2,2',3,4-tetrabromodiphenyl ether
BDE-42	2,2',3,4'-tetrabromodiphenyl ether
BDE-43	2,2',3,5-tetrabromodiphenyl ether
BDE-44	2,2',3,5'-tetrabromodiphenyl ether
BDE-45	2,2',3,6-tetrabromodiphenyl ether
BDE-46	2,2',3,6'-tetrabromodiphenyl ether
BDE-47	2,2',4,4'-tetrabromodiphenyl ether
BDE-48	2,2',4,5-tetrabromodiphenyl ether
BDE-49	2,2',4,5'-tetrabromodiphenyl ether
BDE-50	2,2',4,6-tetrabromodiphenyl ether
BDE-51	2,2',4,6'-tetrabromodiphenyl ether
BDE-52	2,2',5,5'-tetrabromodiphenyl ether
BDE-53	2,2',5,6'-tetrabromodiphenyl ether
BDE-54	2,2',6,6'-tetrabromodiphenyl ether
BDE-55	2,3,3',4-tetrabromodiphenyl ether
BDE-56	2,3,3',4'-tetrabromodiphenyl ether
BDE-57	2,3,3',5-tetrabromodiphenyl ether
BDE-58	2,3,3',5'-tetrabromodiphenyl ether
BDE-59	2,3,3',6-tetrabromodiphenyl ether

Tetrabrominated	
BDE-60	2,3,4,4'-tetrabromodiphenyl ether
BDE-61	2,3,4,5-tetrabromodiphenyl ether
BDE-62	2,3,4,6-tetrabromodiphenyl ether
BDE-63	2,3,4',5-tetrabromodiphenyl ether
BDE-64	2,3,4',6-tetrabromodiphenyl ether
BDE-65	2,3,5,6-tetrabromodiphenyl ether
BDE-66	2,3',4,4'-tetrabromodiphenyl ether
BDE-67	2,3',4,5-tetrabromodiphenyl ether
BDE-68	2,3',4,5'-tetrabromodiphenyl ether
BDE-69	2,3',4,6-tetrabromodiphenyl ether
BDE-70	2,3',4',5-tetrabromodiphenyl ether
BDE-71	2,3',4',6-tetrabromodiphenyl ether
BDE-72	2,3',5,5'-tetrabromodiphenyl ether
BDE-73	2,3',5',6-tetrabromodiphenyl ether
BDE-74	2,4,4',5-tetrabromodiphenyl ether
BDE-75	2,4,4',6-tetrabromodiphenyl ether
BDE-76	2',3,4,5-tetrabromodiphenyl ether
BDE-77	3,3',4,4'-tetrabromodiphenyl ether
BDE-78	3,3',4,5-tetrabromodiphenyl ether
BDE-79	3,3',4,5'-tetrabromodiphenyl ether
BDE-80	3,3',5,5'-tetrabromodiphenyl ether
BDE-81	3,4,4',5-tetrabromodiphenyl ether

Pentabrominated	
BDE-82	2,2',3,3',4-pentabromodiphenyl ether
BDE-83	2,2',3,3',5-pentabromodiphenyl ether
BDE-84	2,2',3,3',6-pentabromodiphenyl ether
BDE-85	2,2',3,4,4'-pentabromodiphenyl ether
BDE-86	2,2',3,4,5-pentabromodiphenyl ether
BDE-87	2,2',3,4,5'-pentabromodiphenyl ether
BDE-88	2,2',3,4,6-pentabromodiphenyl ether
BDE-89	2,2',3,4,6'-pentabromodiphenyl ether
BDE-90	2,2',3,4',5-pentabromodiphenyl ether
BDE-91	2,2',3,4',6-pentabromodiphenyl ether

Pentabrominated		
BDE-92	2,2',3,5,5'-pentabromodiphenyl ether	
BDE-93	2,2',3,5,6-pentabromodiphenyl ether	
BDE-94	2,2',3,5,6'-pentabromodiphenyl ether	
BDE-95	2,2',3,5',6-pentabromodiphenyl ether	
BDE-96	2,2',3,6,6'-pentabromodiphenyl ether	
BDE-97	2,2',3',4,5-pentabromodiphenyl ether	
BDE-98	2,2',3',4,6-pentabromodiphenyl ether	
BDE-99	2,2',4,4',5-pentabromodiphenyl ether	
BDE-100	2,2',4,4',6-pentabromodiphenyl ether	
BDE-101	2,2',4,5,5'-pentabromodiphenyl ether	
BDE-102	2,2',4,5,6'-pentabromodiphenyl ether	
BDE-103	2,2',4,5',6-pentabromodiphenyl ether	
BDE-104	2,2',4,6,6'-pentabromodiphenyl ether	
BDE-105	2,3,3',4,4'-pentabromodiphenyl ether	
BDE-106	2,3,3',4,5-pentabromodiphenyl ether	
BDE-107	2,3,3',4',5-pentabromodiphenyl ether	
BDE-108	2,3,3',4,5'-pentabromodiphenyl ether	
BDE-109	2,3,3',4,6-pentabromodiphenyl ether	
BDE-110	2,3,3',4',6-pentabromodiphenyl ether	
BDE-111	2,3,3',5,5'-pentabromodiphenyl ether	
BDE-112	2,3,3',5,6-pentabromodiphenyl ether	
BDE-113	2,3,3',5',6-pentabromodiphenyl ether	
BDE-114	2,3,4,4',5-pentabromodiphenyl ether	
BDE-115	2,3,4,4',6-pentabromodiphenyl ether	
BDE-116	2,3,4,5,6-pentabromodiphenyl ether	
BDE-117	2,3,4',5,6-pentabromodiphenyl ether	
BDE-118	2,3',4,4',5-pentabromodiphenyl ether	
BDE-119	2,3',4,4',6-pentabromodiphenyl ether	
BDE-120	2,3',4,5,5'-pentabromodiphenyl ether	
BDE-121	2,3',4,5',6-pentabromodiphenyl ether	
BDE-122	2',3,3',4,5-pentabromodiphenyl ether	
BDE-123	2',3,4,4',5-pentabromodiphenyl ether	
BDE-124	2',3,4,5,5'-pentabromodiphenyl ether	
BDE-125	2',3,4,5,6'-pentabromodiphenyl ether	

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Pentabrominated	
BDE-126	3,3',4,4',5-pentabromodiphenyl ether
BDE-127	3,3',4,5,5'-pentabromodiphenyl ether

Hexabrominated	
BDE-128	2,2',3,3',4,4'-hexabromodiphenyl ether
BDE-129	2,2'3,3',4,5-hexabromodiphenyl ether
BDE-130	2,2',3,3',4,5'-hexabromodiphenyl ether
BDE-131	2,2',3,3',4,6-hexabromodiphenyl ether
BDE-132	2,2',3,3',4,6'-hexabromodiphenyl ether
BDE-133	2,2',3,3',5,5'-hexabromodiphenyl ether
BDE-134	2,2',3,3',5,6-hexabromodiphenyl ether
BDE-135	2,2',3,3',5,6'-hexabromodiphenyl ether
BDE-136	2,2',3,3',6,6'-hexabromodiphenyl ether
BDE-137	2,2',3,4,4',5-hexabromodiphenyl ether
BDE-138	2,2',3,4,4',5'-hexabromodiphenyl ether
BDE-139	2,2',3,4,4',6-hexabromodiphenyl ether
BDE-140	2,2',3,4,4',6'-hexabromodiphenyl ether
BDE-141	2,2',3,4,5,5'-hexabromodiphenyl ether
BDE-142	2,2',3,4,5,6-hexabromodiphenyl ether
BDE-143	2,2',3,4,5,6'-hexabromodiphenyl ether
BDE-144	2,2',3,4,5',6-hexabromodiphenyl ether
BDE-145	2,2',3,4,6,6'-hexabromodiphenyl ether
BDE-146	2,2',3,4',5,5'-hexabromodiphenyl ether
BDE-147	2,2',3,4',5,6-hexabromodiphenyl ether
BDE-148	2,2',3,4',5,6'-hexabromodiphenyl ether
BDE-149	2,2',3,4',5',6-hexabromodiphenyl ether
BDE-150	2,2',3,4',6,6'-hexabromodiphenyl ether
BDE-151	2,2',3,5,5',6-hexabromodiphenyl ether
BDE-152	2,2',3,5,6,6'-hexabromodiphenyl ether
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether
BDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether
BDE-155	2,2',4,4',6,6'-hexabromodiphenyl ether
BDE-156	2,3,3',4,4',5-hexabromodiphenyl ether
BDE-157	2,3,3',4,4',5'-hexabromodiphenyl ether

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Hexabrominated	
BDE-158	2,3,3',4,4',6-hexabromodiphenyl ether
BDE-159	2,3,3',4,5,5'-hexabromodiphenyl ether
BDE-160	2,3,3',4,5,6-hexabromodiphenyl ether
BDE-161	2,3,3',4,5',6-hexabromodiphenyl ether
BDE-162	2,3,3',4',5,5'-hexabromodiphenyl ether
BDE-163	2,3,3',4',5,6-hexabromodiphenyl ether
BDE-164	2,3,3',4',5',6-hexabromodiphenyl ether
BDE-165	2,3,3',5,5',6-hexabromodiphenyl ether
BDE-166	2,3,4,4',5,6-hexabromodiphenyl ether
BDE-167	2,3',4,4',5,5'-hexabromodiphenyl ether
BDE-168	2,3',4,4',5',6-hexabromodiphenyl ether
BDE-169	3,3',4,4',5,5'-hexabromodiphenyl ether

Heptabrominated	
BDE-170	2,2',3,3',4,4',5-heptabromodiphenyl ether
BDE-171	2,2',3,3',4,4',6-heptabromodiphenyl ether
BDE-172	2,2',3,3',4,5,5'-heptabromodiphenyl ether
BDE-173	2,2',3,3',4,5,6-heptabromodiphenyl ether
BDE-174	2,2',3,3',4,5,6'-heptabromodiphenyl ether
BDE-175	2,2',3,3',4,5',6-heptabromodiphenyl ether
BDE-176	2,2',3,3',4,6,6'-heptabromodiphenyl ether
BDE-177	2,2',3,3',4',5,6-heptabromodiphenyl ether
BDE-178	2,2',3,3',5,5',6-heptabromodiphenyl ether
BDE-179	2,2',3,3',5,6,6'-heptabromodiphenyl ether
BDE-180	2,2',3,4,4',5,5'-heptabromodiphenyl ether
BDE-181	2,2',3,4,4',5,6-heptabromodiphenyl ether
BDE-182	2,2',3,4,4',5,6'-heptabromodiphenyl ether
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether
BDE-184	2,2',3,4,4',6,6'-heptabromodiphenyl ether
BDE-185	2,2',3,4,5,5',6-heptabromodiphenyl ether
BDE-186	2,2',3,4,5,6,6'-heptabromodiphenyl ether
BDE-187	2,2',3,4',5,5',6-heptabromodiphenyl ether
BDE-188	2,2',3,4',5,6,6'-heptabromodiphenyl ether
BDE-189	2,3,3',4,4',5,5'-heptabromodiphenyl ether

Heptabrominated	
BDE-190	2,3,3',4,4',5,6-heptabromodiphenyl ether
BDE-191	2,3,3',4,4',5',6-heptabromodiphenyl ether
BDE-192	2,3,3',4,5,5',6-heptabromodiphenyl ether
BDE-193	2,3,3',4',5,5',6-heptabromodiphenyl ether

Octobrominated	
BDE-194	2,2',3,3',4,4',5,5'-octabromodiphenyl ether
BDE-195	2,2',3,3',4,4',5,6-octabromodiphenyl ether
BDE-196	2,2',3,3',4,4',5',6-octabromodiphenyl ether
BDE-197	2,2',3,3',4,4',6,6'-octabromodiphenyl ether
BDE-198	2,2',3,3',4,5,5',6-octabromodiphenyl ether
BDE-199	2,2',3,3',4,5,5',6'-octabromodiphenyl ether
BDE-200	2,2',3,3',4,5,6,6'-octabromodiphenyl ether
BDE-201	2,2',3,3',4,5',6,6'-octabromodiphenyl ether
BDE-202	2,2',3,3',5,5',6,6'-octabromodiphenyl ether
BDE-203	2,2',3,4,4',5,5',6-octabromodiphenyl ether
BDE-204	2,2',3,4,4',5,6,6'-octabromodiphenyl ether
BDE-205	2,3,3',4,4',5,5',6-octabromodiphenyl ether

Nonabrominated	
BDE-206	2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether
BDE-207	2,2',3,3',4,4',5,6,6'-nonabromodiphenyl ether
BDE-208	2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether

Decabrominated	
BDE-209	decabromodiphenyl ether

Appendix 2 – Chemistry of PBDE bromination and debromination reactions

Introduction

This appendix addresses the chemical principles that govern the formation (bromination) reactions of the commercial PBDE products and also an overview of what is known of the chemical principles that apply for debromination reactions. The chemical principles indicate that a specific group of congeners will dominate the formation reaction (described below), and these congeners are formed under kinetic control of the geometry of the reaction. Therefore, debromination reactions are unlikely to reproduce the same congener distribution seen in the commercial products because these are not necessarily the most thermodynamically stable congeners, and it is unlikely that kinetic considerations will lead to similar product mixtures for debromination reactions compared with bromination reactions, due to the very different mechanisms under consideration.

The chemical principles support the observations where the product mixtures seen under debrominating conditions contain different congeners and congener ratios compared with the two commercial products developed by bromination reactions, pentaBDE and octaBDE.

Formation reactions

The production of PBDEs utilises electrophilic aromatic substitution starting with diphenyl ether, and using Br₂ and a Lewis acid catalytic species such as FeBr₃. The isomer selectivity of the aromatic substitution reactions is very widely known Substituents on a benzene ring are categorised according to their "directing" properties as either ortho,para (electron donating) directors or meta (electron withdrawing) directors; also as to whether they activate or deactivate the benzene ring towards electrophilic aromatic substitution relative to unsubstituted benzene. The information on the basic organic chemistry of the electrophilic aromatic substitution process is obtained from Morrison & Boyd (1992).

The directing and activating properties are generally linked, with ortho, para directors commonly also activating the benzene ring and Meta directors deactivating the ring. This occurs because the main effect of the substituent is on the relative stability of the reaction intermediate for reaction at the ortho or para position; deactivating substituents deactivate the ortho and para positions more than they do the meta positions. As the directing effect relates to the stability of the reaction intermediate, the control of the reaction geometry derives from the different rates of formation of the possible products (kinetic control), and is not related to the relative thermodynamic stability of the possible isomers. Due to the large activation energy required for the substitution reaction or its reverse reaction, rearrangement of the products to give the thermodynamically favoured congeners following substitution does not normally occur apart from the special case of sulfonation reactions.

The final product mix formed by a series of electrophilic aromatic substitution reactions depends on the directing properties of the substituents, in a stepwise manner. Therefore, if additional substitution reactions occur on an initially monosubstituted benzene ring, the position in which the second additional substituent is most likely to be found depends not only on the directing and activation properties of the substituent introduced in the first reaction. The position of substitution will also be influenced by steric factors; for example a bulky

substituent with (ortho,para) directing properties will give rise to a predominantly parasubstituted reaction product, due to the steric crowding at the ortho position.

In the case of diphenyl ether, the ether group is categorised as moderately activating and (ortho,para) directing. The phenyl ether substituent is quite bulky; therefore, the most probable substitution reaction will occur at the para (4-) position, with ortho substitution (2-) occurring at a much lower yield. A bromine atom deactivates the benzene ring; therefore, a second bromine substitution is most likely to occur on the less substituted ring, again in the para position (4'-). The deactivation of the more substituted ring continues through the sequence of bromination reactions, and results in all major congeners being equally brominated on each ring (in the case of even bromine numbers) or differing in only one bromine atom (odd bromine numbers).

Halogen substituents are an anomaly within the electrophilic aromatic substitution rules, in that they are deactivating, but are also ortho,para directing. In the case of a diphenyl ether ring with a single ortho or para substituent, the bromine atom will tend to direct substitution to the positions meta to the ether bridge (3- or 5-), which are ortho or para to the bromine substituent, while the ether group will direct substitution to the ortho or para positions relative to the ether bridge (2-, 4-, or 6-), as shown below in the case of BDE-15. Arrows indicate the directing properties of the substituent, and the thickness of the arrow indicates the relative strength of the directing effect.



The relative strengths of these effects can be seen by examination of the congener distribution in commercial pentaBDE. La Guardia et al (2006) identified only three tetrabrominated congeners at above their limits of quantification in the two pentaBDE products DE-71 and 70-5DE. Each of the three congeners, BDE-47, 49 and 66 (or 42), have at least one 2,4- substituted ring, while the highly dominant BDE-47 has two 2,4- substituted rings. In DE-71 and 70-5DE, 98.4% and 99.3% of the dibrominated rings in the tetrabrominated congeners are 2,4- substituted, respectively. The second ring in the minor congeners (BDE-49 and BDE-66 or 42) includes one bromine in a meta position relative to the ether bridge; di-ortho substitution does not occur in these minor congeners, showing the importance of the steric effects in promoting para substitution. The dominant pentabrominated and tribrominated congeners also have a disubstituted ring with a 2,4-substitution pattern.

The dominant disubstitution pattern in PBDEs produced by electrophilic aromatic substitution is; therefore, the 2,4- pattern showing the influence of the directing ability and steric properties of the ether group. Addition of a third bromine atom to the 2,4- disubstituted ring is again influenced by the directing properties of the ether group and of the bromine atoms. The two bromine atoms both direct substitution to the 3- or 5- positions, while the ether group directs substitution to the 6- position, as illustrated below for BDE-47.



Examination of the patterns of trisubstitution in commercial pentaBDE can again give insight into which of these are more important. The three most important pentabrominated congeners include a 2,4- disubstituted ring in combination with each of the possible trisubstitution patterns based on bromination of a 2,4- disubstituted ring. These are BDE-85 (2,3,4-), BDE-99 (2,4,5-) and BDE-100 (2,4,6-). In DE-71, La Guardia et al (2006) found the proportions to be 3.0%, 48.6%, and 13.1% (based on the whole formulation) respectively. This indicates that the directing power of two bromines is higher than that of the ether group, favouring 5- over 6- substitution, but the steric difficulties associated with adding the third bromine between two existing substituents reduce the likelihood of 3- substitution. The relative importance of 2,4,5- trisubstitution compared with 2,4,6- trisubstitution is also seen in the hexabrominated series BDE-153, 154 and 155.

Detailed analysis of the addition of a fourth bromine atom is difficult, based on the presence of more than one major starting substitution pattern. However, there are only three possible tetrasubstitution patterns, with the single hydrogen in either an ortho, meta or para position. As all major starting substitution patterns include a bromine at the para position, only the two patterns of 2,3,4,5- and 2,3,4,6- tetrasubstitution are expected to occur as a result of the direct bromination of diphenyl ether. Only a single pentasubstitution pattern is possible. Examination of the nonasubstituted impurities in commercial decaBDE formulations shows that the 2,3,4,5- tetrasubstitution pattern in BDE-206 appears to be preferred over the 2,3,4,6- tetrasubstitution in BDE-207, although the results for the commercial octaBDE formulations appear to show a reverse preference. The presence of BDE-208, with one missing para bromine, suggests that other factors, such as thermal decomposition of BDE-209 during formation, may also influence the product distribution for these more labile higher brominated congeners.

Debromination reactions

While the mechanism of the bromination reactions to form PBDE congeners from diphenyl ether is extremely well characterised, the debromination reactions, whether thermal, photolytic, reductive (eg using zero valent iron) or biological, are not well studied. As the full reaction pathways are not known, no predictions can be made as to the kinetic factors associated with the stereochemistry, or the relative importance of kinetic or thermodynamic factors. Thermodynamic factors are expected to favour debromination at ortho positions, as stability of PBDE congeners for a given degree of bromination is reduced with increasing ortho substitution as indicated by theoretical calculations (Hu et al, 2005; Grabda et al, 2007).

As the commonly found congeners in environmental and biomonitoring studies are those that also dominate the commercial products, it is important to consider whether it is likely that debromination reactions commencing with highly brominated PBDEs, particularly BDE-209, are likely to produce similar congeners to those produced during the bromination reactions. The lack of mechanistic information for the debromination reactions makes *a priori* prediction very difficult; however, it is not possible to attribute exceptional stability to these

common congeners based on the calculations showing that other congeners have higher stability. For example, BDE-66 and 77 are both calculated to be significantly more stable than BDE-47 (Hu et al, 2005). The dominance of a less thermodynamically stable congener in the commercial mixture pentaBDE further indicates that rearrangement to form the most stable congeners does not occur.

While thermal degradation of BDE-209 is reported to be a concern under GC measurement conditions, little information is available on the extent of thermal breakdown or its products. More information is available on other breakdown routes, including metabolic debromination, in mammals, fish and microorganisms, photolytic debromination and chemical reduction. Each of the latter debromination pathways have been shown to be possible under specific laboratory conditions, but the confirmation that any of these are important in the environment has not been established. In particular, the laboratory experiments using specific microbial cultures, photolysis in organic solvents, and chemical reduction have given highly complex mixtures of products that may contain particular congeners found in the environment, but always in conjunction with many more congeners that are not known from environmental samples. This implies that the debromination reactions occur via pathways that do not replicate the congener mixtures that are found in the commercial products.

The complexity of the product mixtures gives some insight into the different mechanisms involved in these reactions, and it also provides an opportunity to establish unambiguously if a particular sample includes congeners that are likely to derive from debromination of BDE-209.

One example of such a congener is the octabrominated BDE-202, which has been identified in studies in two species of fish (Stapleton et al, 2006). This congener has not been identified in any studies of the congener distribution in the commercial mixtures and, as it has no bromine atoms in para positions (favoured in the formation reactions for the commercial mixtures), it is unlikely that even traces would be present in the commercial products. Excluding the possibility of rearrangement reactions, the only route for formation of this congener is debromination of the very minor nonabrominated congener BDE-208. Further, the formation of BDE-208 by microbial debromination of BDE-209 has been demonstrated by shifts in nonabrominated congener ratios (Gerecke et al, 2005). Based on the results of the theoretical studies indicating that highly ortho substituted congeners are not the most stable congeners for a given degree of bromination (Hu et al, 2005; Grabda et al, 2007), formation of BDE-202 by rearrangement is not likely. This indicates that para debromination is a major metabolic reaction of BDE-209, potentially leading to a suite of debrominated congeners lacking one or more para bromines.

Electrochemical reduction, chemical reduction using elemental iron or sulphides and photolysis in organic solvents have been shown to debrominate BDE-209 to provide very complex mixtures of products. BDE-99 and 47 have been shown to be products in each of these reactions (Konstantinov, 2008; Keum and Li, 2005; Bezares-Cruz et al, 2004), but not dominant products. Konstantinov (2008) found preferential removal of meta and para bromines in electrochemical reduction. Keum and Li (2005) identified that 112 different PBDE congeners were formed in the reaction with elemental iron, and the chromatograms shown in the paper indicate that approximately 17 pentabrominated congeners were formed apart from BDE-99 and 100. Following photolysis of BDE-209 in hexane, Bezares-Cruz et al (2004) found 43 different congeners, of which only a small proportion could be identified by comparison with known standards. This included up to 11 different hexabrominated

congeners. These findings, which include many congeners not found in commercial mixtures and for which standards are not available, indicate that the mechanisms for these reactions are indiscriminate compared with the bromination reactions and lead to complex and potentially identifiable product mixtures.

Again, opportunities for identifying the contribution of debromination of higher congeners to the overall environmental PBDE mixture can be identified. Bezares-Cruz et al (2004) identified a number of tetrabrominated congeners following exposure of BDE-209 in hexane to sunlight, with the chromatogram at 27.8 h clearly showing three congeners with approximately equal concentrations; BDE-47, 49 and 66, which are congeners often identified in the environment due to their presence in commercial pentaBDE and the ready availability of standards. Accordingly, the ratios of these congeners in abiotic environmental samples may be able to be used to indicate if a similar reaction has occurred in the environment, even though all are likely to be present due to the contribution of pentaBDE. It should be noted that none of these congeners were found in a more environmentally relevant photolysis study where the BDE-209 was added to dry soil or moistened sediment (Soderstrom, 2004).

Appendix 3: Determination of Sources of PBDE in Australian Homes

NICNAS commissioned a study of the distribution of PBDEs in household dust which commenced with identification of all potential sources with the house by determination of bromine using handheld X-Ray Fluorescence (XRF) equipment, with the objective of more closely linking the concentrations of the PBDEs in dust to the proximity of PBDE containing sources.

In this study four major scenarios were targeted:

- a) DecaBDE used in back casing of television sets;
- b) PentaBDE used in furniture foams;
- c) DecaBDE in monitor back casings and pentaBDE in circuit boards in home offices; and
- d) DecaBDE used in flame retarded textiles.

These scenarios were chosen based on their correspondence to major uses of the flame retardants, the variety of possible release mechanisms, including blooming, physical breakdown of the matrix, and volatilisation and, in the case of the computer circuit boards and polyurethane foams, literature where such release had been directly or indirectly measured. Other likely sources of PBDEs in the houses were also checked using the XRF unit, to determine if likely interferences would be present in the vicinity of the chosen scenarios.

Following calibration for the major sample types, the hand held XRF unit was used to determine a semiquantitative level of bromine in each of the articles associated with the major scenarios within 22 houses in and around Adelaide, South Australia. Bromine measurements were conducted on accessible parts of the articles. Readings varied between not detected to >100000 ppm (>10%) in different hard plastic articles that were examined. The instrument calibration for bromine in hard plastics indicated that the nominal and actual levels are likely to be similar. Foams and fabrics required different calibration, and the results could not be directly compared between hard plastics and foams or fabrics. From the results of the instrument calibration for fabrics, and considering the non-optimal sampling geometry for foams and fabrics, it is likely that the actual level of bromine is much greater than the nominal level for these substrates. Variability in bromine levels was also seen for foams and fabrics.

The measured bromine content for each type of article varied widely. For each type of article analysed apart from the back panels of television sets, the majority of results were either non-detected bromine, or detection of <1% bromine. Among the electrical items, such as television sets, small electronics and miscellaneous items, much lower numbers of items showed 1-5% bromine than >5% bromine. Given that the normal loadings for a BFR to be effective are >5% (IPCS, 1994), this is expected. Reasons for the observation of low level bromine signal may include "breakthrough" readings resulting from the X-ray beam reaching BFRs in inaccessible parts at a greater depth within the article, eg diffuse X-ray fluorescence from BFRs (commonly TBBPA) in circuit boards within the article, or other bromine-containing contaminants such as sea spray. For foam and fabrics, nominal readings >0.1% were considered to be likely to indicate the presence of a BFR.

The presence of a bromine signal cannot necessarily be taken to indicate that a certain PBDE mixture is present. A variety of BFRs may be in use and, particularly at lower bromine levels in the low ppm range, other sources of bromine may contribute. The higher results, >1%, are taken to be indicative of the presence of a BFR. Among the major scenarios identified above,

it is known that decaBDE is the dominant BFR used in HIPS back casings of CRT televisions, and likely also in CRT monitors, whereas a high bromine level determined by XRF is a good indicator of the presence of decaBDE. The other scenarios are less certain, as alternative flame retardants may be present in furniture foams, textile backcoatings, and circuit boards. Home offices are also characterised by regular updating of equipment, and the contribution of historical contents need to be considered in this case. In particular, the type of monitor in common use has changed from CRT to LCD, and these may differ in the use of flame retardants.

As these PBDEs have also been reported to be used in other types of products, the next step was to examine the "second list" of articles for the presence of PBDEs. These included electrical hardware, such as switches, cables and powerboards, casings of small electronic equipment, plastic parts of whitegoods, and blinds. These were examined to obtain information about the prevalence of PBDEs in these articles and also to determine any likely interfering sources of PBDEs in dust within a room.

While the analysis of the results of this study was underway, a study of the prevalence of bromine detection in articles in the USA was published (Allen et al. 2007). The methodologies used for this study were very similar to those used in the study commissioned by NICNAS, although variations in calibration methods may result in lack of comparability of the absolute values reported. Comparison of the studies indicate that similar ranges of bromine levels were seen, and that the prevalence of detection in similar types of articles was generally higher in the USA, but not to a major extent.

Following the determination of the nature and distribution of potential bromine sources within the houses, a number of specific representative examples for the major scenarios of decaBDE in televisions, curtains and home office equipment, and pentaBDE in furniture foam and home office equipment, were selected. Selection criteria included lack of alternate interfering potential sources in the vicinity, the ability to sample dust both near and far from the source, and the presence of suitable sites within the house for use as a control. The history of the contents of the rooms was also requested from home owners, to determine the likelihood of contributions from past room contents to the levels of PBDEs in dust.

For each of the selected scenarios, dust was collected using a vacuum cleaner from an area in the vicinity of the potential source, and from an area distant from the selected source. Dust collection areas were 1 m2 to 2 m2, depending on floor covering type. For each selected house, dust was also collected at a single control site.

The dust was analysed by GC-MS for the concentrations of the following PBDE congeners: BDE-17, BDE-28 + 33, BDE-30, BDE-47, BDE-49, BDE-66, BDE-71, BDE-77, BDE-85, BDE-99, BDE-100, BDE-119, BDE-126, BDE-138 + 166, BDE-139, BDE-140, BDE-153, BDE-154, BDE-156 + 169, BDE-171, BDE-180, BDE-183, BDE-184, BDE-191, BDE-196, BDE-197, BDE-201, BDE-203, BDE-204, BDE-205, BDE-206, BDE-207, BDE-208 and BDE-209.

Primary analysis of the results focussed on the eight congeners BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209. The first six of these are major constituents of commercial pentaBDE; BDE-183 served as a marker for any contribution from commercial octaBDE, while BDE-209 showed the presence of commercial decaBDE. The results of the dust analysis are summarised in Table A3.1.

Table A3.1. Levels of major PBDE congeners in dust at specific locations in fourAustralian homes

Location		BDE	BDE	BDE	BDE	BDE	BDE	Sum	BDE	BDE	Total	Source
		-28	-47	-99	-	-	-	penta	-	-		
					100	153	154		183	209		
House 10												
Bedroom 2	Near TV	6.8	760	1450	270	180	140	2800	24	230	3270	TV back
Bedroom 2	Away from TV	2.8	300	650	120	140	77	1287	310	1330	3640	
Bedroom 1	Away from foam underlay	74	9050	16900	2430	1710	1200	31290	200	4100	38200	Underlay
Study	Near computer	<10	220	360	63	110	54	807	55	1760	3380	Monitor
Study	Away from computer	8.3	200	330	59	58	42	689	28	450	1290	
House 12												
Entry	Control	2.8	120	150	31	15	13	329	3.4	310	690	
Bedroom 1	Near curtains	2.3	98	200	37	23	20	378	0.82	360	800	Curtain
Bedroom 1	Away from curtains	3.3	260	610	110	82	65	1127	18	1040	2340	
Bedroom 2	Near mattress	1.2	47	74	14	7.2	6.2	148.4	1.3	85	250	Mattress
Bedroom 2	Away from mattress	<3	150	320	58	36	32	596	5.8	400	1100	
Bedroom 3	Near mattress	1.7	110	240	48	34	28	460	6	260	780	Mattress
Lounge	Near TV	3.4	100	160	31	65	19	375	230	4540	5770	TV back
Lounge	Away from TV	10	370	410	83	45	37	945	5.9	510	1580	
House 13												
Bedroom 1	Near curtains	<1	42	62	11	7.3	5.3	127.6	1.5	130	280	Curtain
Bedroom 1	Away from curtains	2.4	79	120	20	14	10	243	2.9	190	490	
Bedroom 3	Control	5.6	270	490	84	56	42	942	8.9	740	1810	
Study	Near desk chair	20	5340	13700	2230	2290	1520	25080	120	5790	32900	Desk Chair
Study	Away from desk chair	12	3070	6030	1060	770	630	11560	37	1030	13500	

Location		BDE -28	BDE -47	BDE -99	BDE - 100	BDE - 153	BDE - 154	Sum penta	BDE - 183	BDE - 209	Total	Source
House 16												
Bedroom 4	Control	3.4	59	94	13	8.8	5.6	180.4	3.6	350	590	
Bedroom 3	Near curtains	<2	18	49	7.4	19	4.6	98	55	400	690	Curtains
Bedroom 3	Away from curtains	<2	34	82	12	12	6.5	146.5	11	500	780	
Upstairs Living	Near sofa	<2	25	100	13	27	12	177	110	760	1340	Sofa
Upstairs Living	Away from Sofa	<9	79	120	18	36	10	263	92	1600	2280	
Bedroom 1	Near TV	3.5	59	110	15	8	5	197	9.2	300	580	TV Back
Bedroom 1	Away from TV	<1	43	77	12	9.5	5.6	147.1	11	320	540	

Sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154

In House 10, the area selected as control, in Bedroom 1, proved to have the highest values for both pentaBDE and decaBDE of any of the rooms in the entire study. This was attributed to the presence of a foam underlay on the bed, although it is possible that previous room contents, particularly furniture containing polyurethane foam, may have contributed. The dust samples taken elsewhere in House 10 showed that the high values for the pentaBDE-related congeners were specific to Bedroom 1. The reason for the elevated level of BDE-209 in this room is not clear, because no specific likely sources for decaBDE were identified. The curtain in Bedroom 1 gave low readings using the handheld XRF. It is also noted that the sample point in Bedroom 1 was close to a door and only metres away from the sample points in the Study and Bedroom 2, where much lower levels of all the PBDEs were found. This indicates that there is very high variability of PBDE concentrations in dust throughout a house, and that the migration from a source covers short distances.

Bedroom 1 in House 10 reportedly had a history of being used as a home office, and the sources identified by the XRF would not necessarily be the only contributors to the PBDE levels in dust in the room. In particular, it was confirmed that a desktop computer, which is a possible source of pentaBDE, had been present in the Study for some time in the past, and that a monitor which gave high XRF readings for bromine in the back casing, had only recently been moved into the room. The Study results showed somewhat elevated BDE-209 results in the vicinity of the monitor, but comparatively low results for the pentaBDE-related congeners. A second home office scenario was examined in House 13. In this case, the only major bromine source was a desk chair seat cushion, assumed to be a potential source of pentaBDE. The monitor present contained very low levels of bromine, but, as this was two years old, it is probable that previous room contents, particularly older monitors, would also have contributed to PBDE levels in the dust. The highest level of BDE-209 (5790 ng/g dust) in the study was found in this room, with the likely source being an older monitor. Very high levels of pentaBDE-related congeners (25080 ng/g dust) were attributed to the foam in the desk chair cushion, as the level decreased to less than half at a distance of 2 m away from the desk chair.

Bedroom 2 in House 10 was selected for examination of the television scenario. In this case, higher levels for BDE-209 were actually found more distant from the television than adjacent to it. This suggests that the TV set was not a major source of BDE-209. The more elevated readings at the far side of the room may result from air circulation, preferential retention of PBDEs in a rug compared with floorboards, or closer proximity to the Study and Bedroom 1. Other television scenarios were examined in House 12 Lounge and House 16 Bedroom 1. In House 16, no elevated levels of BDE-209 were seen in the vicinity of the television, although in House 12, a clear gradient in BDE-209 concentration was seen between the vicinity of the television and a remote area of the same room. The vicinity of the television in this case had the second highest BDE-209 concentration in the study.

Curtains were the focus of three scenarios, in House 12, Bedroom 1, House 13, Bedroom 1, and House 16, Bedroom 3. In no case was an elevated level of BDE-209 found in the dust in the vicinity of the curtain. From these results, it is not possible to determine whether the curtains contain BDE-209 but do not emit it at high levels, or whether the bromine detection in the curtains arises from an alternative BFR.

Apart from the desk chair in the Study of House 13 and the mattress underlay in Bedroom 1 in House 10, two other foam scenarios were examined. One related to mattresses in Bedroom 2 and Bedroom 3 of House 12. In this case, the two bedrooms were similarly furnished, with identical mattresses, both containing bromine. However XRF analysis of the dust from the two bedrooms showed much higher bromine in Bedroom 2 than Bedroom 3. The house owner advised that a swag with a foam component was rolled up under the bed in Bedroom 2, which appeared to be the main point of difference. However the XRF results on the dust were not confirmed by GC/MS, suggesting that an alternative flame retardant was present. No gradient in pentaBDE-related congeners was seen around the sofa in the Upstairs Living room in House 16, which may again indicate that an alternative BFR was present. The reason for the increase in BDE-209 away from the sofa is not clear, as no potential sources were identified closer to this sample point than the sample point near the sofa.

House 16 was unique among the sampled houses in that it was newly constructed (around 2 years old) and little influence of historical sources would be expected.

The study was not intended as a survey of the overall PBDE levels in household dust, but rather to determine major sources contributing to these levels. The variability observed in this study is such that doubt is cast on the overall value of single point or single room dust studies in representing the exposure of an individual within the house to PBDEs. High values for pentaBDE-related congeners were found in individual rooms chosen for their potential inclusion of specific sources. The highest values found in this study were comparable with the highest value seen in a study in the USA by Stapleton et al (2005). In the Stapleton study, samples were collected in the main family room, without specific reference to the contents of this room. However, given that the samples collected for this study were intended to represent specific "hot spots" in houses that were specifically chosen for the presence of potential sources, they are not inconsistent with the overall comparatively low values for pentaBDE-related congeners in past Australian studies (Sjodinet al. 2006; Toms et al. 2006).

The findings of the study clearly indicated that the presence of foam in furniture was a major factor in contributing to the lower brominated PBDEs in household dust. The release of pentaBDE-related congeners from the foam is unlikely to differ greatly internationally, except for the impact of climatic factors such as temperature and sunlight exposure causing embrittlement, and this is likely to be high in the Australian climate. The frequency of

detection of bromine in chairs and sofas by XRF differs very little between Australia (71% of chairs and 72% of sofas) and the USA (67% of chairs and 81% of sofas). However, in the more general surveys of PBDE concentrations in household dust, Australia was found to have much lower overall levels of the pentaBDE-related congeners BDE-47 and BDE-99 than seen in the USA or Canada. This may be attributable to more widespread use of pentaBDE substitutes in Australian furniture foam, although this cannot be independently confirmed.

While some variability of dust concentrations of BDE-209 was seen within the study, no "hot spots" of the same magnitude as those seen for the pentaBDE-related congeners were identified. The potential for release of BDE-209 from television sets is not clear, given that the highest concentrations of BDE-209 on a dust weight basis were found in the vicinity of television sets and monitors, but that this finding was not replicated with all television sets examined. Importantly, the maximum levels of BDE-209 found in these specific locations were not reflected throughout the house.

International studies of PBDEs in dust have been conducted by a variety of protocols, for example by sampling the contents of the bag of a vacuum cleaner in use within the house, or by controlled vacuuming of a uniform sized area at a specific location within a house. The studies have generally not reported any details of the items in the proximity of the area where sampling was undertaken. Sampling of the bag of the household vacuum cleaner may be particularly affected by uses such as directly vacuuming furniture or cars (Wilford, 2005).

In comparison with the results of the international studies, the analysis of the predicted "hot spots" has given useful information. The maximum level of pentaBDE-related congeners seen in this study is very similar to the highest level seen in the controlled sampling study by Stapleton (2005) in the USA, suggesting that the observations of Stapleton may be in a region with similar surroundings to the maximum "hot spot" in the Australian study. This would imply that the major difference between the median levels of PBDEs in house dust in Australia and the USA would be in the prevalence of such "hot spots" around pentaBDEcontaining foam in furniture. In the case of decaBDE, the maximum international dust levels have generally been seen in the UK (Harrad et al. 2007; Sjodin et al. 2006; Santillo, 2003). The highest level recorded by Harrad et al was 520000 ng/g dust, of the order of 100x the highest level seen in a "hot spot" in Australian homes. Sjodin et al (2006) report that that 95% of all upholstery materials in the UK are flame retarded to comply with fire safety regulations, and that this is the only country within the European Union that has regulation specifying the level of flame retardancy for domestic upholstery. Wilford et al (2005) conclude that flame-retarded textiles may be a more likely source of particles/fibres than hard plastics, but the release mechanisms have not been well characterised. Textile backcoatings are reported to be composed of a latex material, with a high content of around 30% decaBDE. Specifications for performance of the backcoatings refer to the number of washes of the textile after which the flame retardant performance is maintained; however, performance may be maintained even following significant loss of flame retardant. The release rate for the flame retardant from the backcoating has not been characterised. It is possible to speculate that constant exposure to UV radiation in the case of curtain materials may cause significant crosslinking of the latex material, leading to embrittlement and flaking off as the textile flexes.

Lack of findings of elevated levels of BDE-209 in the vicinity of curtains in the Australian study may indicate that this mechanism is of minor importance in Australian homes. However this cannot be confirmed, as there are also possibilities that the backcoating had not commenced to break down, or that the backcoating contained a BFR other than

decaBDE. As the findings in the scenarios that were examined in the Australian homes (televisions and monitors) do not account for the magnitude of the BDE-209 levels in the UK, and as the UK has both much higher levels of BDE-209 in dust than seen in any other countries, reportedly due to the strictest textile flame retardancy requirements among major countries, it is plausible to attribute these extreme levels of BDE-209 in dust to the use of BFRs in textiles.

9 References

Alaee M, Luross J, Sergeant DB, Muir DCG, Whittle DM, Solomon K (1999). Distribution of polybrominated diphenyl ethers in the Canadian environment. Organohalogen Compd. **40**:347–350.

Al Bitar F (2004). Hazardous chemicals in Belgian house dust: report on chemical content in house dust samples collected in Belgian homes and offices. Greenpeace. Available at http://www.greenpeace.org/raw/content/belgium/fr/press/reports/hazardous-chemicals-in-belgian-2.pdf

Allen JG, McClean MD, Stapleton HM, Nelson JW, Webster TF (2007). Personal exposure to polybrominated diphenyl ethers (PBDEs) in residential indoor air. Environmental Science and Technology, **41**:4574-4579.

Allen JG, McClean MD, Stapleton HM, Webster TF (2008). Critical factors in assessing exposure to PBDEs via house dust. Environ Int **34**:1085–1091.

AMAP (1998). AMAP Assessment Report: Arctic Pollution Issues. Oslo, Arctic Monitoring and Assessment Programme.

American Chemical Council (2002). Voluntary Children Chemical Evaluation Program (VCCEP): Data summary: decaBDE (a.k.a. decabromodiphenyl oxide, DBDPO), CAS#1163-19-5. Arlington, Virginia, American Chemistry Council's Brominated Flame Retardant Industry Panel. Accessed at <u>http://www.tera.org/peer/VCCEP/DECA/DBDPO%20Assessment.pdf</u>

Anderson O & Blomkist G (1981). Polybrominated aromatic pollutants found in fish in Sweden. Chemosphere 10: 1051–1060, cited in Alaee M and Wenning RJ (2002) The significance of brominated flame retardants in the environment: current understanding, issues and challenges. Chemosphere, **46**:579–582.

Anim AK, Drage DS, Goonetilleke A, Mueller JF, Ayoko GA (2017) Distribution of PBDEs, HBCDs and PCBs in the Brisbane River estuary sediment. Marine Pollution Bulletin, **120**:165:173.

ATSDR (2004). Toxicological profile for polybrominated biphenyls and polybrominated diphenyl ethers (PBBs and PBDEs). U.S. Department Of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Accessed <u>http://www.atsdr.cdc.gov/toxprofiles/tp68.html#bookmark11</u>

Bartrons M, Catalan J, Penuelas J (2016) Spatial and Temporal Trends of Organic Pollutants in Vegetation From Remote and Rural Areas. Scientific Reports 6:25446, May 2016.

Besis A and Samara C (2012). Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments - A review on occurrence and human exposure. Environ Pollut **169**:217-229.

Bett KS (2008) Unwelcome guest: PBDEs in indoor dust. Environ Health Perspect, **116**:A202-8.

Bezares-Cruz J, Jafvert CT & Hua I (2004). Solar photodecomposition of decaBDE: Product and quantum yield. Environmental Science and Technology, **38**:4149-4156.

Boyd AW, & Morrison RT (1992) Organic Chemistry (6th Edn) Prentice Hall, Eaglewood Cliffs NJ

Brommer S, Harrad S, van den Eede N, Covaci A (2012). Concentrations of organophosphate esters and brominated flame retardants in German indoor dust samples. J Environ Monit; **14**:2482-2487.

BSEF (Bromine Science and Environmental Forum) <u>http://www.bsef.com/</u>. (Accessed 2005).

Bull K, Basu N, Zhang S, Martin JW, Bursian S, Martin P, Chan LH. Dietary and in utero exposure to a pentabrominated diphenyl ether mixture did not affect cholinergic parameters in the cerebral cortex of ranch mink (Mustela vison) Toxicol Sci. 2008; **96**:115–122.

Cetin & Odabasi (2005). Measurement of Henry's Law Constants of seven polybrominated diphenyl ether (PBDE) congeners as a function of temperature. Atmospheric Environment, September 2005; **39**:5273-5280.

Chao H, Wang S, Lee W, Wang Y, & Papke O (2006). Levels of polybrominated diphenyl ethers (PBDEs) in breast milk from central Taiwan and their relation to infant birth outcome and maternal menstruation effects. Environment International **33**:239-245. doe:10.1016/j.envint.2006.09.013.

Chemical Gazette (2006). Australian Government Chemical Gazette, January 2006.<u>https://www.nicnas.gov.au/news-and-events/chemical-gazette</u>

Chemical Gazette (2007). Australian Government Chemical Gazette, February 2007. https://www.nicnas.gov.au/news-and-events/chemical-gazette

Chemical Gazette (2007). Australian Government Chemical Gazette, March, 2007. <u>https://www.nicnas.gov.au/news-and-events/chemical-gazette</u>

Chen L, Mai B, Bi X, Chen S, Wang X, Ran Y, Luo X, Sheng G, Fu J, & Zeng EY (2006). Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. Environmental Science and Technology, **40**:1190-1196.

Chen L, Mai B, Xu Z, Peng X, Han J, Ran Y, Sheng G and Fu J (2008). In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. Atmospheric Environmental, **42**:78-86.

Chen SJ, Ma YJ, Wang J, Chen D, Luo XJ, Mai BX. 2009. Brominated flame retardants in children's toys: concentration, composition, and children's exposure and risk assessment. Environ Sci Technol., **43**:4200–4206.

Chen D, Hale RC (2010) A global review of polybrominated diphenyl ether flame retardant contamination in birds. Environment International, **36**:800-811.

Chen Q, Yu LQ, Yang LH, Zhou BS (2012) Bioconcentration and metabolism of decabromodiphenyl ether (BDE-209) result in thyroid endocrine disruption in zebrafish larvae Aquatic Toxicology **110**:141-148.

Clarke B, Porter N, Symons R, Marriott P, Ades P, Stevenson G, Blackbeard J (2008) Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge. Chemosphere, **73**:980:989.

Clarke BO, Porter NA, Symons RK, Marriott PJ, Stevenson GJ Blackbeard JR (2010) Investigating the distribution of polybrominated diphenyl ethers through an Australian wastewater treatment plant. Science of the Total Environment **408**:1604-1611.

Coakley JD, Harrad SJ, Goosey E, Ali N, Dirtu AC, Van den Eede N, Covaci A, Douwes J, Mannetje A' (2013). Concentrations of polybrominated diphenyl ethers in matched samples of indoor dust and breast milk in New Zealand. Environ Int. **59**:255-61.

Costner, P., B. Thorpe, and A. McPherson. 2005. Sick of Dust: Chemicals in Common Products - A Needless Health Risk in Our Homes. Clean Production Action. Available: <u>http://www.safer-products.org/downloads/Dust%20Report.pdf</u>.

Cramer PH, Ayling RE, Thornburg KR, Stanley JS, Remmers JC, Breen JJ, & Schwemberger J (1990). Evaluation of an analytical method for the determination of polybrominated dibenzo*p*-dioxins/dibenzofurans (PBDD/PBDF) in human adipose tissue. Chemosphere, **20**: 821-827, cited in IPCS (1998) Environmental Health Criteria 205: Polybrominated Dibenzo-p-dioxins and Dibenzofurans. Geneva, World Health Organisation, International Program on Chemical Safety.

De Boer J, Wester PG, Rodriguez DP, Lewis WE, and Boon JP (1998). Polybrominated biphenyls and diphenyl ethers in sperm whales and other marine mammals - a new threat to ocean life? Organohalogen Compounds, **35:**383-386.

De Carlo VJ (1979). Studies on brominated chemicals in the environment. Ann. N. Y. Acad. Sci. 320: 678–681, cited in Alaee M and Wenning RJ (2002) The significance of brominated flame retardants in the environment: current understanding, issues and challenges. Chemosphere **46**:579–582.

EBFRIP (2008). Sweden Reverses Deca Ban, European Brominated Flame Retardant Industry Panel website. Accessed at

http://www.ebfrip.com/statements/EBFRIP%20statement_sweden_13052008.pdf

EC (European Commission) (2002a). European Union Risk Assessment Report. Bis(pentabromophenyl) ether, CAS No: 1163-19-5 EINECS No: 214-604-9. (Series: 1st Priority List, Volume: 17). European Commission – Joint Research Centre, Institute for Health and Consumer Protection, European Chemicals Bureau (ECB). Luxembourg, Office for Official Publications of the European Communities.

https://echa.europa.eu/documents/10162/da9bc4c4-8e5b-4562-964c-5b4cf59d2432.

EC (2002b). Opinion on the results of the Risk Assessment of: Bis(pentabromophenyl)ether -Environmental and Human Health Part (CAS No.: 1163-19-5 EINECS No.: 214-604-9). Opinion expressed at the 35th CSTEE plenary meeting Brussels, 31st October 2002.

http://europa.eu.int/comm/health/ph_risk/committees/sct/documents/out165_en.pdf

EC (European Commission) (2004a). Update of the risk assessment of bis(pentabromophenyl) ether (decabromodiphenyl Ether). R013-0404-env. European Commission Joint Research Centre (<u>http://ecb.jrc.it/existing-chemicals/</u>).

EC (2004b). Opinion on "Update of the risk assessment of bis(pentabromophenyl) ether(decabromodiphenyl ether)". SCHER. European Commission Health & Consumer Protection Directorate-General.

ECHA, European Chemicals Agency, (2013). Draft background document for Bis(pentabromophenyl)ether (decabromodiphenyl ether; decaBDE). Document developed in the context of ECHA's fifth Recommendation for the inclusion of substances in Annex XIV. 24 June 2013.

ECHA (2014), Multiple Framework Contract with Re-opening of competition for Scientific Services for ECHA. Reference:ECHA/2011/01. Service Request SR14. Support for an Annex XV Dossier on Bis-(pentabromophenyl) ether (DecaBDE). European Chemicals Agency.

Eljarrat E, Marsh G, Labandeira A, Barcelo D (2008) Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. Chemosphere **71**:1079-1086.

Environment Canada (2006a). Canadian Environmental Protection Act, 1999 Ecological Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs). Accessed at <u>http://www.ec.gc.ca/CEPARegistry/documents/subs_list/PBDE_SAR/PBDEs_SAR_EC_June_200</u> <u>6_(en).pdf</u>.

Environment Canada (2006b) Risk Management Strategy for Polybrominated Diphenyl Ethers (PBDEs). <u>http://www.ec.gc.ca/Toxics/docs/substances/PBDE/PBDE_RMS/EN/toc.cfm</u>.

Environment Canada (2010) Ecological State of the Science Report on the Bioaccumulation and Transformation of Decabromodiphenyl Ether. <u>https://www.ec.gc.ca/lcpe-</u> <u>cepa/documents/substances/decabde/ess_report_decabde-eng.pdf</u>.

Environmental Working Group (2005). Body burden: the pollution in newborns. Environmental Working Group. <u>http://www.ewg.org/reports/bodyburden2/</u>

Environmental Working Group (2006). Mother's milk. Environmental Working Group. <u>http://www.ewg.org/reports/mothersmilk/es.php</u>.

EPHC (2009) Environmental risk assessment guidance manual for industrial chemicals. Environmental Protection and Heritage Council, Commonwealth of Australia, 109 pp.

Fischer D, Hooper K, Athanasiadou I, & Bergman A (2006). Children show highest levels of polybrominated diphenyl ethers in a California family of four: a case study. Environmental Health Perspectives, **114**:1581-1584.

Fromme H, Korner W, Shahin N, Wanner A, Albrecht M, Boehmer S, Parlar H, Mayer R, Liebl B, Bolte G. 2009. Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicated diet study, indoor air, house dust, and biomonitoring in Germany. Environ Int **35**:1125–1135.

Fukata, H., Omori-Inoue M, Osada H, Todaka E, Omori N, Kawashiro Y, Takahashi S, Takigami H, Sakai S, & Mori C (2005). Current status of maternal and fetal exposure to brominated flame retardants, PCBs and dioxins in Japan. IN: Organohalogen Compounds Volume 67, CD-ROM of proceedings of Dioxin 2005 AND ISPAC-20. Edited by E. Reiner and M.Alaee: 1617 – 1619.

FSANZ (2007). Polybrominated diphenyl ethers (PBDE) in food in Australia. Food Standards Australia and New Zealand.

http://www.foodstandards.gov.au/_srcfiles/PBDE_Report_Dec_07.pdf#search=%22pbde%22

Gallen C, Drage D, Kaserzon S, Baudel C, Gallen M, Banks A, Broomhall S, Mueller JF (2016) 'Occurrence and distribution of brominated flame retardants and perfluoroalkyl substances in Australian landfill leachate and biosolids. Journal of Hazardous Materials, **312**:55-64.

Gerecke AC, Hartmann PC, Heeb NV, Kohler H-PE, Giger W, Schmid P, Zennegg M & Kohler M (2005) Anaerobic degradation of decaBDE. Environmental Science and Technology, **39**: 1078-1083.

Gevao B, Al-Bahloul M, Al-Ghadban AN, Al-Omair A, Ali L, Zafar J, Helaleh M & (2006). House dust as a source of human exposure to polybrominated diphenyl ethers in Kuwait. Chemosphere, **64**: 603-608.

Government of Canada (2008). Polybrominated diphenyl ethers regulations (Notice). Chemical Gazette, 9 July 2008; **142**(14).

Government of Canada (2006). Publication of the final results of investigations and recommendations for the substance – Polybrominated diphenyl ethers that have the

molecular formula C12H(10-n)BrnO in which $4 \le n \le 9 -$ (Subsection 77(6) of the Canadian Environmental Protection Act, 1999). Canada Gazette, 1 July 2006; **140**.

Grabda M, Oleszek-Kudlaka S, Shibata E & Nakamura T (2007) Gas phase thermodynamic properties of PBDEs, PBBs, PBPs, HBCD and TBBPA predicted using DFT method. Journal of Molecular Structure: Theochem **822**: 38-44

Hagmar L & Bergman A (2001). Human exposure to BFRs in Europe. The Second International Workshop on Brominated Flame Retardants, Swedish Chemical Society, Stockholm, 2001.

Hale, R.C., M.J. La Guardia, E. Harvey and T.M. Mainor. 2002. Potential role of fire retardanttreated polyurethane foam as a source of brominated diphenyl ethers to the U.S. environment. Chemosphere **46**: 729–735.

Hale RC, Alace M, Manchester-Neesvig JB, Stapleton HM, Ikonomou MG (2003). Polybrominated diphenyl ether flame retardants in the North American environment. Environ. Int. **29**: 771–779.

Harden F, Müller J & Toms L (2005). Organochlorine Pesticides (OCPs) and Polybrominated Diphenyl Ethers (PBDEs) in the Australian Population: Levels in Human Milk, Environment Protection and Heritage Council of Australia and New Zealand <u>http://www.ephc.gov.au/pdf/EPHC/OCP_PBDE_human_milk_jan%202005.pdf</u>

Harrad S, Ibarra C, Diamond M, Melymuk L, Robson M, Douwes J, Roosens L, Dirtu AC (2008). Polybrominated diphenyl ethers in domestic indoor dust from Canada,New Zealand, United Kingdom and United States. Environment International, **34**:232-238.

He J, Yang D (2011) Chronic zebrafish low dose decabrominated diphenyl ether (BDE-209) exposure affected parental gonad development and locomotion in F1 offspring. Ecotoxicology, **20**:1813-1822.

Health Canada (2012) Human Health State of the Science Report on Decabromodiphenyl Ether (decaBDE).

https://www.ec.gc.ca/lcpe-cepa/documents/substances/decabde/ess_report_decabdeeng.pdf.

Hearn LK, Hawker DW Mueller JF (2012) Dispersal patterns of polybrominated diphenyl ethers in the vicinity of an automotive shredding and metal recycling facility. Atmospheric Pollution Research **3**: 317-324.

Hu J, Eriksson L, Bergman Å, Jakobsson E, Kolehmainen E, Knuutinen J, Suontamo R, Wei X (2005) Molecular orbital studies on brominated diphenyl ethers. Part II—reactivity and quantitative structure–activity (property) relationships .Chemosphere, **59** 1043–1057.

Huwe JK & Smith DJ (2007). Accumulation, whole-body depletion, and debromination of decabromodiphenyl ether in male Sprague-Dawley rats following dietary exposure. Environmental Science and Technology, **41**:2371-2377. DOI 10.1021/es061954d.

Huwe, JK., Hakk, H., and Birnbaum, LS, (2008). Tissue distribution of polybrominated diphenyl ethers in male rats and implications for biomonitoring. Environ. Sci. Technol. **42**: 7018–7024.

IARC (International Agency for Research on Cancer) (1990). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 48: Some flame retardants and textile chemicals, and exposure in the textile manufacturing industry: Summary of data reported

and evaluation. Lyon, IARC. Accessed at: <u>http://monographs.iarc.fr/ENG/Monographs/vol48/mono48-8.pdf</u>.

IARC (International Agency for Research on Cancer) (1999). Decabromodiphenyl oxide. Volume 71. IARC. Lyon. Summary of data reported and evaluation. Lyon, IARC. Accessed at: <u>http://monographs.iarc.fr/ENG/Monographs/vol48/mono71-8.pdf</u>.

Ibhazehiebo, K., T. Iwasaki, J. Kimura-Kuroda, W. Miyazaki, N. Shimokawa and N. Koibuchi (2011). "Disruption of thyroid hormone receptor-mediated transcription and thyroid hormone-induced Purkinje cell dendrite arborization by polybrominated diphenyl ethers." Environmental health perspectives, **119**: 168-175.

ICL Industrial Products (2005). Flame retardants home page. <u>http://www.dsbg.com/brome/brome.nsf/ENTRY?readform&mf=viewFramesetSearchByGlobal</u> <u>Code/Pbu22?OpenDocument&ws=Pbu22</u> (Accessed 2005).

Inoue K, Harada K, Takenaka K, Uehara S, Kono M, Shimizu T, Takasuga T, Senthilkumar K, Yamashita F, & Koizumi A (2006). Levels and concentration ratios of polychlorinated biphenyls and polybrominated diphenyl ethers in serum and breast milk in Japanese mothers. Environmental Health Perspectives, **144**:1179-1185 (and supplementary tables).

IPCS (International Programme on Chemical Safety) (1994). Environmental Health Criteria 162: Brominated diphenyl ethers. Geneva, World Health Organization.

IPCS (International Programme on Chemical Safety) (1997). Environmental Health Criteria 192: Fire retardants: a general introduction. Geneva, World Health Organisation.

Jakobsson K et al. (2002). Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. Chemosphere, **46**:709-716. (cited in Jakobbson 2005).

Jakobsson K, Athanasiadou M, Christiansson A, Bergman A, & Hagmar L (2005). Polybrominated diphenyl ethers (PBDEs) in serum from Swedish men 1988-2002. A longitudinal study. IN: Organohalogen Compounds, CD-ROM of proceedings of Dioxin 2005 AND ISPAC-20. Edited by E. Reiner and M.Alaee: 533-536.

Jansson B, Asplund L, Olsson M (1987). Brominated flame retardants – ubiquitous environmental pollutants? Chemosphere, **16**:2343–2349.

Johnson-Restrepo B and Kannan K (2009). An assessment of sources and pathways of human exposure to polybrominated diphenyl ethers in the United States. Chemosphere, **76**:542-548.

Jones-Otazo HA, Clarke JP, Diamond ML, Archbold JA, Ferguson G, Harner T, et al. 2005. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. Environ Sci Technol., **39**:5121–5130.

Julander A, Westberg H, Engwall M, & van Bavel B (2005). Distribution of brominated flame retardants in different dust fractions in air from an electronics recycling facility, Science of the Total Environment, **350**:151-160.

Kajiwara N, Noma Y, Takigami H (2008) Photolysis studies of technical decabromodiphenyl ether (DecaBDE) and ethane (DeBDethane) in plastics under natural sunlight. Environmental Science and Technology, **42**:4404-4409.

Kajiwara N, Desborough J, Harrad S, Takigami H (2013a) Photolysis of brominated flame retardants in textiles exposed to natural sunlight. Environmental Science: Processes and Impact,s **15**:653-660.

Kajiwara N, Takigami H (2013b) Emission behaviour of hexabromocyclododecanes and polybrominated diphenyl ethers from flame-retardant-treated textiles. Environmental Science: Processes and Impacts, **15**:1957-1963.

Karlsson M, Julander A, van Bavel B, & Hardell L (2007). Levels of brominated flame retardants in blood in relation to levels in household air and dust. Environment International, **33**:62-69.

Kemmlein S, Hahn O and Jann O (2003). Emission of Flame Retardants from Consumer Products and Building Materials, Atmospheric Environment, **37**: 5485-5493.

Keum Y-S & Li Q. X (2005) Reductive debromination of polybrominated diphenyl ethers by zerovalent iron. Environmental Science and Technology, **39**: 2280-2286.

Kim TH, Lee YJ, Lee E, Kim MS, Kwack SJ, Kim KB et al (2009). Effects of gestational exposure to decabromodiphenyl ether on reproductive parameters, thyroid hormone levels ,and neuronal development in Sprague Dawley rats offspring. J Toxicol Environ Health **72**:1296-303.

Kim J, Kang JH, Park H, Baek SY, Kim YH and Chang YS (2012). Assessment of polybrominated diphenyl ethers (PBDEs) in serum from the korean general population. Environmental Pollution, **164**:46-52.

Kim M, Guerra P, Theocharides M, Barclay K, Smyth SA, Alaee M (2013) Polybrominated diphenyl ethers in sewage sludge and treated biosolids: effect factors and mass balance. Water Research, **47**:6496-6505.

Knoth W, Mann W, Meyer R, Nebhuth J. (2002). Polybrominated diphenylether in house dust. Organohalogen Compounds, **58**:213-216.

Kohler M, Zenegg M (2008) Temporal trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss lake sediments. Environmental Science and Technology, **42**: 6378-6384.

Konstantinov A, Bejan D, Bunce NJ, Chittim B, McCrindle R, Potter D & Tashiro C (2008) Electrolytic debromination of PBDEs in DE-83TM technical decabromodiphenyl ether. Chemosphere, **72**: 1159-1162.

Kuo YM Sepulveda MS (2010) Bioaccumulation and biotransformation of decabromodiphenyl ether and effects on daily growth in juvenile lake whitefish (Coregonus clupeaformis). Ecotoxicology, **19**:751-760.

La Guardia M, Hale R & Harvey E (2006). Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environmental Science and Technology, **40**: 6247–6254.

Lagalante AF, Oswald TD, Calvosa FC (2009). Polybrominated diphenyl ether (PBDE) levels in dust from previously owned automobiles at United States dealerships. Environ Int, **35**:539–544

Lee SJ, Ikonomou MG, Park H, Baek SY, Chang YS (2007). Polybrominated diphenyl ethers in blood from Korean incinerator workers and general population. Chemosphere, **67**: 489-497.

Liu PY, Zhao YX, Zhu YY, Qin ZF, Ruan XL, Zhang YC, Chen BJ, Li Y, Yan SS, Qin XF, Fu S, Xu XB (2012). Determination of polybrominated diphenyl ethers in human semen. Environ Int. **42**: 132-137.

Lopez D, Athanasiadou M, Athanasiadis I, Estrada LY, Diaz-Barriga F & Bergman A (2004). A Preliminary study on PBDEs and decaBDED in blood and milk from Mexican women. The Third International Workshop on Brominated Flame Retardants, BFR 2004 Abstracts p 483-487.

Lorber M (2008). Exposure of Americans to polybrominated diphenyl ethers. Journal of Exposure Science and Environmental Epidemiology, **18**: 2-19.

Lowell Center for Sustainable Production (2005). Decabromodiphenylether: An investigation of non-halogen substitutes in electronic enclosure and textile applications Available online at http://www.safer-products.org/downloads/Deca%20BDE%20Substitutes%20Report.pdf.

MacGregor J & Nixon W (1997). Decabromodiphenyl oxide (DBDPO): Determination of noctanol/water partition coefficient. Project Number 439C-101. Wildlife International, Easton, Maryland. 13 July 1997. Unpublished.

Manning T, Ross, GA, Symons R (2008) Environmental contaminants in white-bellied seaeagles (Haliaeetus leucogaster) found in Sydney, Australia. Australasian Journal of Ecotoxicology, **14**:21-30.

McGrath TJ, Morrison PD, Sandiford CJ, Ball AS (2016) Widespread polybrominated diphenyl ether (PBDE) contamination in urban soils in Melbourne, Australia. Chemosphere, **164**:225-232.

McGrath TJ Ball AS, Clarke BO (2017) Critical review of soil contamination by poybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs); concentrations, sources and congener profiles. Environmental Pollution, **230**:741-757.

McPherson A, Thorpe B, & Blake A (2004). Brominated flame retardants in dust on computers: the case for safer chemicals and better computer design. Clean Production Action. Available online at <u>www.computertakeback.org</u>.

Mizukawa H, Nomiyama K, Nakatsu S, Yamamoto M, Ishizuka M, Ikenaka Y, Nakayama SMM Tanabe S (2017) Anthropogenic and Naturally Produced Brominated Phenols in Pet Blood and Pet Food in Japan. Environmental Science and Technology, **51**:11354-11362.

NHMRC (2003). The dietary guidelines for children and adolescents in Australia incorporating the infant feeding guidelines for health workers. Canberra, National Health and Medical Research Council, Commonwealth of Australia.

NICNAS (1999). Polybrominated flame retardants (PBFRs): Priority Existing Chemical Assessment Report No. 20. Sydney, National Industrial Chemicals Notification and Assessment Scheme.

NICNAS (2007). Interim Public Health Risk Assessment of Certain PBDE Congeners. Sydney, National Industrial Chemicals Notification and Assessment Scheme.

https://www.nicnas.gov.au/_data/assets/pdf_file/0003/4944/Final-Interim-Report-PBDE-March.pdf.

Norwegian Pollution Control Authority [SFT] (2008). Ban on deca-BDE. Publication No. 2401. Accessed at <u>http://www.sft.no/publikasjoner/2401/ta2401.pdf</u>.

Noyes PD, Hinton DE (2011) Accumulation and debromination of decabromodiphenyl ether (BDE-209) in juvenile fathead minnows (Pimephales promelas) induces thyroid disruption and liver alterations. Toxicological Sciences, **122**:265-274.

Noyes PD, Lema SC, Macaulay LJ, Douglas NK, Stapleton HM (2013) Low level exposure to the flame retardant BDE-209 reduces thyroid hormone levels and disrupts thyroid signalling in fathead minnows. Environmental Science and Technology, **47**: 10012-10021.

OECD (1994). Risk reduction monograph no. 3. Selected brominated flame retardants. Environmental Monograph Series No. 102 [OCDE/GD(94)96]. Paris, Organisation for Economic Cooperation and Development.

Orihel DM, Bisbicos T, Darling CTR, Dupuis AP Williamson M, Muir DCG (2016) Probing the debromination of the flame retardant decabromodiphenyl ether in sediments of a boreal lake. Environmental Toxicology and Chemistry, **35**:573-583.

OSPAR (2004). Certain brominated flame retardants – polybrominated diphenylethers, polybrominated biphenyls, hexabromo cyclododecane, 2001 (2004 Update). OSPAR Priority Substances Series, OSPAR Commission. Accessed at:

http://www.ospar.org/eng/html/sap/welcome.html#hazardous%20substances

Peters AK, van Londen K, Bergman Å, Bohonowych J, Denison MS, van den Berg M, & Sanderson JT (2004). Effects of polybrominated diphenyl ethers on basal and TCDD-induced ethoxyresorufin activity and cytochrome P450-1A1 expression in MCF-7, HepG2, and H4IIE cells. Toxicological. Sciences, **82**:488-496.

Pettersson A, Westberg H, Engwall M, & Ohlson CG (2001). Concentrations in air and dust of polybrominated diphenyl ethers and tetrabromobisphenol A, The Second International Workshop on Brominated Flame Retardants, Swedish Chemical Society, Stockholm, 2001.

Pettersson-Julander A, van Bavel B, Engwall M, & Westberg H (2004). Personal air sampling and analysis of polybrominated diphenyl ethers and other bromine containing compounds at an electronic recycling facility in Sweden. J. Environ. Monit, **6**: 874-880.

Qin X, Xia X (2010) Thyroid disruption by technical decabromodiphenyl ether (DE-83R) at low concentrations in Xenopus laevis. Journal of Environmental Sciences **22**:744-751.

Qu W, Bi X, Sheng G, Lu S, Fu J, Yuan J, & Li L (2007). Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. Environment International. doi:10.1016/j.envint.2007.05.009 (http://dx.doi.org.ezproxy2.library.usyd.edu.au/10.1016/j.envint.2007.05.009)

Ren, G., Z. Wang, Z. Yu, Y. Wang, S. Ma, M. Wu, G. Sheng, and J. Fu. (2013). Primary investigation on contamination pattern of legacy and emerging halogenated organic pollutions in freshwater fish from Liaohe River, Northeast China. Environmental Pollution, **172**:94-99.

Ridoutt CVL Kingsford RT (2011), Organohalogenated pollutants in Australian white ibis (Threskiornis molucca) eggs. Report by the Australian Wetlands and Rivers Centre, University of New South Wales, Sydney.

Roach A, Symons R, Stevenson G, Manning T (2008) Levels PBDEs in sediment and sea eagles from Sydney harbour, Australia: Spatial patterns and profiles. Organohalogen Compounds, **70**:000114.

Roosens L., Abdallah M.A.E., Harrad S., Neels H., Covaci A. (2009). Factors influencing concentrations of polybrominated diphenyl ethers (PBDEs) in students from Antwerp, Belgium. Environmental Science and Technology, **43**:3535-3541.

Saini A, Thaysen C, Jantunen L, McQueen RH, Diamond ML (2016) From Clothing to Laundry Water: Investigating the fate of Phthalates, Brominated Flame Retardants, and Organophosphate Esters, Environmental Science and Technology, **50**:9289-9297.

Santillo D, Labunska I, Davidson H, Johnston P, Strutt M & Knowles O (2003a). Consuming chemicals: Hazardous chemicals in house dust as an indicator of chemical exposure in the home (Part 1- UK). Greenpeace Research Laboratories Technical Note 01/2003 (GRL-TN-01-2003) <u>http://www.greenpeace.to/publications/housedust_uk_2003.pdf</u>

Santillo D, Labunska I, Davidson H, & Johnston P (2003b). Consuming chemicals #2: Hazardous chemicals in house dust as an indicator of chemical exposure in the home. Greenpeace Research Laboratories Technical Note 02/2003 (GRL-TN-02-2003). http://www.greenpeace.to/publications/consuming_chemicals_VO_mp.pdf

Schecter A, Pavuk M, Papke O, Ryan JJ, Birnbaum L, & Rosen R (2003). Polybrominated diphenyl ethers (PBDEs) in USA mothers' milk. Environmental Health Perspectives, **111**: 1723-1729.

Schecter A, Papke O, Joseph JE & Tung K-C (2005). Polybrominated diphenyl ethers (PBDEs) in U.S. computers and domestic carpet vacuuming: possible sources of human exposure. Journal of Toxicology and Environmental Health, Part A, **68**:501 – 513.

Shanmuganathan, D., 2010 'Polybrominated Diphenyl Ethers in South Australian Environment: Human Health Risk Assessment and Toxicity to Biota', PhD. Thesis, University of South Australia.

Sharp R & Lunder S (2004). In the dust: toxic fire retardants in American homes. Environmental Working Group 2004 Report available at <u>http://www.ewg.org/reports/inthedust/index.php</u>.

She J, Holden A, Sharp M, Williams-Derry C, & Hooper K (2005). PBDEs greater than PCBs in 30% of breast milk samples from the Pacific Northwest. IN: Organohalogen Compounds Volume **67**, CD-ROM of proceedings of Dioxin 2005 AND ISPAC-20. Edited by E. Reiner and M. Alaee.

Sifleet SD (2009) Toxicology of decabromodiphenyl ether in avian embryos: Disposition of the flame retardant BDE-209 in yolk-injected chicken embryos (Gallus gallus). Thesis presented to the faculty of the school of medical science, The College of William and Mary in Virginia, USA.

Sjodin A & Hagmar L (1999). Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. Environmental Health Perspectives, **107**: 643-648.

Sjodin A, Carlsson H, Thuresson K, Sjolin S, Bergman A, & Ostman C (2001) Flame retardants in indoor air at an electronic recycling plant and at other work environments. Environmental Science & Technology, **35**:448-454.

Sjodin A, Papke O, McGahee III E, Jones R, Focant J-F, Pless-Mulloli T, Toms L-M, Wang R, Zhang, Y, Neeham L, Herrmann T, & Patterson Jr D (2004). Concentration of polybrominated diphenyl ethers (PBDEs) in house hold dust from various countries - inhalation a potential route of human exposure. Organohalogen Compounds, **66**:3817-3822.

Sjodin A, Papke O, Focant J-F, Jones R, Pless-Mulloli T, Leontjew Toms L-M, Herrmann T, Mueller J, Neeham L, Patterson Jr D (2006). Concentration of Polybrominated Diphenyl Ethers (PBDEs) in Household Dust from Various Countries – Is Dust a Major Source of Human Exposure? Organohalogen Compounds, **68**:2181-2185. Söderström G, Sellstrom U, de Wit C & Tysklind M (2004) Photolytic debromination of decabromodiphenyl ether (BDE 209). Environmental Science and Technology, **38**(1): 127-132.

Standards Australia (1990) AS 3758-1990: Guide to the evaluation of the effectiveness of fire retardants. Homebush, Standards Australia.

Standards Australia (1993) SAA HB37.1 - 1993: Handbook of Australian fire standards. Part 1: Fire – General. Homebush, Standards Australia.

Stapleton HM, Dodder NG, Offenberg JH, Shantz MM, Wise SA (2005). Polybrominated diphenyl ethers in house dust and clothes dryer lint. Environmental Science & Technology, **39**:925-931.

Stapleton H, Brazil B, Holbrook D, Mitchelmore C, Benedict R, Konstantinov A and Potter D (2006). In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by Juvenile Rainbow Trout and Common Carp. Environmental Science and Technology, **40**:4653-4658.

Stapleton HM, Dodder NG (2008) Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. Environmental Toxicology and Chemistry **27**:306-312.

Stenzel J and Markley B, (1997). Decabromodiphenyl Oxide (DBDPO): Determination of the Water Solubility. Project Number 439C-102. Wildlife International, Easton, Maryland. 10 June 1997. Unpublished.

Stenzel J and Nixon W, (1997). Decabromodiphenyl Oxide (DBDPO): Determination of the Vapour Pressure Using a Spinning Rotor Gauge. Project Number 439C-115. Wildlife International, Easton, Maryland. 13 July 1997. Unpublished.

Strandberg B, Dodder NG, Basu I, Hites RA (2001). Concentrations and spartial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes Air. Environmental Science & Technology, **35**:1078-1083.

Sun B, Hu Y, Cheng H Tao S (2016) Kinetics of Brominated Flame Retardant (BFR) Releases from Granules of Waste Plastics. Environmental Science and Technology, **50**:13419-13427.

Tan J, Cheng SM, Loganath A, Chong YS, & Obbard JP (2007). Polybrominated diphenyl ethers in house dust in Singapore. Chemosphere, **66**:985-992.

The Court of Justice (2008). Judgement of the Court (Grand Chamber) 1 April 2008 In Joined Cases C 14/06 and C 295/06. Accessed from website of European Court of Justice. http://curia.europa.eu/en/transitpage.htm

Thomas GO, Wilkinson M, Hodson S, Jones KC (2006). Organohalogen chemicals in human blood from the United Kingdom. Environmental Pollution, **141**:30-41.

Thuresson K (2004). Occupational exposure to brominated flame retardants with emphasis on polybrominated diphenyl ethers, Doctoral thesis, Department of Environmental Chemistry, Stockholm University.

Thuresson K, Bergman A., Jakobsson K (2005). Occupational exposure to commercial decabromodiphenyl ether in workers manufacturing or handling flame-retarded rubber. Environmental Science and Technology, **39**:1980-6.

Thuresson K, Hoglund P, Hagmar L, Sjodin A, Bergman A Jakobsson K (2006). Apparent halflives of hepta- to decabrominated diphenyl ethers in humans as determined in occupationally exposed workers. Environmental Health Perspectives, **114**:176-181.

Tokarz III JA, Ahn M-Y, Leng J, Filley TR, Nies L (2008) Reductive debromination of polybrominated diphenyl ethers in anaerobic sediment and a biomimetic system, Environmental Science and Technology, **42**:1157-1164.

Toms L, Mueller J, Bartkow M, Symons R (2006a). Assessment of concentrations of polybrominated diphenyl ether flame retardants in indoor environments in Australia. Australian Government Department of the Environment and Heritage, Canberra.

Toms LML, Harden F, Hobson P, Papke O, Ryan JJ, Muller J (2006b). Assessment of the concentrations of polybrominated diphenyl ether flame retardants in the Australian population: levels in blood. Australian Government Department of the Environment and Heritage, Canberra.

Toms LML, Mueller J, Mortimer M, Symons R, Stevenson G & Gaus C (2006c). Assessment of concentrations of polybrominated diphenyl ether flame retardants in aquatic environments in Australia, Australian Government Department of the Environment and Heritage, Canberra.

Toms LM, Harden FA, Symons RK, Burniston D, Furst P, Muller JF (2007). Polybrominated diphenyl ethers (PBDEs) in human milk from Australia. Chemosphere, **68**:797–803.

Toms LML, Hearn L, Kennedy K, Harden F, Bartkow M, Temme C and Mueller JF (2009). Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. Environ Int. (<u>https://www.ncbi.nlm.nih.gov/pubmed/19351571</u>) **35**: 864-9.

UNEP (2007) Risk profile on commercial octabromodiphenyl ether. UNEP/POPS/POPRC.3/20/Add.6, Persistent Organic Pollutants Review Committee.

UNEP (2014). Risk profile of decabromodiphenyl ether (commercial mixture, c-decaBDE), prepared by the ad hoc working group on decabromodiphenyl ether Persistent Organic Pollutants Review Committee. **UNEP**/POPS/POPRC.10/10/Add.2 at;

http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC12/MeetingDo cuments/tabid/5191/Default.aspx].

UNEP (2016). UNEP/POPS/POPRC.10/10/Add.2 at;

http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC10/MeetingDo cuments/tabid/5191/Default.aspx].

UNEP (2016). UNEP/POPS/COP.8/CRP.21 at;

http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC10/MeetingDo cuments/tabid/5191/Default.aspx].

UNECE (2009). Globally Harmonised System of Classification and Labelling of Chemicals (GHS) United Nations, 2009. Third edition. Accessed at https://www.unece.org/trans/danger/publi/ghs/ghs_rev03/03files_e.html

US EPA (1987). Polyhalogenated dibenzo-p-dioxins/dibenzofurans; testing and reporting requirements; final rule 40 CFR Parts 707 and 766. Federal Register, Friday 5 June 1987; **52**:21412–21450.

US EPA (1997). Exposure factors handbook. National Center for Environmental Assessment, Washington, DC; EPA/600/P-00/002B. Available from: National Information Service, Springfield, VA; PB2003-101678 and <u>http://www.epa.gov/ncea</u>

US EPA (2008). Toxicological Review of Decabromodiphenyl ether (BDE-209) (CASRN 1163-19-5) in support of summary information on the Integreted Risk Information System (IRIS) – . Washington DC, US Environmental Protection Agency. June 2008.

US EPA (2010). Polybrominated Diphenyl Ethers (PBDEs) Action Plan.

Vieth B, Herrmann T, Mielke H, Ostermann B, Papke O, & Rudiger T (2004). PBDE levels in human milk: the situation in Germany and potential influencing factors – a controlled study. Organohalogen Compounds, **64**:2643-2648.

Watanabe O, Kashimoto T, Tatsukawa (R) (1987). Polybrominated biphenyl ethers in marine fish, shellfish and river and marine sediments in Japan. Chemosphere 16:2389–2396. Cited in Alaee M and Wenning RJ (2002). The significance of brominated flame retardants in the environment: current understanding, issues and challenges. Chemosphere, **46**:579–582.

Watanabe I, Tatsukawa R. (1990). Anthropogenic brominated aromatics in the Japanese environment. In: Proceedings of Workshop on Brominated Aromatic Flame Retardants, Skokloster, Sweden, 24-26 October 1989. Swedish National Chemicals Inspectorate, KEMI, Solna, Sweden, 1990, p. 63-71

Webster TF, Harrad S, Millette JR, Holbrook RD, Davis JM, Stapleton HM (2009) Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. Environ Sci Technol. **43**:3067–3072.

Wilford BH, Shoeib M, Harner T, Zhu Jiping & Jones KC (2005). Polybrominated Diphenyl Ethers in Indoor Dust in Ottawa, Canada: Implications for Sources and Exposure. Environ. Sci. Technol., **39**:7027 –7035.

Wolf M, Riess M, Heitmann D, Schreiner M, Thoma H, Vierle O, & van Eldik R (2000). Application of a purge and trap TDS-GC/MS procedure for the determinations of emissions from flame retarded polymers. Chemosphere, **41**:693-699.

WHO (2001). World Health Organisation, Report of the Expert Consultation on the Optimal Duration of Exclusive Breastfeeding. Department of Nutrition for Health and Development & Department of Child and Adolescent Health and Development. <u>www.who.int/child-adolescent-health/New_Publications/NUTRITION/WHO_CAH_01_24.pdf</u>

Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, la Guardia M, McClean M, Webster TF (2007). Human exposure to PBDEs: associations of PBDE body burdens with food consumption and house dust concentrations. Environmental Science and Technology, **41**:1584-1589. doi10.1021/es0620282.

Wu Q., Baek S.Y., Fang M., Chang Y.S. (2010). Distribution and fate of polybrominated diphenyl ethers in indoor environments of elementary schools. Indoor Air, **20**: 263-270.

Xiao, H., L. Shen (2012). Atmospheric concentrations of halogenated flame retardants at two remote locations: the Canadian High Arctic and the Tibetan Plateau. Environ Pollut., **161**: 154-161.

Zenneg M, Munoz M, Schmid P, Gerecke AC (2013) Temporal trends of persistent organic pollutants in digested sewage sludge (1993-2012). Environment International, **60**:202-208.

Zweidinger RA, Cooper SD, Erickson MD, Michael LC, Pellizzari ED (1979). Sampling and analysis for semivolatile brominated organics in ambient air. ACS Symp. Ser. 94:217–231. Cited in De Wit C (2002). An overview of brominated flame retardants in the environment. Chemosphere, **46**:583-624.

www.nicnas.gov.au