Australian Government
Department of Health
National Industrial Chemicals Notification and Assessment Scheme

Pentabromodiphenyl Ether

Priority Existing Chemical Assessment Report
Assessment No. 43

Date: 5 MAY 2020

National Industrial Chemicals Notification and Assessment Scheme

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Preface

The Minister for Health (then Health and Ageing) declared, by notice in the Chemical Gazette of 3 January 2006, pentabromodiphenyl ether (pentaBDE), CAS No. 32534-81-9, to be a Priority Existing Chemical (PEC) under Division 5 of the Industrial Chemicals (Notification and Assessment) Act 1989 (the ICNA Act).

Within 28 days of this declaration, importers of pentaBDE were required to apply in the approved form for the chemical to be assessed. By notice in the Chemical Gazette, the Director of NICNAS required all persons who introduced the chemical during the period beginning 12 months before the date of the notice and ending 12 months after that date, to provide information about the chemical. Under section 56(2) of the ICNA Act, only persons who had applied for the assessment of chemical (the Applicants) could introduce the chemical into Australia during the assessment period of the chemical.

Two Applicants (and other users of pentaBDE) provided information about the chemical, such as the properties of the chemical, the quantities of the chemical that had been, or were proposed to be imported or manufactured (including handling and storing and methods of manufacture), uses or potential uses of the chemical and other matters specified under Section 58 of the ICNA Act.

The human health and environment risk assessment was then conducted and this report was prepared by officers in the Office of Chemical Safety (OCS) within the Australian Government Department of Health, in accordance with the ICNA Act. Officers from the Australian Government Department of Agriculture, Water and the Environment (DAWE) contributed to the environmental sections of this report.

In accordance with the ICNA Act, publication of this report revokes the declaration of this chemical as a PEC. Therefore, introducers wishing to introduce this chemical in the future do not need to apply for assessment. However, introducers need to be aware of their duty to provide any new information to the Director, as required under Section 64 of the ICNA Act.

From 1 July 2020, the Industrial Chemicals Act 2019 (the IC Act) replaces the ICNA Act. Section 100 of the IC Act obliges introducers of pentaBDE to provide any additional information about pentaBDE that has become available to them, to the Executive Director of the Australian Industrial Chemicals Introduction Scheme (AICIS).

For the purposes of Section 78(1) of the ICNA Act, copies of NICNAS assessment reports (including this and other PEC reports) are freely available from the NICNAS website. Hard copies are available free of charge from NICNAS from the following address:

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You can find more information on the NICNAS website.

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
DAWE	Australian Government Department of Agriculture, Water and the Environment
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

The Minister for Health (formerly Health and Ageing) declared pentabromodiphenyl ether (pentaBDE), CAS Number 32534-81-9, a Priority Existing Chemical (PEC) for full risk assessment under the ICNA Act by notice in the Commonwealth Chemical Gazette of 3 January 2006. PentaBDE was declared because:

- it represented about 19% (72 tonnes) of all polybrominated flame retardants (PBFRs) imported into Australia in 1998-1999
- some animal studies reported that pentaBDE caused liver degeneration and affected liver enzymes as well as thyroid hormone levels in vitro
- there was evidence that exposure to congeners in the commercial formulation during neonatal brain development in mice caused neurobehavioural changes
- congeners derived from pentaBDE were the main PBFRs found in human breast milk in Australia
- it is highly toxic to aquatic organisms and has been shown to be persistent and bioaccumulative with potential for long-term adverse environmental effects.

Polybrominated diphenyl ethers (PBDEs) with 3-10 bromine atoms are used commercially as additive flame retardants. Flame retardants are used to retard fire in both natural and synthetic polymeric materials, such as cotton textiles and thermoplastic resins. The commercial PBDE products, pentaBDE and octabromodiphenyl ether (octaBDE), have been used as flame retardants; however, the production of these chemicals ceased by 2005 (European Communities, 2001a; Great Lakes Chemical Corporation, 2005). The only PBDE product in current production is commercial decabromodiphenyl ether (decaBDE).

The commercial formulation of pentaBDE is listed in Annex A of the Stockholm Convention on Persistent Organic Pollutants (the Stockholm Convention) as ‘c-pentaBDE’, which consists mostly of tetrabrominated (BDE-47), pentabrominated (BDE-99, BDE-100) and hexabrominated (BDE-153, BDE-154) diphenyl ether congeners. Parties to the Convention must take measures to stop the production and use of pentaBDE.

PentaBDE (including tetra- and pentabrominated congeners) are listed in Annex III of the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (the Rotterdam Convention). As a result, importation of the mixture of the chemicals are subject to the prior informed consent (PIC) procedure.

Introduction and uses

PentaBDE has never been manufactured in Australia. Data provided to NICNAS during the assessment of PBFRs in 1999 and the call for information for PBFRs in 2004 indicated no manufacture of pentaBDE in Australia. Consultation with the applicants for assessment of pentaBDE (known past importers of pentaBDE) in 2005 and in 2017 (1 past importer), confirmed that importation of pentaBDE as a pure chemical or as a component in chemical products ceased in 2005. On 6 March 2007, the then Minister of Health and Ageing also prohibited the manufacture and import of pentaBDE while the chemical remains a PEC. The immediate prohibition was based on a precautionary approach to the regulation of pentaBDE.

In Australia, pentaBDE was used as an additive flame retardant for flexible polyurethane foam at a level of 2.5-15% of the polyol mixture (equivalent to a final pentaBDE concentration of 1.63-9.75%). The polyurethane foam containing pentaBDE was used in commercial furniture, such as transport seats, and domestic furniture, such as beds. PentaBDE was also used as an additive flame retardant for rigid polyurethane, epoxy, unsaturated polyesters and flexible PVC compounds. Epoxy resin formulations containing pentaBDE were also supplied to the aerospace industry and used in potting agents, and in laminating and adhesive systems.

An unknown quantity of pentaBDE has been imported in articles in the past. These, as well as articles produced in Australia, are likely to remain in use for some time. These are mostly polyurethane foam-containing articles, for example transport seats and mattresses.

Health effects

Based on toxicity studies of pentaBDE, tetra- to hexabrominated PBDEs have low acute toxicity by oral, dermal or inhalation routes. They are not skin or eye irritants, or skin sensitisers. Available information shows that they are neither genotoxic, nor result in foetal death or malformation when administered during pregnancy. No information is available on the carcinogenic potential; however, they are not considered to be human carcinogens.

Following single and repeated dosing of laboratory animals, liver enlargement and induction of metabolic enzymes was seen at comparatively low doses. More subtle effects of pentaBDE and individual congeners on specific mechanisms of toxicity, particularly during development, were further examined in a large number of studies. These studies indicated that certain developmental effects, particularly on the brain and the reproductive organs, occurred at low doses following treatment in rat or mouse pregnant dams or neonates.

A number of studies reported effects on the brain resulting in changes in neurobehavioural development. The offspring of pregnant rat dams treated with BDE-99 or BDE-47 showed higher activity levels, along with ultrastructural changes in the ovaries of female offspring and decreased sperm production, without any other changes in sexual function, in the male offspring. Reduced thyroid hormone (thyroxine) levels were seen in the dams following treatment; the effects in pups could be correlated to the change in maternal thyroxine levels. The maternal thyroxine reduction and effects in pups were seen in dams dosed at 0.06 mg/kg bw BDE-99, the lowest dose tested.

Changes in thyroxine levels in dams or pups have been implicated in the developmental effects in the brain and reproductive organs. There are physiological differences between rodents and humans that make rodents more susceptible to thyroid-mediated effects of this type. Therefore, the rodent results must be considered as conservative compared with humans.

Occupational exposure

PentaBDE is no longer imported into Australia as a raw material; however, it is likely to be present in Australia in articles historically manufactured or imported. Therefore, occupational exposures to pentaBDE in the form of pure chemical or chemical mixture is not expected.

The major route of occupational exposure is expected to be due to release from articles such as foam furnishings. Since articles containing pentaBDE are no longer imported in Australia, occupational exposure from use of articles is expected to decline to minimal levels with the global phase-out of pentaBDE. In addition, pentaBDE is not expected to be bioavailable for exposure after it is incorporated into the polymer matrix.

Public exposure

Public exposure includes direct consumer exposure through use of materials containing pentaBDE and indirect exposure via the environment. Exposure to pentaBDE is mostly by indirect exposure via the environment, through:

- inhalation or ingestion of pentaBDE-containing dust released from articles within a household
- consumption of food and water.

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 (Waller et al., 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 decabrominated congeners. In most cases, the dominant congeners were BDE-209, -99 and -47; 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 pentaBDE based on XRF results. The dust samples targeting TVs as a source gave variable results and did not show any clear pattern or extreme decaBDE concentrations.

Breast milk samples collected were dominated by pentaBDE-related congeners, BDE-47, -99, -100, -153 and -154. These congeners accounted for 91% of the total congeners analysed, with a reported mean value of 10 and 11.4 ng/g lipid weight in 2002-03 and in 1993, respectively.

A tetrabrominated congener, BDE-47, was the dominant congener (50% of total PBDEs) reported in all pooled breast milk.

Environmental effects

Based on available ecotoxicity data, pentaBDE is considered to be toxic to aquatic organisms. PentaBDE can bioaccumulate in fish, and biomagnification of the chemical can occur in birds that eat contaminated fish. Available test data confirm that the congeners found in commercial pentaBDE are highly bioaccumulative and can biomagnify through the food chain. The available data show that where exposure occurred through both food and water, the tetrabrominated congener (BDE-47), pentabrominated congeners (BDE-99 and BDE-100), and hexabrominated congener (BDE-153) were highly bioaccumulative with log bioaccumulation factors (logBAF) values >5 (BAF >100000). Sediment organisms also have the potential to accumulate congeners found in pentaBDE when exposed through sediment with BAFs of 4 (BDE-99) to 9.1 (BDE-154) found for tetra- through to hexabrominated congeners.

Modelled and measured levels of pentaBDE in remote environments indicates that pentaBDE and the congeners in commercial formulations can undergo long-range transport (LRT). The LRT ability of pentaBDE was a criterion for its classification as a persistent organic pollutant (POP) substance.

Environmental exposure

PentaBDE can be released and distributed into the environment through many channels, including:

- release into the atmosphere or waste water from its industrial uses and disposal
- emission or dust from pentaBDE-containing articles
- leaching and emission from landfill.

The most significant environmental compartment to which pentaBDE is predicted to partition into is the soil, except if release is all to water, in which case partitioning will be mostly to sediments.

There are measured data available for Australian sediments, and indoor and outdoor air. Combined measured concentration of congeners BDE-47, 99, 100, 153 and 154 levels, or $\sum_{26}$BDE (sum of total bromodiphenyl ether congeners), is used to represent the dust exposure level of pentaBDE. Overall, the dust PBDE levels in office sites were higher than in homes.

The highest levels of penta- and tetrabrominated congeners in Australia were found in:

- sediment samples from Port Phillip Bay in the lower Yarra area in Victoria
- the Molonglo sewage treatment plant (STP) in Canberra (in the Australian Capital Territory).

The combined levels of pentabrominated related congeners at Port Phillip Bay and Molonglo STP were 6.9 and 3.75 µg/kg dw, respectively.

Recommendations

This section provides the recommendations arising from the priority existing chemical assessment of the declared chemical, pentaBDE.

Considering the human health and environmental effects of pentaBDE and its fate in the environment, and noting that pentaBDE formulation (tetraBDE and pentaBDE) is for elimination listed on Annex A of the Stockholm Convention and on Annex III of the Rotterdam Convention, where importation is subject to prior informed consent (PIC) procedure, NICNAS makes the following recommendations:

Recommendation 1

- that pentaBDE be considered for evaluation under the Industrial Chemicals Act 2019 (commencing 1 July 2020), to determine whether pentaBDE should be removed from the Australian Inventory of Industrial Chemicals.

Recommendation 2

- that the Department of Agriculture, Water and the Environment, in consultation with states and territories develop a plan to address the environmental risks of pentaBDE, including in existing products and articles, 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 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 Act) the applicants, as well as any other importers or manufacturers of the notified chemical, have post-assessment regulatory obligations to notify NICNAS when any relevant 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 pentaBDE, or degradants of pentaBDE;
- additional information has become available to the person as to an adverse effect of degradants of pentaBDE on occupational health and safety, public health, or the environment.

or

Under Section 64(2) of the Act; if

- the chemical (pentaBDE) is to be used for any other purpose than either (a) those purposes disclosed to the Director through the call for information to industry or (b) for a purpose subject to specific exemption as defined by Part IV to 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.

Please note that, from 1 July 2020, the Industrial Chemicals (Notification and Assessment) Act *1989* will be replaced by the Industrial Chemicals Act 2019 (the IC Act), wherein Section 100 of the IC Act sets out obligations on the introducers of pentaBDE to provide any additional information about pentaBDE, that has become available to them, to the Executive Director of Australian Industrial Chemicals Introduction Scheme (AICIS).

1 Introduction

1.1 Declaration

Pentabromodiphenyl ether (pentaBDE; benzene, 1,1'-oxybis-, pentabromo derivative, Chemical Abstracts Service Registration Number (CAS RN) 32534-81-9), was declared a priority existing chemical (PEC) for a full risk assessment under the Industrial Chemicals (Notification and Assessment) Act 1989 (Cwlth) (the ICNA Act) by notice in the Commonwealth Chemical Gazette of 3 January 2006. PentaBDE was declared because it represented approximately 19% (72 tonnes) of all polybrominated flame retardants (PBFRs) imported into Australia in 1998/99. PentaBDE was used as an additive flame retardant for flexible polyurethane foam, rigid polyurethane, epoxy, unsaturated polyesters and flexible polyvinyl chloride (PVC) compounds. The polymer urethane foam was used in furniture such as transport seats and beds. Epoxy resin formulations were used in the aerospace industry, as potting agents for electronic components, and in laminating and adhesive systems.

In animal studies, evidence existed that pentaBDE caused liver degeneration, and adverse effects on liver enzyme and thyroid hormone levels in vitro. There was also evidence that exposure to pentaBDE during a critical phase of neonatal brain development caused neurobehavioural changes in mice. Congeners derived from commercial formulation of pentaBDE were the main polybrominated flame retardants found in human breast milk in Australia. The properties of pentaBDE indicate that it is highly toxic to aquatic organisms, and it has shown to be both persistent and bioaccumulative, thereby potentially have continuing adverse environmental effects.

1.2 Objectives

The objectives of this assessment are to:

- identify the extent and patterns of use of pentaBDE
- identify the health and environmental hazards of pentaBDE 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 pentaBDE.

No current importers of pentaBDE or products containing pentaBDE have been identified.

Information on the uses and quantities of pentaBDE imported into Australia in its pure form or as a component in chemical products was provided by companies previously importing pentaBDE. Information was also obtained from published papers identified in a comprehensive literature search of several online databases and retrieved from other sources, particularly the 1994 review by the International Programme on Chemical Safety (IPCS) of polybrominated diphenyl ethers (PBDEs) (IPCS, 1994), the 2001 Risk Assessment Report on pentaBDE published by the European Union (EU RAR) (European Communities, 2001b), the 2006 Report of the Persistent Organic Pollutants Review Committee (POPRC) on the risk profile on commercial pentaBDE (UNEP, 2006) and the 2007 Report of the POPRC on risk management evaluation on commercial pentaBDE (UNEP, 2007a). The POPRC documents (risk profile and risk management evaluation) were accepted by the Stockholm Convention Conference of the Parties (UNEP, 2006, 2007b). Summaries of the relevant health and environmental effects were taken from these documents.

Data provided to NICNAS by industry for an assessment of polybrominated flame retardants (PBFRs) in 1999 (NICNAS, 2001) and the call for information for PBFRs in 2004 indicated no manufacture of pentaBDE in Australia. Applicants for assessment of another PBFR, decabromodiphenyl ether (decaBDE), who were consulted in 2005, indicated that importation of pentaBDE as a pure chemical, or in chemical products, ceased prior to the declaration on pentaBDE as a PEC. However, an unknown quantity of pentaBDE was imported in articles, particularly articles (such as furniture) containing polyurethane foam and these articles, as well as those produced in Australia in the past, may still be in use.

The characterisation of human exposure to pentaBDE in Australia was partly based upon information from a group of monitoring studies commissioned by the Environmental Protection and Heritage Council (EPHC) and the Australian Government Department of Environment and Heritage (DEH) (now the Department of Agriculture, Water and the Environment). Final reports from these studies were published in January 2005 (breast milk) (Harden et al., 2005) and March 2007 (human serum, indoor environments, sediment) (Toms et al., 2006a; Toms et al., 2006b; Toms et al., 2006c). Overseas use patterns and occupational exposure models were also considered in the assessment.

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

Brenntag Australia Pty Ltd

260 - 262 Highett Road

HIGHETT, VIC 3190

Foamco Industries Pty Limited

27 Pembury Road

MINTO, NSW 2566

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 does 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 the effectiveness of a flame retardant by itself. Its effectiveness is related to:

- the particular materials or products to which it is applied or into which it is incorporated
- the specified incorporation/application method
- the specified loading/application rate/retention
- the particular fire hazard characteristic assessed, and
- the assessment conditions.

There are accepted test methods for measuring fire performance of materials and products. Generally the tests used to assess the fire performance of 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 used for fire hazard assessments, quality control and setting of specifications for a product 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-retardant treated 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, work wear, children’s wear, military fabrics, and
- polymer components inside mass transit vehicles (aeroplanes, 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 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 (or rate) to which blooming may occur is dependent on a number of factors, which include:

- size and shape of the flame retardant molecule/polymer
- geometric structure of the plastic matrix
- stability of the flame retardant molecule/compound in the 'melt' (that is compatibility of the flame retardant 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. The physical structure of polyurethane foams will essentially preclude blooming.

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.

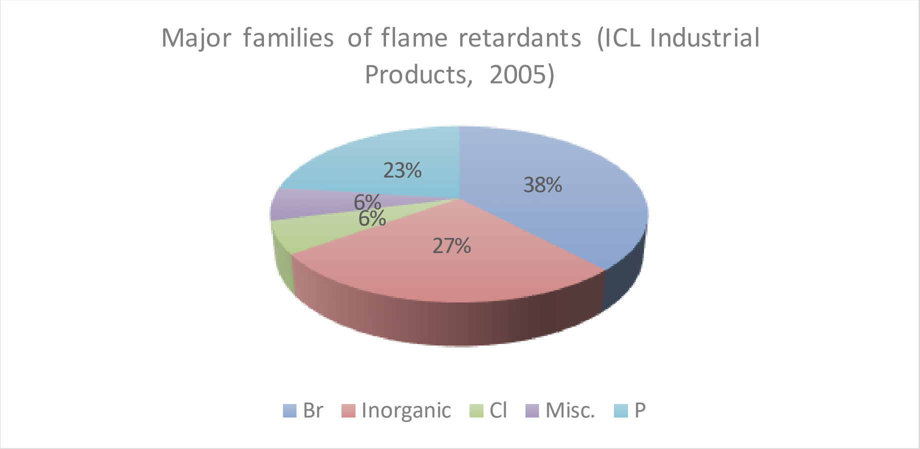
The choice of a given flame retardant depends on the type of application; a flame retardant cannot necessarily be substituted with another for any particular application. Their suitability is subject to variables such as the material requiring treatment, the fire safety standards with which the product must comply, cost considerations and recyclability. For base chemicals requiring treatment, 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 effectiveness as a flame retardant.

The graph below was produced by a major producer of flame retardants. It 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 3 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 (Van-Esch, 1997).

Polybrominated diphenyl ethers

Polybrominated diphenyl ethers (PBDEs) are a group of aromatic brominated compounds in which 1-10 hydrogen atoms in the diphenyl ether structure are replaced by bromine atoms. There are 209 possible PBDE congeners containing 1-10 bromine atoms (See Appendix 1 – Nomenclature for PBDE congeners), although most of these are unlikely to be commercially available. PBDEs with 3-10 bromine atoms are used commercially as additive flame retardants.

The only PBDE product in current production is commercial decabromodiphenyl ether (decaBDE). 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 2 flame retardants in 2005 due to concerns over health effects (Great Lakes Chemical Corporation, 2005). In Europe, the marketing and use of pentaBDE was prohibited in 2003 (European Communities, 2001a). However, due to the production and use of these chemicals in the past, many articles incorporating these flame retardants are still in use. Another commercial PBDE product, tetrabromodiphenyl ether (tetraBDE), is reported to have been used in Japan but no longer in production since 1994 (IPCS, 1994). The reported characteristics of tetraBDE indicate that its composition was similar to that of pentaBDE but with higher relative proportions of lower brominated species. See Appendix 1 for discussion of the congener distribution in these older products.

Commercial PBDE products are mixtures of individual congeners. TetraBDE, pentaBDE and octaBDE are commercial formulations containing a mix of 3-6, 4-6 and 6-10 bromine atoms, respectively. Current formulations of decaBDE contain ≥97% BDE-209 (BDE-209 refers to a fully brominated PBDE conger with 10 bromine atoms), with the major impurities being lower brominated diphenyl ethers, predominantly the 3 nonabrominated diphenyl ether congeners (IPCS, 1994).

This report considered the pentaBDE product as consisting of a number of pure congeners, particularly BDE-47 (a tetrabrominated congener), and BDE-99 and BDE-100 (pentabrominated congeners), with smaller quantities of other congeners including hexabrominated congeners, in addition to other tetra- and pentabrominated congeners.

2.2 International perspective

The growth of international interest in PBDEs

The 3 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 being detected in outdoor and indoor air, dust, sewage sludge, sediment, fish, aquatic birds, marine mammals and other wildlife (Chen and Hale, 2010; Jansson et al., 1987; Watanabe et al., 1987). Human monitoring showed the same trends; increasing levels of 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 (Krüger, 1988).

In response to these early findings, the following international engagements were initiated:

- International Programme on Chemical Safety (IPCS, 1994) report on the effects of PBDEs on human health and environmental quality
- voluntary agreement to not produce PBDE mixtures apart from pentaBDE, octaBDE, and decaBDE by international flame retardant producers and
- 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 concerning persistence and bioaccumulation, PBDEs potentially produce brominated dioxins and furans at some stage of their life cycle (IPCS, 1994). In the USA, 8 brominated flame retardants including pentaBDE, octaBDE and decaBDE were subject to a Toxic Substances Control Act (TSCA) test rule (published 5 June 1987), requiring analyses for the presence of brominated dioxins and furans [US Federal Register 52: 21412] (USEPA, 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 pentaBDE. Major assessments included:

- 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)
- the International Programme on Chemical Safety (IPCS) publication of Environmental Health Criteria (EHC 162) monograph on Brominated Diphenyl Ethers in 1993 (IPCS, 1994)

- the European Chemicals Bureau publication of the European Union Risk Assessment Report (EU RAR): diphenyl ether, pentabromo derivative (pentabromodiphenyl ether). 1st Priority List, Volume 5 (European Communities, 2001b)
- Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers (PBBs and PBDEs) (Pohl et al., 2004)
- Ecological Screening Assessment Report on PBDEs (Government of Canada, 2006a) and
- State of the Science Report for a Screening Health Assessment on PBDEs (Government of Canada, 2006c).

The Furniture Flame Retardancy Partnership, which is a voluntary partnership program initiated by the US EPA's Design for the Environment (DfE) Program, published a report in September 2005 on Environmental profiles of chemical flame-retardant alternatives for low-density polyurethane foam, Volume 1 and 2 (USEPA, 2005).

The US EPA has also produced an assessment of the potential health risk of pentaBDE to children as part of its Voluntary Children's Chemical Evaluation Program Pilot (VCCEPP), under the US EPA's 'Chemical Right to Know' initiative. The assessment was sponsored by Chemtura (formerly Great Lakes Chemical Corporation) (Environ International Corporation, 2003). Under its Integrated Risk Information System (IRIS) program, the US EPA produced a toxicological review of the pentaBDE congener, BDE-99, that was released in June 2008 (USEPA, 2008), and an exposure assessment of PBDEs was published in May 2010 (USEPA, 2010).

Assessment and risk management activities in Europe

Risk Assessment under Council Regulation No. 793/93

PentaDE was the subject of a risk assessment carried out in accordance with the European Economic Community (EEC) Council Regulation No 793/93, of 23 March 1993, on the evaluation and control of the risks of 'existing' substances. Under EEC Regulation 793/93, the European Commission was required to draw up a list of priority substances and allocate these to Member States for evaluation. PentaBDE was listed as a priority substance in the European Commission (EC) Regulation 2268/95, of 27 September 1995, concerning the second list of priority substances as foreseen under EEC Regulation 793/93. In accordance with this, the UK government undertook a risk assessment of pentaBDE, with results published in a European Union Risk Assessment Report (EU RAR) in 2001 (European Communities, 2001b). The EU RAR identified polyurethane foam manufacture and processing as the source of exposure to pentaBDE occupationally and environmentally, while consumer exposure was deemed negligible. PentaBDE was found to be not readily biodegradable, with its congeners widely detected in the environment, including in predatory birds and mammals. Identified risks included those to organisms living in aquatic sediments and soil compartments, and secondary poisoning of top predators. Possible formation of brominated dibenzo-p-dioxins and dibenzofurans from combusted articles was also noted.

The environmental aspect of the report identified some problems, including: the absence of more accurate data on actual releases from the various lifecycle stages of pentaBDE; uncertainty regarding historical use of the substance in other polymeric materials which may have been imported into the EU that could not be accounted for quantitatively despite the possible contributions to regional emissions; the lack of quantification of regional emissions from landfills and incinerators which may increase its long-term levels; and the implications of its presence in the tissues of higher organisms.

The potential for bioaccumulation of the congeners contained in pentaBDE in humans is of concern as well as the chloracne-like response reported in repeated dose dermal studies. The absence of carcinogenicity and fertility data as well as the absence of consensus as to the significance (if any) of the neurobehavioural effects seen in the single exposure of neonatal mice, were limitations that influenced risk characterisation. The potential risk through breast milk consumption in infants and the lack of toxicokinetic information relating to this, including multi-generational reproduction study of the effects of breast milk, were also of concern.

Apart from recommending information provision to address some data gaps, the EU RAR recommended future revision be considered when issues such as increases in tissue concentration in higher organisms have been documented. The EURAR further recommended that, due to the properties of pentaBDE, risk reduction measures need to be initiated at the policy level immediately without waiting for results of the recommended studies.

As a consequence, regulatory actions to protect both human health and the environment were adopted in 2001. Member States implemented a Risk Reduction Strategy for pentaBDE followed by a European Commission Recommendation, which requested marketing and use restrictions under Directive 76/769/EEC. Annex 1 to the Directive 76/769/EEC states the following restrictions for pentaBDE:

1. May not be placed on the market or used as a substance or as a constituent of substances or of preparations in concentrations higher than 0.1% by mass and
2. Articles may not be placed on the market if they, or flame-retarded parts thereof, contain this substance in concentrations higher than 0.1% by mass (European Communities, 2001b).

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 and in promoting the collection and recycling of such equipment, called the Restriction of Hazardous Substances (RoHS) Directive (Directive 2002/95/EC). The RoHS Directive restricts (with exceptions) the use of 10 hazardous materials, including PBDEs, 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 to ensure that new electrical and electronic equipment placed in the market of any Member State does not contain more than the agreed levels of lead, cadmium, mercury, hexavalent chromium, PBBs and PBDEs. The maximum concentration level for PBDEs is 0.1% by weight of homogeneous materials.

The RoHS is closely linked with the Waste Electrical and Electronic Equipment (WEEE) Directive (Directive 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.

Under this Directive, plastics in waste electrical and electronic equipment that contain brominated flame retardants require selective treatment. The waste must be diverted from landfill and removed from other collected WEEE, and disposed of, or recovered in compliance with the Waste Framework Directive (Directive 2008/98/EC on waste and repealing certain Directives).

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 4 kg per inhabitant per year. The collection rates were revised to 45% of the weight of electrical and electronic products entering the market. This Directive requires the recovery or disposal of waste without endangering human health and without using processes or methods that could harm the environment.

Assessment and risk management activities in North America

United States of America (USA)

At the state level, legislation prohibiting the use of pentaBDE and octaBDE exists in California, Hawaii, Illinois, Maine, Maryland, Michigan, Minnesota, New York, Oregon, Rhode Island and Washington. Complementing the phase-out of pentaBDE and octaBDE in many states, and the voluntary phase-out by Chemtura (formerly Great Lakes Corporation – the only manufacturer in the USA) which took effect on 31 December 2004, the United States Environmental Protection Agency (US EPA) promulgated a Significant New Use Rule (SNUR) under the Toxic Substances Control Act (TSCA) in June 2006 covering 6 groups of PBDEs (tetra-, penta-, hexa-, hepta-, octa- and nonabrominated diphenyl ethers) and any combinations of these chemicals, requiring notification to US EPA at least 90 days before commencement of manufacture or import for any use on or after 1 January 2005. 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 (USEPA, 2013).

Another response to the phase-out of pentaBDE and octaBDE was the creation of the Furniture Flame Retardancy Partnership in December 2003, a US EPA (Design for the Environment) initiated program that not only involves the furniture industry and chemical manufacturers but also environmental groups, fire safety advocates and other government agencies. This voluntary partnership program was established to identify chemical alternatives to pentaBDE that are safer to human health and the environment.

Another US EPA initiative under the Office of Pollution Prevention and Toxics is the Voluntary Children's Chemical Evaluation Program (VCCEP). This program aims to give citizens information on the effects of chemicals on children to enable informed choices in the home and marketplace. A total of 23 substances, including pentaBDE, octaBDE and decaBDE, which were deemed to be most ubiquitous in children, were chosen for evaluation.

By the end of 2004, pentaBDE and octaBDE formulations were voluntarily withdrawn from the US marketplace by their manufacturers, 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.

In April 2012, the US EPA issued a proposed rule that would amend the TSCA section 5(a) SNUR for certain PBDEs, and that would require persons who manufacture, import, or process any of 3 commercial PBDEs (i.e. penta-, octa- or decaBDE), including in articles, for any use after 31 December 2013, to conduct testing under TSCA section 4(a).

Canada

In Canada, human health and ecological screening assessments were conducted on PBDEs as required by the Canadian Environmental Protection Act*, 1999* (CEPA 1999). The assessment reports, State of the Science Report for a Screening Health Assessment (Government of Canada, 2006c) and Ecological Screening Assessment (Government of Canada, 2006a), were published in 2006. Although the health screening assessment identified data gaps and limitations to determine a more meaningful population exposure to PBDEs, the ecological screening assessment concluded that PBDEs were entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Based on the ecological assessment, PBDE congeners (tetra- to decabrominated) were added to the List of Toxic Substances in Schedule 1 of CEPA 1999 in December 2006. Furthermore, the screening assessment concluded that tetra- penta-, and hexabrominated congeners meet the criteria for persistence and bioaccumulation as defined by the Persistence and Bioaccumulation Regulations under CEPA 1999. The 3 PBDEs met the condition for mandatory addition to the Virtual Elimination List due to their presence resulting from human activity. The Virtual Elimination List aims to reduce the amount or concentration of listed toxic substances to below a defined level of quantification (Government of Canada, 2006b).

As a first step in the risk management process, regulations prohibiting manufacture, use, sale, offer for sale, and import of tetra-, penta- and hexabrominated congeners or any resin, polymer or other mixture containing these PBDEs were published in the Canada Gazette (Government of Canada, 2008).

In 2013, a Federal Environmental Quality Guideline (FEQG) for PBDEs was developed in addition to the risk assessment or risk management identified for PBDEs. The FEQG is intended to protect all forms of aquatic life and wildlife from exposure to water, sediment and biological tissue containing PBDEs (Government of Canada, 2013).

Status of pentaBDE under International Conventions and Councils

The Stockholm Convention

The objective of the Stockholm Convention on Persistent Organic Pollutants (the Stockholm Convention) is to protect human health and the environment from persistent organic pollutants by maintaining measures to reduce and eliminate the intentional and unintentional release of persistent organic pollutants (POPs), including from stockpiles and wastes. The signatories of the Stockholm Convention (which include Australia) have agreed to eliminate the production and use of chemicals listed under Annex A; to restrict the production and use of chemicals listed under Annex B; and to reduce the unintentional release of chemicals listed under Annex C. However, Australia has not ratified the listing of pentaBDE under Annex A, B or C of the Stockholm Convention.

In January 2005, Norway, as a Party to the Stockholm Convention, submitted a proposal to list pentaBDE in Annex A to the Convention. The Persistent Organic Pollutant Review Committee (POPRC) concluded in its review, that the commercial product pentaBDE referred to as ‘c-pentaBDE’ meets the screening criteria specified in the Annex D of the Stockholm Convention for a substance to be considered persistent, bio-accumulative and possessing the potential for long-range environmental transport; therefore, pentaBDE should be considered as a persistent organic pollutant (UNEP, 2005). PentaBDE is a mixture of bromodiphenyl ether congeners in which the main components are 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47; CAS Number 40088-47-9) and 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99; CAS Number 32534-81-9), with both having the highest concentration by weight compared to the other components of the mixture.

A Risk Profile prepared by the POPRC was adopted in 2006 and, subsequently, a Risk Management Evaluation was prepared and considered in 2007 (UNEP, 2006, 2007a). Both reports concluded that risk management would be best served by a global ban on production and use of pentaBDE, covering all sectors, and that listing components of pentaBDE mix under Annex A of the Stockholm Convention would be the most appropriate measure, given that most developed countries have already banned production. Therefore, it was recommended that Conference of the Parties (UNEP-FAO, 2013) to the Convention consider listing 2,2', 4,4'- tetrabromodiphenyl ether (BDE-47, CAS No. 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99, CAS No. 32534-81-9) and other tetra- and pentabrominated congeners present in commercial pentaBDE. Due to the predominance of BDE-47 (tetrabrominated congener) and BDE-99 (pentabrominated congener) in pentaBDE, these were used as markers for enforcement purposes in Annex A of the Stockholm Convention (UNEP, 2007a). At the 4th Meeting of the Conference in May 2009, the Conference agreed to list tetra- and pentabrominated congeners as the main components of commercial pentabromodiphenyl ether in Annex A of the Stockholm Convention, with specific exemption for articles containing either of these in accordance with the provisions of Part IV to Annex I. The provisions of Part IV allow the recycling of articles that contain or may contain penta- and tetrabrominated congeners. In addition, the provisions also allow the use and final disposal of articles manufactured from recycled materials that contain or may contain either of these, provided that the recycling and disposal is carried out in an environmentally sound manner and does not lead to recovery of these chemicals for the purpose of their reuse.

Rotterdam Convention

The aim of the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (the Rotterdam Convention) is ‘to protect human health and the environment from potential harm by promoting shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals, and by contributing to the environmentally sound use of those hazardous chemicals through exchange of information about their characteristics as well as provision of national decision-making process on their import and export, and by disseminating these decisions to Parties’. The Rotterdam Convention entered into force in 2004, and it requires the notifications of 2 Parties of final regulatory control actions taken in relation to a chemical to institute a ban or severely restrict a chemical under the Convention. Australia is party to the Convention.

At the 6th Meeting of the Conference of the Parties in 2013, the Conference agreed to list pentaBDE (including tetra- and pentabrominated congeners), in Annex III of the Rotterdam Convention and adopted the decision-guidance document (UNEP-FAO, 2013) with the effect that the mixture of the chemicals are subject to the prior informed consent (PIC) procedure, where Parties are requested to make an informed decision as to whether or not they consent to the future import of the pentaBDE (including tetra- and pentabrominated congeners). In

Australia, pentaBDE is subject to an interim ban and the decision as to whether or not to consent the future import of the chemical has not yet been finalised.

2.3 Australian perspective

Polybrominated flame retardants (PBFRs) 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 ICNA Act). This was 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, and
- labels, material safety data sheets and other hazard communication materials be revised to reflect the information on hazards already available for these chemicals (NICNAS, 2007c).

In 2005, decaBDE was declared as a PEC for full risk assessment, with the declaration notice for decaBDE covering its degradation products, which included penta- and octaBDE. PentaBDE and octaBDE were also declared on 3 January 2006 as PECs for full risk assessment under the ICNA Act (NICNAS, 2006). The reasons for declaration for pentaBDE and octaBDE were that in animal studies, pentaBDE and octaBDE caused liver and thyroid effects, and changes in neurobehavioural development when individual congeners were administered to neonatal mice during a critical phase of brain development. OctaBDE showed toxicity to embryos in rats and rabbits, while pentaBDE and octaBDE had components that are known to bioaccumulate, and these have been detected in breast milk in Australia (NICNAS, 2007c).

Due to the absence of assessment applications for octaBDE, indicating that it is not imported or manufactured in Australia, it was removed from the Australian Inventory of Chemical Substances (AICS). Therefore, future manufacture and importation of octaBDE are not permitted in Australia, except as laboratory standards for analytical determination. Persons importing octaBDE for analytical purposes must comply with annual reporting obligations as required under the ICNA Act (NICNAS, 2007a).

A monitoring study in Australia commissioned by the Australian Government the Department of the Environment and Heritage (DEH, now the Department of Agriculture, Water and the Environment (DAWE)) indicated low levels of PBDEs in breast milk. The study reported a mean PBDE level in breast milk of 11 ng/g lipid weight (lw) (range 6-18 ng/g lw). The PBDE levels detected were higher than those reported in Europe and Japan, but lower than in North America and Canada (Harden et al., 2005).

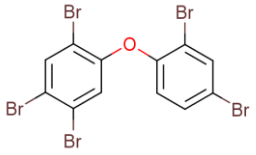
In 2004, 3 separate studies were commissioned by the DEH to measure levels of PBDEs in human serum, indoor dust and sediments. In the Australian population, the highest levels of

PBDEs were detected in the blood of young children, and at lower levels in women of child bearing age (Toms et al., 2006a). Indoor dust measurements showed that concentrations of PBDE were greater indoor air than in outdoor air. PBDE levels in Australian indoor air were generally lower than or similar to other countries, such as Canada and USA (Toms et al., 2006c). In the aquatic environment, levels in Australia were found to be lower compared with samples from industrialised countries such as Europe and North America (Toms et al., 2006b).

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 pentaBDE) (NICNAS, 2007c). 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, due to the developmental effects reported 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 applying an interim prohibition to the importation and/or manufacture of pentaBDE and mixtures containing pentaBDE into Australia, which took effect on 6 March 2007 (NICNAS, 2007b).

3 Identity, Composition and Properties

3.1 Chemical identity

Chemical identity information	
IUPAC name	benzene, 1,1'-oxybis-, pentabromo derivative
Chemical name	pentabromodiphenyl ether
CAS no:	32534-81-9
EINECS No:	251-084-2
SMILES representation	c1ccccc1Oc1ccccc1.[*]Br.[*]Br.[*]Br.[*]Br.[*]Br
Synonyms	PeBDE; PentaBDE; PeBDPE; PeBBE; PeBBO; PeBDPO; pentabromo biphenyl oxide; pentabromodiphenyl oxide; pentabromo phenoxybenzene; benzene 1,1′ oxybis-, pentabromo derivative; pentabromobiphenyl ether; pentabromophenyl ether
Trade name	DE 71, Bromkal 70-5 DE, Bromkal 70, Bromkal G 1, Saytex 125, FR 1205, FR 1215, DE 60FTM, Planelon PB 501, Tardex 50
Molecular formula	$C_{12}H_5Br_5O$ (nominal)
Molecular weight	564.75 (nominal) 485.82 - 643.62 (range for more common congeners)
Structural formula	

PentaBDE is a member of a class of chemicals known as PBDEs. This class includes all chemicals with the diphenyl ether structure where 1 or more of the hydrogens have been substituted by bromine, and the members of this class range from monobrominated to decabrominated. In total, there are 209 different chemicals (congeners) in the category of PBDEs once the positional isomerism is taken into account (Appendix 1). Of these, only a small number have industrial use. These derive from the commercial products tetraBDE (stated to be no longer in production in 1994 (IPCS, 1994), pentaBDE, octaBDE and decaBDE. PentaBDE and octaBDE consist of a range of congeners of different bromination levels of around 5 moles of bromine per mole of diphenyl ethyl and 8 moles of bromine per mole of diphenyl ethyl, respectively. DecaBDE is close to a pure single congener as currently produced.

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

3.2 Composition of Commercial Product

PentaBDE has been reported to contain a mix of bromination levels ranging from tribrominated to hexabrominated. The average degree of bromination is close to 5 bromine atoms per molecule, with a bromine content of around 71%. The name 'pentabromo derivative' derives from the stoichiometry of the preparative reaction and does not necessarily reflect the actual composition of the final product, which may contain high levels of tetrabrominated congeners. PentaBDE contains mostly congeners in the tetrabrominated (BDE-47), pentabrominated (BDE-99 and BDE-100) and hexabrominated (BDE-153 and BDE-154) range.

The commercial products are produced by direct bromination of diphenyl ether by an electrophilic aromatic substitution reaction, in the presence of a Lewis acid (Friedel-Crafts) catalyst such as aluminium tribromide ($AlBr_3$). The products of nucleophilic aromatic substitution reactions are generally formed under kinetic control of orientation, ie the most reactive sites on the aromatic ring are most rapidly substituted. Substituents on an aromatic ring may be defined as to whether they activate or deactivate the aromatic ring towards electrophilic substitution, and as to whether they direct substitution towards ortho and para positions, or towards meta positions (Pohl et al., 2004).

Control of substitution in bromination of diphenyl ether depends both on the properties of the ether substituent and the properties of each added bromine substituent. The ether group has a stronger directing effect than the bromine, but both are ortho, para directing groups. Accordingly, the strongest directing influence from the ether group will result in dominance of ortho or para substituents, at least for lower levels of bromination. In the presence of comparatively bulky groups, such as the phenyl ether substituent in diphenyl ether, it is common that the para position is much more readily substituted than the ortho positions, and accordingly all major components of pentaBDE are substituted in both para positions (4,4′).

Breakdown products

PentaBDE is expected to break down in the environment by similar mechanisms to decaBDE (i.e. photolysis, metabolic debromination or hydrodebromination) (Refer to Appendix 2). The debromination reactions of decaBDE are also discussed in detail in the NICNAS risk assessment of decaBDE (NICNAS, 2019). It is known that the photolysis of congeners in the bromination range covered by pentaBDE in organic solvents is much slower than that for decaBDE, and reports have indicated that the photolysis products in aqueous systems may be dominated by brominated dibenzofurans and dibenzodioxins. Congeners with a bromination level as low as 4 were seen in the breakdown of decaBDE in organic solvents (Bezares-Cruz et al., 2004).

The breakdown products may be various and dependent on different possible mechanisms of breakdown (i.e. photolytic, metabolic by species, or pyrolytic). Both metabolism and photolysis in aqueous systems have shown to be the major breakdown pathways that include reductive debromination, or formation of oxygenated species. Limited information is available on debromination reactions of pentaBDE, particularly as the commercial product is already a mix of congeners. It is also noted that very little information is available on the identity, concentrations, or the effects of the breakdown products of PBDEs other than lower brominated diphenyl ethers.

Based on the limited range of congeners present in pentaBDE, compared with the theoretical possibility of all congeners arising from stepwise breakdown of decaBDE, it is likely that certain congeners in the lower bromination ranges can arise from decaBDE but not from pentaBDE.

The risk profile for pentaBDE, prepared by the Persistent Organic Pollutants Review Committee (POPRC), states that pentaBDE is persistent and has potential for bioaccumulation and biomagnification. PentaBDE has a long environmental half-life in sediment, soil and air. In the gastrointestinal tract, a pentabrominated congener was reductively debrominated to BDE-47 (a tetrabrominated congener). It is assumed that major congeners in pentaBDE (BDE-47 and BDE-99), are considered to be more toxic and bioaccumulative than other PBDE congeners. Furthermore, the potential for debromination of higher congeners to more toxic congeners with less bromine substituents in the environment is of concern. The characteristics of pentaBDE and its components, particularly those relating to long-range transport, bioaccumulation and toxicity in a range of aquatic organisms and mammals triggered global regulatory action to voluntarily phase out, or prohibit, the manufacture and use of pentaBDE worldwide.

3.3 Physical and chemical properties

Physical properties

PentaBDE appears as an amber viscous liquid or semi solid. The individual pentabrominated congeners, BDE-99 and BDE-100, which are abundant in the commercial mix, are generally white crystalline solids. Due to its application as a flame retardant, it is assumed to not have flammability properties (Pohl et al., 2004).

Information on selected physical properties of pentaBDE are provided in Table 3 below.

Table 3.2 Physical properties of pentaBDE

Property	Value	Reference
Melting point	-7 to -3°C	(European Communities, 2001b)
Decomposition temperature	>200°C	(European Communities, 2001b)
Specific gravity	2.25 to 2.28	(European Communities, 2001b)
Water Solubility	2.4 µg/L at 25°C	(European Communities, 2001b)
	2.4 µg/L at 25°C	(Tittlemier et al., 2002)
	40 µg/L at 25°C (BDE-100)	
Dissociation constant (pKa)	Not expected to dissociate under normal environmental conditions.	
Vapour pressure (Pa)	4.69×10^{-5} at 21°C	(European Communities, 2001b)
	1.76×10^{-5} (BDE-99) at 25 °C	(Tittlemier et al., 2002)
	2.86×10^{-5} (BDE-100) at 25°C	
Partition coefficient (Log K_{ow})	6.57*	(European Communities, 2001b)
	7.32 (BDE-99)	(Braekevelt et al., 2003)
	7.24 (BDE-100)	

Property	Value	Reference
Henry's Law Constant	0.6 Pa.m^3/mol (BDE-99)	(Cetin and Odabasi, 2005)
	0.24 Pa.m^3/mol (BDE-100)	
log K_{oc}	4.48 (BDE-99)	EPIWin v3.11

*6.5 (measured – generator column method based on OECD Test Guideline 105 and EPA 40 CFR Ch. 1 §)

PentaBDE has low water solubility and is expected not to readily dissolve in surface water (relatively hydrophobic). It has high partition coefficients (log K_{ow}), which suggests a great absorption capacity for organic carbon in soils and sediments, and a tendency for bioaccumulation (USEPA, 2010).

The vapour pressures of PBDEs are low, with the vapour pressures decreasing with added bromine atoms and increasing molecular weight (USEPA, 2010; Wong et al., 2001).

Chemical properties

PentaBDE does not contain any functional groups that are able to dissociate under normal environmental conditions.

PentaBDE is unstable at high temperatures, and formation of polybrominated dibenzofurans and dibenzodioxins during incineration may occur. It also decomposes photolytically (European Communities, 2001b).

4 Manufacture, Importation and Use

4.1 Manufacture

PentaBDE has never been manufactured in Australia. Data provided by industry in 1999 (NICNAS, 2001) and in a call for information for PBFRs in 2004, indicated that there was no manufacture of pentaBDE in Australia.

Following growing concerns over pentaBDE in the 1990's, industry voluntarily ceased production of pentaBDE in Europe in 1997 (European Communities, 2001a), and in the US at the end of 2004 (Great Lakes Chemical Corporation, 2005). PentaBDE is not manufactured in Japan and pentaBDE has been voluntarily withdrawn from the market since 1990 (Kajiwara et al., 2004).

It has been reported that pentaBDE of different composition to the originally produced commercial products was available from China after 1999 (UNEP, 2006). However, China has enacted a set of controls over hazardous substances similar to that in use in the RoHS Directive for electrical and electronic equipment. In 2007, pentaBDE was phased out in China and production ceased at the same time (UNEP, 2006).

Data provided by Bromine Science and Environmental Forum (BSEF), the major industry group of manufacturers of PBFRs, indicated that the worldwide demand for pentaBDE declined from 8500 tonnes in 1999 to 7500 tonnes in 2001 (BSEF, 2001). Prior to the establishment of regulatory controls, pentaBDE was manufactured in Israel, Japan, USA and EU (UNEP, 2006).

4.2 Importation of pentaBDE

Data collected from industry indicated that only one pentaBDE product, Great Lakes DE-60F Special, was imported into Australia from 1998 to 2005. Great Lakes DE-60F Special is a proprietary blend including brominated diphenyl ethers. The MSDS for DE-60F Special specifies that it contains >65% of pentaBDE, and <35% aromatic phosphates.

Table 4 Amount of pentaBDE imported into Australia 1998-2006

Chemicals	Import period			
	1998-99	2003-04	2004-05	2005-06
Great Lakes DE-60F Special	72 tonnes	48 tonnes	27.5 tonnes	0 tonnes (projected)
PentaBDE	46.8 tonnes	31.2 tonnes	17.9 tonnes	0 tonnes (projected)

The amount of pentaBDE imported into Australia was reported as 72, 48 and 27.5 tonnes in 1998-99, 2003-04, and 2004-05, respectively. Importation of pentaBDE ceased at the end of June 2005. In 2006, companies listed by the Australian importer as downstream users for the product were contacted and it was confirmed that old stocks of pentaBDE had been used up, and they were no longer using the chemical. An importer also relayed, in January 2006, that the phase-out of pentaBDE use in Australia was almost complete.

A range of formulated products containing pentaBDE were also imported into Australia under the trade name, Epocast. Approximately 400 kg/year were imported for use in the aerospace industry.

4.3 Uses of pentaBDE

In Australia, the product Great Lakes DE-60 F Special was used as an additive flame retardant for flexible polyurethane foam at concentrations of 2.5-15%, which equates to a final pentaBDE concentration of 1.63-9.75%. The polyurethane foam containing pentaBDE was used in both commercial furniture such as transport seats, and domestic furniture, such as beds.

Other uses of the product indicated in the Great Lakes technical information sheet include use as an additive flame retardant for rigid polyurethane, epoxy, unsaturated polyesters and flexible polyvinyl chloride (PVC) compounds. Recommended uses for other pentaBDE products marketed worldwide included use in laminates, adhesives and coatings. It is not known if pentaBDE was ever used for these applications in Australia.

The Epocast products containing pentaBDE are epoxy resin formulations. They are supplied to the aerospace industry and used as potting agents, and in laminating and adhesive systems.

In a review of the use of pentaBDE prepared for the United Kingdom (UK) Department of Environment, Transport and the Regions in 2000, it was estimated that 95% of pentaBDE used in Europe at that time went into the manufacture of flexible polyurethane foam, with the remaining 5% going into non-foamed polyurethanes (RPA Ltd., 2000).

The use of pentaBDE in the following sectors was also identified internationally (UNEP, 2006):

- Electrical and electronic appliances including computers, home electronics, office equipment, household appliances, items containing printed circuit laminates, plastic outer casings and internal plastic parts such as small run components with rigid polyurethane elastomer instrument casings
- Transportation (cars, trains, aircraft and ships) having plastic and textile interiors, and electrical components
- Building materials such as foam fillers, insulation boards, foam insulation, pipes, wall and floor panels, plastic sheetings and resins
- Furniture such as upholstered furniture, furniture covers, mattresses, flexible foam components
- Textiles including curtains, carpets, foam underlay for carpets, tents, tarpaulins, work clothes and protective clothing and
- Polyurethane foam based packaging materials.

The most common use reported for pentaBDE was in polyurethane foam since 1999 (Hale et al., 2002). The polyurethane foams contain 10-18% pentaBDE and are mainly used for furniture and upholstery in domestic furnishing, and in the automotive and aviation industries. In 2000, global production and use of pentaBDE in polyurethane foam production was estimated to be 150,000 tonnes/year polyurethane (equivalent to 15,000 to 27,000 tonnes pentaBDE/year) (European Communities, 2001b).

4.4 PentaBDE in imported articles

No information was collected from the Australian industry regarding the past importation of pentaBDE in imported articles such as furnishings, car parts, or electrical and electronic equipment.

Due to the prohibition of the substance in Europe, it is unlikely any imports of new articles manufactured in Europe into Australia will contain pentaBDE. The use of pentaBDE in electrical and electronic appliances ceased in Europe in July 2006.

The sole manufacturer of pentaBDE in the US voluntarily ceased production in 2004. Therefore, it is unlikely newly manufactured items originating from the US will contain pentaBDE. A number of American states have also restricted the use of pentaBDE.

The main uses of products/articles treated with pentaBDE were identified internationally (RPA Ltd., 2000) as follows:

- Automobile applications including headrests, seating, steering wheels, acoustic management systems, dashboards, door panels and carpeting. PentaBDE is particularly effective in reducing the risk of ignition and the rate of burn and meeting emission levels for volatiles set by the automotive industry
- Production of phosphorus-free pentaBDE-based foams for domestic furniture, some of which includes cot mattresses
- Production of various small run and prototype components, such as rigid polyurethane elastomer instrument casings. Other minor uses identified were in the packaging of electronic equipment within the European countries. It was also noted that scraps from polyurethane were exported from Europe to the US for manufacture of carpet underlay, and
- Use in printed circuit boards and in manufacture of rubber conveyor belts in the mining industry.

The articles in which the PBDEs have been used typically have long useful lives, and accordingly many of the older articles that may contain pentaBDE are expected to be still in use.

5 Human Health and Environmental Effects

5.1 Human Health Effects

Several hazard assessments have been published to investigate the adverse effects PBDEs, including pentaBDE. The current consensus is that there are significant data limitations concerning the toxicity and modes of actions, half-life and metabolism of pentaBDE in experimental animals and in humans (UNEP, 2006). However, data suggest that exposure to lower doses of pentaBDE over extended periods of time may cause health effects, since pentaBDE accumulates in the human body. Possible health effects in vulnerable groups including pregnant women, embryos and infants cannot be ignored, as adverse effects on thyroid hormone levels, and development of the foetal central nervous system have been reported in animal studies. The thyroid hormones play a significant role during pregnancy. Infants may further be exposed to pentaBDE through their mother's milk, since pentaBDE is lipophilic and accumulates in the milk (VKM, 2005). A major uncertainty is that the thyroid hormone system in rodents is much more sensitive than humans to thyroid-mediated effects (NICNAS, 2007c)

No epidemiological studies of workers or populations specifically exposed to pentaBDE are available. Several studies have attempted to relate health outcomes with exposure to PBDEs, including pentaBDE or congeners derived from pentaBDE. A health assessment was conducted for a group of 35 workers exposed for at least 6 weeks to polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) during manufacture. A higher than normal prevalence of primary hypothyroidism with elevated serum concentrations of thyrotropin and low or borderline-low serum total T_4 (thyroxine) and free thyroxine indexes was seen in 4 of these workers (Bahn et al., 1980b). A significant reduction in sensory and fibular motor nerve velocities was also observed. Three of these workers were re-evaluated 1 year after the initial study. Partial reversibility was seen in 1 worker (Bahn et al., 1980a).

Other studies have also been conducted to measure the levels of PBDE in adipose tissue. Samples were taken from 77 Swedish hospital patients of both sexes, 28-85 years of age. Some of the subjects were diagnosed with cancer. In persons without malignancies, the mean BDE-47 level was 5.1 ng/g lipid. Higher levels of tetrabrominated BDE-47 were seen in patients with non-Hodgkin lymphoma (NHL), at 13 ng/g lipid, than in patients without malignancies (Lindström, 1998). Although a link between PBDEs and NHL cannot be excluded, no causal link can be drawn from this work, particularly in the absence of consideration of other contributing factors.

5.2 Environmental Effects

A number of studies were conducted in various organisms in the environment to determine the ecotoxicity of pentaBDE. These studies have been reproduced in this report from various international reports and summarised in Table 5 below. The summary table should be read in conjunction with the references provided.

There is distinct lack of data for avian toxicity; however, biomagnification in fish-eating birds may occur in PBDEs, particularly pentaBDE, which has been detected in birds, including in fish eating birds (KemI, 1999).

5.2.1 Avian Toxicity

There are no data available.

5.2.2 Aquatic and Terrestrial Toxicity

Table 5 Summary of pentaBDE effects on organisms in the environment

Substance	Species	Study Endpoint	Result	Reference
Aquatic compartment				
Pentabrominated congeners (54.6%)	*Oryziaz latipes* (Orange-red killifish)	Fish acute toxicity (LC50 after 48 hours)	> 500 mg/L	(CITI, 1982)
Pentabrominated congeners (54.6%)	*Onchorhyncus mykiss* (Rainbow trout)	Fish acute toxicity (LC50 after 96 hours)	> 21 µg/L	(Palmer et al., 1997b)
Pentabrominated congeners (55.1%)	*Onchorhyncus mykiss* (Rainbow trout)	Early life stage toxicity study (NOEC after 87 day exposure; consisted of 27 day hatching and 60 day post hatch period)	≥ 16 µg/L	(Wildlife International Ltd., 2000d)
BDE-99	*Onchorhyncus mykiss* (Rainbow trout)	Early life stage toxicity study (NOEC after 87 day exposure consisted of 27 day hatching and 60 day post hatch period)	> 12 µg/g egg	(Hornung et al., 1996)
BDE-47	*Pimephales promelas*	Fish acute toxicity – QSAR predictions (LC50 after 96 hours)	27.3-52.2 µg/L	(European Communities, 2001b)
Pentabrominated congeners (54.6%)	*Daphnia magna*	Acute immobilisation test (EC50 after 48 hours)	14 µg/L NOEC of 4.9 µg/L	(Palmer et al., 1997a)
Pentabrominated congeners (54.6%)	*Daphnia magna*	Acute immobilisation test (EC50 after 96 hours and days 7-21)	17 µg/L (96 hours) 14 µg/L (7-21 days) NOEC of 5.3 µg/L based on reduction in length and weight at 9.8 µg/L	(Drottar and Krueger, 1998)

Substance	Species	Study Endpoint	Result	Reference
BDE-99	*Daphnia magna*	QSAR predictions (EC50 after 48 hours)	6.4-13.3 µg/L	(European Communities, 2001b)
BDE-99	*Daphnia magna*	QSAR predictions (NOEC 16 days)	0.38-0.85 µg/L	(European Communities, 2001b)
Pentabrominated congeners (54.6%)	*Selenastrum capricornutum* Fresh water algae	Growth of freshwater microalgae and/or cyanobacteria (EC10 after 24 hours)	3.1 µg/L based on cell density	(Palmer et al., 1997c)
BDE-99	*Selenastrum capricornutum* Fresh water algae	QSAR predictions (EC50 72-96 hours)	3.6-7.6 µg/L	(European Communities, 2001b)
Pentabrominated congeners (55.10%)	*Hyalella azteca*	Sediment toxicity test (EC50 after 28 days)	> 50 mg/kg dry weight	(Wildlife International Ltd., 2000b)
			LOEC of ≥ 13 mg/kg dry weight based on increase in mortality	
			NOEC of 6.3 mg/kg dry weight	
Pentabrominated congeners (55.10%)	*Chironomus riparius*	Sediment toxicity test (EC50 after 28 days)	> 50 mg/kg dry weight LOEC of 50 mg/kg dry weight (nominal) based on decrease in mean development time NOEC of 25 mg/kg dry weight (nominal)	(Wildlife International Ltd., 2000a)
	Lumbriculus variegatus		> 50 mg/kg dry weight	(Krueger et al., 2001)

Substance	Species	Study Endpoint	Result	Reference
Pentabrominated congeners (55.10%)		Sediment toxicity test (EC50 after 28 days)	LOEC of 6.3 mg/kg dry weight based on survival/reproduction	
			NOEC of 3.1 mg/kg dry weight	
Terrestrial Compartment				
Pentabrominated congeners (55.10%)	Soil amended with Lucerne meal	Toxicity to soil microorganisms- Nitrogen transformation test (NOEC after 28 days)	> 1 mg/kg dry weight	(Inveresk, 1999)
Pentabrominated congeners (55.10%)	*Zea mays* (corn)	Seedling emergence and seedling growth test (NOEC after 21 days)	16 mg/kg dry weight (corn)	(Great Lakes Chemical Corporation, 2000)
	Allium cepa (onion)		≥ 1000 mg/kg dry weight (onion, rye grass, soybean, cucumber)	
	Lolium perenne (rye grass)			
	Cucumis sativus (cucumber)			
	Glycine max (soybean)			
	Lycopersicon esculentum (tomato)		125 mg/kg dry weight (tomato)	
Pentabrominated congeners (55.10%)	*Eisenia fetida*	Earthworm – Acute toxicity test (NOEC after 14 days)	> 500 mg/kg dry weight	(Wildlife International Ltd., 2000c)

5.2.3 Atmosphere

No test data on animals exposed through the gas phase are available.

Although volatilisation to the atmosphere from foams containing pentaBDE is predicted, only very low concentrations in the atmosphere are expected. Removal is likely to be mainly via wet and dry deposition, although photodegradation may also occur to some extent. Thus, abiotic effects such as global warming, ozone depletion in the stratosphere and acidification are unlikely to occur (European Communities, 2001b).

6 Release and Fate

6.1 Release

PentaBDE has never been manufactured in Australia. Importation of pentaBDE into Australia ceased by June 2005. Up to that time, the product was used primarily as an additive flame retardant for flexible polyurethane foam at a concentration of up to 15% and a final pentaBDE concentration in the finished foam of up to 9.75%. The polyurethane foam containing pentaBDE was used in both commercial furniture (such as transport seats) and domestic furniture (such as beds). Significant volumes of pentaBDE may also have been imported in the past in finished articles. However, due to the current global prohibition on the manufacture and use of pentaBDE, it is unlikely that newly manufactured articles originating overseas will contain pentaBDE.

Release of pentaBDE to the environment can occur during formulation of flame retardant mixtures, the manufacture of articles, the service life of articles containing flame retardants, and on disposal (whether through landfill, incineration or recycling). Widespread release is likely to result from emission during service life or on disposal of articles containing pentaBDE, to landfill, although past direct release of pentaBDE in industrial wastewater may account for high localised concentrations. Landfill is expected to be the predominant route of environmental exposure to pentaBDE at the end of the useful life of articles, as incineration is seldom practised in Australia. Due to the lack of incineration and recycling facilities in Australia, products or articles containing pentaBDE are likely to be disposed of to landfill at the end of their useful lives.

In Australia, representative data on local and national release levels are not available. After the technical lifetime of a landfill, a slow but long-lasting flow of non-degraded substances into the environment is expected to take place.

Release during product use

No estimate of the levels of pentaBDE contained in articles, and disposed of to Australian landfills, can be made given the lack of data on likely quantities imported in articles. However, following global regulatory action, the amount disposed of through this route is expected to diminish over time as fewer articles containing the substance will require disposal.

PentaBDE is used as a liquid flame retardant additive in the production of polymer foams and electrical products. Given that pentaBDE-treated products are used in various domestic products such as household furniture, carpets and appliances, release of pentaBDE from these articles has been detected in indoor house dust (Shoeib et al., 2004; Stapleton et al., 2005; Wilford et al., 2005). The concentrations of PBDEs in house dust have been reported in various studies and are discussed in Section 8.2 (Public exposure). The dominant congeners found in house dust were those of pentaBDE and decaBDE.

In polymer foams, pentaBDE can migrate within the solid matrix and a minimal amount can volatilise from the surface of foams during their life cycle. However, each PBDE congener will have its own distinctive migration and volatility levels (UNEP, 2006). Although pentaBDE can volatilise from pentaBDE-treated articles, the flame retardants when emitted are likely to adsorb to particles and adhere to surfaces in the appliances or any other surfaces in the indoor environment, or spread to the outdoor environment when airing rooms (European Communities, 2001b).

Another route for release to the environment is from distribution of pentaPBDE-containing foam fragments when polyurethane foams become brittle and disintegrate at the end of their useful lives. A polyurethane foam treated with pentaBDE showed evidence of disintegration within 4 weeks of exposure to direct sunlight at temperatures between 30 to 35 °C and humidity of 80% or greater (Hale et al., 2002). Therefore, low density foam particles may be transported via stormwater runoff or air currents and will serve as an exposure route to organisms via inhalation or ingestion of particles containing pentaBDE. The inclusion of pentaBDE in the manufacture of coatings, cables and shoe soles can also result in slow release of pentaBDE to the environment. Articles with high wear rates such as car undercoating and shoe soles are expected to have higher amounts of pentaBDE released in the environment (European Communities, 2001b).

Release from waste containing pentaBDE

The main routes of emission of substances from landfills, depending on the properties of the substance include leaching into groundwater, transport with landfill gas, and diffusion into the atmosphere. Some emission factors may include particulates caused by abrasion/degradation of the article. Ultimately, all particulates will be removed or settle, and losses will be transferred to soil or water as a result of wash-down.

Emission of pentaBDE from waste articles may occur, for example, through 'blooming' where the chemical moves to the surface of the article, from which it may volatilise or be washed off. When articles are disposed of to landfill, in theory pentaBDE could leach into groundwater or volatilise from the surface of articles as they degrade. The levels of organic chemicals leaving landfill as leachate will be influenced by the degree of degradation in the landfill. Data available indicate that the rates of both aerobic and anaerobic degradation of pentaBDE are likely to be very slow.

Abrasion of discarded articles and degradation of foams may release particles containing pentaBDE within the landfill and this may provide a transport mechanism for entry into leachate water. Releases from products or articles containing pentaBDE can also be expected due to weathering, wearing and leaching at the end of service life during disposal and recycling operations (dismantling, handling of waste, transport and storage). In the EU, the annual releases of polyurethane products at end of use were estimated to be distributed in various compartments as follows: 75% to soil, 0.1% to air and 24.9% to surface water (European Communities, 2001b).

In general, the average concentration of pentaBDE in home and electrical appliances is estimated to be 34 mg/kg, with the highest concentration found in the plastic portions (125 mg/kg) (Morf et al., 2005). Limited information is available about waste generated from pentaBDE from other uses such as in electrical and electronic appliances in the EU. Some appliances are recycled for their metal content; however, many are burned in municipal waste incinerators. In the EU, a ruling to separate plastic wastes containing PBDEs prior to recovery and recycling has been enacted since (EU, 2012).

The majority of used vehicles containing solid or foam components containing pentaBDE are stored outdoors and eventually dismantled in shredder plants. Materials containing pentaBDE are treated as hazardous wastes in some countries. Wastes from building materials, textiles and furniture are disposed off in landfills or incinerated. Where municipal waste incinerators are used, almost all flame retardants are destroyed at their operating temperatures (Danish EPA, 1999). Both gaseous and particulate fractions have been detected above background levels of pentaBDE in the air close to the vicinity of municipal waste incinerators. Brominated dibenzo-p-dioxins and dibenzofurans may have been produced during incineration of articles containing pentaBDE, and these chemicals may have been released to the environment (UNEP, 2006).

A Swiss experimental study reported a flow analysis for the life cycles of pentaBDE, octaBDE, decaBDE and tetrabromobisphenol A (TBBPA). In this study, electrical and electronic equipment was reported to be the largest contributor to waste followed by automotive shredder residues and construction waste. Vehicles produced in 1980 contained 0.089 g/kg pentaBDE as a plastic component (excluding its electrical and electronic components), while vehicles built in 1998 had 0.044g/kg pentaBDE. Much higher quantities of up to 50g pentaBDE/kg of resin were used in manufacturing rail vehicles in 1980 (UNEP, 2006).

6.2 Fate

The main components of pentaBDE (tetra-, penta- and hexabrominated congeners) have low water solubilities and vapour pressures along with high octanol-water partition coefficients (log K_{ow}). These factors indicate that congeners will partition strongly to organic carbon and be unlikely to volatilise to the atmosphere. However, the Henry's Law Constant indicates that where available in the water column, tetra- and pentabrominated congeners may be moderately volatile. Where found in water and the atmosphere, congeners in pentaBDE are most likely to be sorbed to particulate matter, which reduces volatilisation.

The half life values of pentabrominated congener, BDE-99, in various environmental media were predicted using Epi Suite (formerly referred to as EPIWIN program). The estimated half-life values are summarised in Table 6.1.

Table 6.1 Summary of estimated half life values for BDE-99 in various environmental compartments (UNEP, 2006)

Environmental compartment	Estimated half life (day)	References
Soil	150	(Palm, 2001; Palm et al., 2002)
Aerobic sediment	600	(Palm, 2001; Palm et al., 2002)
Water	150	(Palm, 2001; Palm et al., 2002)
Air	19	(Palm et al., 2002)
Air	11	(Vulykh et al., 2004)

6.2.1 Abiotic degradation

Photodegradation

Rates of photodegradation of PBDEs have been shown to decrease with decrease in levels of bromination. While rate constants for photolysis of the pentaBDE congeners have been determined in a methanol/water mixture, the relevance of these to environmental reaction rates is uncertain. BDE-47 (tetrabrominated congener) is expected to be more resistant to photolysis than the penta- and hexabrominated components. BDE-47 was reported to have a half-life of 12 days with a rate constant of 4×10^{-5}/min. BDE-99 had a half-life of 2.4 days (rate constant 2×10^{-4}/min) while BDE-138 had a half-life of 1.2 days (rate constant = 4×10^{-4}/min). Actual photolytic breakdown products are not well investigated (Eriksson et al., 2001).

From available data, (NICNAS, 2019), it appears the photochemical reaction of higher brominated congeners follows a consecutive debromination to 6 bromine-substituted (hexabrominated) PBDEs. Chemicals with fewer than 6 bromine substitutions were possibly polybrominated dibenzofurans (PBDFs) and these are expected to be susceptible to further photodegradation.

A study on the photodegradation of PBDEs including BDE-28, -47, -99, -100, -153 and -183 congeners dissolved in hexane reported photodegradation half lives of 4.97, 2.53, 0.32, 6.46, 0.29 and 0.26 hours, respectively. In general, the higher brominated BDE congeners degraded at a faster rate than the lower brominated congeners. BDE-47 photodegraded to form tribrominated species (BDE-17 and BDE-28), which further debrominated to form dibrominated congeners. BDE-99 photodegraded to form tetabrominated congeners (BDE-66, -49 and -47), which subsequently underwent further photolysis. BDE-100 photodegraded to form tetrabrominated congeners (BDE-75 and-47) (Fang et al., 2008).

In the environment, pentaBDE will be initially found in bulk matrices, hence exposure to light would only occur for a very small proportion of the available compounds. In addition, the low vapour pressure, water solubility and high log K_{ow} indicate that the majority of pentaBDE released to the environment would partition onto suspended particulate matter (eventually forming part of the sediments) or soil. Here, it is likely to be immobile and only the surface layer is likely to be exposed to light. Further, in sediments, the amount of light reaching the sediment surface would be low and other external factors such as the presence of humic acid (shown to decrease the rate of photolysis) are likely to be present (Wildlife International Ltd., 2000b).

Therefore, it can be expected that only a small fraction of the total pentaBDE present in the environment would have the potential for photodegradation.

Atmospheric Photooxidation

When sorbed to atmospheric particles, the breakdown of tetra- and pentabrominated congeners through reaction with hydroxyl radicals is likely to be very slow. A rate constant for reaction of these compounds (BDE-47 and BDE-99) with OH radicals (kOH) in the atmosphere was calculated to be 15×10^{-13} and 5.5×10^{-13} cm^3/molecule/second, respectively (AOPWIN Program (Atmospheric Oxidation Program for Microsoft Windows 3.1, Version 1.91)). Using the diurnally and seasonally averaged concentration of tropospheric hydroxyl radicals of $1.5\times10^6/cm^3$, the half-life for the degradation of BDE-47 by hydroxyl radicals (12:12 hours light:dark) was calculated to be 7.1 days while that for BDE-99 was calculated to be 19.4 days.

Atmospheric half-lives for penta-, octa-, and decabrominated congeners have been estimated to be 29, 140 and 476 days, respectively. The atmospheric half lives were calculated using quantitative structure activity relationships (QSAR) and hydroxyl radical concentration of $5 \text{ X } 10^5$ hydroxy radicals/cm^3 (Pohl et al., 2004). A degradation rate constant of $1.27 \text{ X } 10^{-12}$ cm^3/molecule/second for pentabrominated congener (BDE-99) was also estimated using the same hydroxyl radical concentration (European Communities, 2001b).

Hydrolysis

The main congeners found in pentaBDE are expected to be hydrolytically stable. However, there is evidence to suggest that they may be susceptible to hydrolysis reactions through reaction with nucleophiles (Rahm et al., 2005). The method used the second order rate constant for the reaction with sodium methoxide in methanol/N,N-dimethylformamide (DMF) as an indicator of relative susceptibility toward hydrolysis. The higher brominated compounds rapidly solvolysed through nucleophilic aromatic substituents (half-lives <1 hour for octabrominated (BDE-203), through decabrominated (BDE-209) congeners). The rate of reaction of lower brominated PBDEs decreased by roughly a factor of 10 for every decrease in the level of bromination. Half-lives for heptabrominated (BDE-183), hexabrominated (BDE-153) and pentabrominated (BDE-100) congeners were calculated to be 5.3 hours, 22.3 hours and 188 hours, respectively, with the longest half-lives of >240 hours found for tetrabrominated (BDE-47) and tribrominated (BDE-28) congeners. This study used a single hard, strong and small nucleophile. Water is a weak nucleophile and it is difficult to extrapolate such findings to potential environmental reactions.

6.2.2 Biodegradation

The congeners found in pentaBDE are generally expected to be biotically stable under aerobic and anaerobic conditions. A composite sample (33.7% tetrabrominated congeners, 54.6% pentabrominated congeners and 11.7% hexabrominated congeners) was shown to be not readily biodegradable in a standard OECD study (European Communities, 2001b).

In 1 anaerobic study, BDE-47 was not degraded (<1% after 32 weeks). Later research using known dechlorinating strains of bacteria indicated that it is unclear as to whether there is potential for these to occur naturally in the environment (European Communities, 2001b).

Biotransformation is a possible route of degradation of PBDEs and there is evidence that organisms can metabolise higher brominated PBDE congeners to lower brominated congeners, particularly BDE-47 (European Communities, 2001b).

6.2.3 Bioaccumulation

Data generated from laboratory and field studies, along with a large volume of data from monitoring levels of PBDEs in biota show that the components of pentaBDE are readily bioavailable, highly bioaccumulative and can biomagnify through the food chain. Bioaccumulation occurs from contact of the aquatic organism with a contaminant in the water column, the sediments, and through the organism’s food chain.

The bioaccumulation factor (BAF) is often used to model the entire process of bioaccumulation. On the other hand, the bioconcentration factor (BCF) has been used to measure accumulation from the water column only. The biomagnification factor (BMF) is the ratio of the concentration of the chemical in an organism to the concentration of the chemical in the diet of the organism. BMF is an indication of the increase in concentration of the chemical as it moves up trophic levels in the aquatic ecosystem (USEPA, 2010).

The available test data show that where exposure occurred through both food and water, tetrabrominated BDE-47, pentabrominated BDE-99 and BDE-100 and hexabrominated BDE-153 were highly bioaccumulative with logBAF values >5 (BAF >100,000). When considering exposure just through food, individual congeners BDE-47, BDE-99 and BDE-100 were demonstrated to biomagnify (BMFs ranging from 2-46). The commercial pentaBDE formulation was shown to biomagnify with BMFs around 20. A similar BMF (20) was demonstrated for BDE-153 from mysid shrimp to common tern. Sediment organisms have the potential to accumulate congeners found in the commercial pentaBDE when exposed through sediment with BAFs of 4 (BDE-99) to 9.1 (BDE-154) found for tetra- through to hexabrominated congeners.

Generally, of the congeners in the pentaBDE formulation, BDE-47 and BDE-99 dominated the levels found in biota, although significant levels of BDE-100 were often present. The relative abundance of the BDE-47 congener (often found at >40% total PBDEs in biotic samples) indicates that organisms either have a preferential uptake and/or retention of this congener, or there is debromination of penta- and hexabrominated congeners to this congener within the organisms; thereby, increasing its concentration relative to that found in the commercial mixture.

The available data indicate that these compounds are bioavailable through different exposure routes such as water, sediment, soil and food. In particular, BDE-47 (present at around 37% in pentaBDE formulations), and the 2 pentabrominated congeners (BDE-99 and BDE-100), have very high BCFs and BAFs, and are generally the dominant congeners measured in biota. Levels of these substances have been measured in marine predators including dolphins, seals, polar bears and birds. The hexabrominated congeners also have very high BCF/BAF values. The occurrence of hexabrominated congeners in biota is smaller by comparison (generally <5% total PBDEs); however, they are also present at lower concentrations compared with other congeners in pentaBDE. Metabolism of these congeners within organisms will lead to lower detections of these congeners and possibly higher levels of lower brominated congeners such as BDE-47.

In addition to bioaccumulation within organisms, evidence shows a strong biomagnification tendency for these PBDE congeners present in pentaBDE. Several food-web studies, and measurements of PBDEs in high trophic marine mammals, support this statement and where tested for, clear biomagnification has been demonstrated. For example, biomagnification from lower trophic level aquatic organisms to fish to marine mammals has been reported for tetrabrominated (BDE-47), pentabrominated (BDE-99 and BDE-100), and hexabrominated (BDE-153 and BDE-154) congeners.

PBDE congeners present in pentaBDE have also been routinely detected in birds and terrestrial mammals. The distribution of congeners differs somewhat based on the evidence with the hexabrominated congeners often appearing more dominant than found in aquatic organisms, particularly for BDE-153 where levels were often of a similar magnitude to BDE-47 and BDE-99.

Terrestrial mammals appear to be exposed to PBDE congeners present in pentaBDE depending on their diet. Based on limited evidence with grizzly bears, those obtaining the majority of their diet through marine food had a PBDE profile dominated by the tetrabrominated congener (BDE-47), while those with a mainly terrestrial diet had a PBDE profile dominated by the decabrominated congener (BDE-209).

A summary of the estimated BAF and BMF for various aquatic species is presented in Table 6.2 below. The UNEP established a criterion of BCF or BAF in aquatic species of greater than 5000 (logBAF = 3.7) for chemicals considered to have a high potential for bioaccumulation (UNEP, 2006).

Table 6.2 Summary of estimated BAF and BMF values for various aquatic species (US EPA, 2010)

PBDE congeners	Species	Factor	References
Bioaccumulation factors (log BAFs)			
BDE-28	Lake trout	7.6	(Tomy et al., 2004)
BDE-47	Lake trout	7.3	(Streets et al., 2006)

PBDE congeners	Species	Factor	References
	Blue mussels	6.1	(Gustafsson et al., 1999)
BDE-66	Lake trout	7.3	(Streets et al., 2006)
BDE-85	Lake trout	2.3	(Tomy et al., 2004)
BDE-99	Lake trout	6.7	(Streets et al., 2006)
	Blue mussels	6.1	(Gustafsson et al., 1999)
	Dreissena polymorpha	1.8	(Lithner et al., 2003)
BDE-10	Lake trout	7.5	(Streets et al., 2006)
Biomagnification factors (BMFs)			
BDE-15	Porpoise	1.6-2.4[a]	(Ramu et al., 2006)
BDE-28	Lake trout	7.6[b]	(Tomy et al., 2004)
	Porpoise	1.6-2.4[a]	(Ramu et al., 2006)
BDE-47	Lake trout	2.1-37.2[b]	(Tomy et al., 2004)
	Porpoise	1.5[a]	(Ramu et al., 2006)
BDE-66	Lake trout	6.4-7.8[b]	(Tomy et al., 2004)
BDE-99	G. wilkitzkii/Copepod	0.65–47.6	(Sormo et al., 2006)
	Porpoise	1.8-2.4[a]	(Ramu et al., 2006)
	Guillemot egg/herring	17	(Sellström, 1996)
	Grey seal/herring	4.3	(Sellström, 1996)
	Salmon/sprat	10	(Burreau et al., 2000)
		5.9	(Burreau et al., 2000)
	Atlantic salmon/small herring	3.8	(Burreau et al., 2000)
	Net plankton/Benthic organisms	7.1	(Alaee and Wenning, 2002)
	Benthic organism/Forage fish	0.8	(Alaee and Wenning, 2002)
	Polar bear/ringed seal	3.4-11	(Muir et al., 2006)
		1.0	
		5.9	
		0.3	(Sormo et al., 2006)
	Ringed seal (various species)	0.6-43.1	(Sormo et al., 2006)
	Ringed seal/polar cod	13.7	(Sormo et al., 2006)
	Lake trout	6.6-35.8[b]	(Tomy et al., 2004)
BDE-100	Lake trout	6.5-45.9[b]	(Tomy et al., 2004)
	Porpoise	1.7-2.4[a]	(Ramu et al., 2006)
BDE-138	Lake trout	3.2-8.7[b]	(Tomy et al., 2004)

PBDE congeners	Species	Factor	References
BDE-153	Lake trout	9.4-19.5[b]	(Tomy et al., 2004)
BDE-154	Lake trout	13.3-3[b]	(Tomy et al., 2004)
BDE-183	Lake trout	3.9-28.4[b]	(Tomy et al., 2004)
BDE-190	Lake trout	1.6-5.1[b]	(Tomy et al., 2004)
BDE209	Lake trout	0.3[b]	(Tomy et al., 2004)

[a] Biomagnification calculated as the ratio of the chemical concentration in the blubber of porpoise to those in its stomach content on a lipid weight basis.

[b] Biomagnification from food spiked with known amounts of each BDE congener (BDE-28, -47, -66, -77, -85, -99, -100, -138, -153, -154, -183, -190, -209).

6.2.4 Potential for long range transport (LRT)

The combination of modelled and measured levels of PBDEs including in remote environments indicates that PBDE congeners present in pentaBDE are capable of undergoing long-range transport. Monitoring studies have also detected the widespread occurrence of PBDEs in the atmosphere.

In the Great Lakes region of North America, tetrabrominated (BDE-47) and pentabrominated (BDE-99) congeners were the main PBDEs detected in air samples collected between 1997 to 1999 from 4 locations. Near Lake Superior, concentrations of PBDEs ranged from 5 pg/m^3 to about 52 pg/m^3 in Chicago. At collection temperatures of about 20 °C, approximately 80% of the tetrabrominated congeners were in the gas phase, and 70% of the hexabrominated congeners were associated with particles (Strandberg et al., 2001). In another study, concentrations of gaseous and particulate PBDEs from the Midwest to the Gulf of Mexico were collected at various sites (urban, semi-urban, agricultural and remote), every 12 days between 2002 to 2003 (Hoh and Hites, 2005). At the Chicago site, the mean concentration of total PBDEs was 100±35 pg/m^3, which is approximately 3-6 times higher than the other sites and significantly higher than the values obtained between 1997 to 1999. The mean pentaBDE concentration (sum of congeners) was 31 pg/m^3, which is approximately 2-4 times higher than the measurements for the other sites.

Harner et al. (Harner et al., 2006) used passive air samplers deployed at several sites in an urban-rural transect of approximately 75 km in Toronto, Canada and analysed samples for PBDEs. Samplers were allowed to integrate gas phase PBDEs over 3 consecutive seasons starting in the summer of 2000. PBDEs were fairly uniform along the transect with air concentrations in Toronto of around 10-30 pg/m^3. Concentrations at the suburban sites reached a maximum of 20.4 pg/m^3, while the rural site showed a lower concentration of 8.2 pg/m^3 in summer and/or autumn, and a higher concentration of 24.3 pg/m^3 in spring and/or summer. The lowest concentrations were observed during the winter and were proposed to be associated with reduced inputs from indoor sources, and a preference for PBDEs to partition to the particle phase at lower temperatures. The PBDEs measured ranged from tri- to heptabrominated congeners and the congener profile was dominated by BDE-47 (1.5-15.84 pg/m^3) followed by BDE-99 (0.53-7.04 pg/m^3). The composition of PBDEs in the air samples did not differ across the transect or for the different seasons.

Organic films were collected from indoor and outdoor window surfaces along an urban-rural transect extending northward from Toronto, Canada and 41 PBDE congeners were analysed (Butt et al., 2004). There were 14 samples in total (9 exterior and 5 interior samples) collected from late July to early August in 2001 at 9 sites. The total PBDEs for exterior urban films ranged from 2.5-14.5 ng/m^2 compared to 0.56-1.1 ng/m^2 at suburban/rural sites. Interior urban films (mean 34.4 ng/m^2) showed levels of PBDEs that were 3 times greater than rural films (10.3 ng/m^2). Congener profiles were dominated by decabromodiphenyl ether (BDE-209; 51.1%). Congeners from the pentaBDE formulation are reported with BDE-99 and BDE-47 congeners accounting for 13.6% and 9.4%, respectively. Based on total PBDEs, the calculated air concentrations as extrapolated from the film measurements were 4.8 pg/m^3 for outdoor and 42.1 pg/m^3 for indoor urban sites.

Indoor air in 74 randomly selected homes in Ottawa, Canada was sampled and also at 7 outdoor sites during the winter of 2002-03 (Wilford et al., 2005). The passive sampling rate (2.5 m^3/day) was determined through a pilot study. In the outdoor sites, no hexabrominated congeners were detected. Tribrominated congeners (BDE-17 and BDE-28) were found at low mean concentrations of 0.017 and 0.095 pg/m^3, respectively. BDE-47 had a mean concentration of 0.87 pg/m^3 while BDE-99 and BDE-100 were found at mean concentrations of 1.1 and 0.11 pg/m^3, respectively. These values were much lower than those reported for indoor air. In the indoor air, hexabrominated congeners (BDE-153 and -154) were found at mean levels of 1.6 and 1.9 pg/m^3, respectively. Levels of indoor BDE-17 and BDE-28 were in orders of magnitude higher than outdoors with mean levels of 12 and 24 pg/m^3, respectively. Indoor air (unlike outdoor air) was dominated by BDE-47, with mean values of 160 pg/m^{3}compared with the pentabrominated congener BDE-99, with mean values of 42 pg/m^3. There were 2 other congeners found indoors but not reported outdoors were tetrabrominated congeners, BDE-71 and BDE-66, with mean levels of 11 and 2.9 pg/m^3, respectively. BDE-100 had mean indoor levels of 10 pg/m^3.

Air samples were collected at 1 rural site in southern England (Stoke Ferry) and 1 semi-rural site in northwestern England (Hazelrigg) during 1997 (spring, summer, autumn and winter) and analysed for PBDEs. Detectable concentrations of tri- to heptabrominated congeners were found and the sum concentrations of BDE-47, BDE-99 and BDE-100 were 11–67 pg/m^3 at Stoke Ferry and 7-28 pg/m^3 at Hazelrigg. PBDE levels have also been measured in several archived air samples from the Arctic (Alert, Northwest Territories, Canada and Dunai Island, eastern Siberia) taken between January 1994 and January 1995. The total concentrations of several di- to hexabrominated congeners were 1-4 pg/m^3 at Alert most of the year, but peaked to as high as 28 pg/m^3 in July, 1994. Total BDE congener concentrations in air samples from Dunai were lower than at Alert, with the highest level also found in summer (7-8 pg/m^3). BDE-47 and BDE-99 were the major congeners found (Besis and Samara, 2012).

Semi-permeable membrane devices were used to collect passive air samples for BDE congeners (BDE-28, -47, -48, -75, -99, -100, -153, -154) at remote, rural and urban locations across 22 countries in Europe for six weeks in 2002. BDEs were detected in approximately 50% of the samples. The equivalent BDE air concentrations estimated from the passive sampler data ranged from 0.5 to 250 pg/m^3. UK sites had the highest concentrations of PBDEs due to history of PBDE production and formulations. High values were also detected in urban centres in mainland Europe, including Athens, Bilthoven, Geneva, Milan and Seville. Values in Eastern Europe were generally low. BDE-47 and BDE-99 contributed to approximately 75% of BDEs, similar to the proportion in pentaBDE (UNEP, 2006).

Concentrations of PBDEs in air and soil on a rural-urban transect across a major UK conurbation were reported (Harrad and Hunter, 2006). Outdoor air samples were collected from 10 sites within the West Midlands conurbation. Sampling sites were located on a southwest (upwind) to northeast (downwind) transect at intervals of between 2 and 17 km across the sample area providing a mix of rural, suburban and urban sampling locations. Passive air samplers (PUF disks) were used. At each sampling point, 4 disks were used. Samples appear to have been taken approximately monthly over 12 months and reported as follows:

- Total PBDEs in the rural areas ranged from 2.84-8.47 pg/m^3. The dominant congener in all rural air samples was BDE-47 (1.63-4.95 pg/m^3). BDE-99 was found at concentrations ranging from 0.49-1.55 pg/m^3 and, BDE-100 between 0.23-0.73 pg/m^3. BDE-153 and BDE-154 were found at similar levels ranging from 0.11-0.20 pg/m^3 and 0.07-0.17 pg/m^3, respectively.
- The suburban sites (2 of 3 sampling locations were reported) had higher levels with total PBDE concentrations ranging from 10.3-14.0 pg/m^3. Levels of BDE-47, BDE-99 and BDE-100 ranged from 5.89-8.22 pg/m^3, 1.98-2.64 pg/m^3 and 0.89-1.23 pg/m^3, respectively. BDE-153 and BDE-154 were found at lower concentrations of 0.40-0.51 pg/m^3 and 0.26-0.29 pg/m^3, respectively.
- The 3 urban sites (including one in the centre of the city of Birmingham) had total PBDE levels ranging from 11.5-23.3 pg/m^3. Levels of BDE-47, BDE-99 and BDE-100 ranged from 6.64-13.73 pg/m^3, 2.22-4.26 pg/m^3 and 0.95-2.08 pg/m^3, respectively.
- Lower concentrations of 0.29-0.63pg/m^3 and <0.1-0.53 pg/m^3 for BDE-153 and BDE-154, respectively, were measured.

Atmospheric concentrations of tri- to heptabrominated congeners (108 samples in total) were measured at 2 rural or semirural sites in England and 1 remote site on the west coast of Ireland in 2001 and 2002 (Lee et al., 2004). Concentrations of total PBDEs at the Irish site ranged from 0.22-5.0 pg/m^3 with BDE-47 at 0.16-1.9 pg/m^3, BDE-99 at 0.28-1.9 pg/m^3 and BDE-100 at 0.07-0.43 pg/m^3. Of the 2 sites in England, one (Hazelrigg) was located on the northwest coast of England and the other (Chilton) around 70 km west of London. These sites showed similar levels. Concentrations of total PBDEs at the Hazelrigg site ranged from 2.8-37 pg/m^3 with BDE-47 at 0.78-15 pg/m^3, BDE-99 at 0.53-11 pg/m^3 and BDE-100 at 0.15-0.46 pg/m^3. Concentrations of total PBDEs at the Chilton site ranged from 3.4-33 pg/m^3 with BDE-47 at 0.72-7.2 pg/m^3, BDE-99 at 0.82-15 pg/m^3 and BDE-100 at 0.17-2.1 pg/m^3.

High-volume (48-hour) air samples previously collected within the Swedish Dioxin Survey, 1 from Hoburgen in southern Sweden (Gotland) and 1 from Ammarnäs in northern Sweden were analysed for PBDEs. The results showed quantifiable amounts of BDE-47, BDE-99 and BDE-100. The total PBDE levels were approximately 1 and 8 pg/m^3. The highest levels of BDE-47 were found on polyurethane foam plugs (gas phase) while high levels of BDE-99 and BDE-100 were found on filters (particulate phase). This corresponds well with the physicochemical properties of these substances, as BDE-47 is more volatile than the other compounds, and would be expected to be in the gas phase to a larger extent. Because these substances were found in air samples from both sites, it was proposed that these substances may have been spread via long-range transport (LRT).

In a comparison of concentrations in air and deposition on an island located in the central basin of the Baltic Sea, total median PBDE concentrations in air (gaseous + particle) of 8.6 pg/m^3 were reported (ter Schure et al., 2004). The PBDE levels were found mainly associated with particles and were dominated by BDE-209 followed by BDE-47 and BDE-99. In what is defined by the study as a remote region, the actual levels of BDE-47 and BDE-99 in air ranged from 0.2-5.6 pg/m^3 and 0.2-4.3 pg/m^3, with median levels of 1.8 and 1.2 pg/m^3, respectively. BDE-100 was also detected at a range of 0.1-1.7 pg/m^3 in air, with median concentration in air of 0.7 pg/m^3. At the same site, BDE-47 and BDE-99 in rain were present at ranges of 0.1-0.3 ng/L and <0.1-0.4 ng/L, respectively.

The LRT potential of PBDEs was assessed using a variety of models (TaPL3, ELPOS, Chemrange and Globo-POP), physical and chemical properties (solubility, vapour pressure, log K_{ow}, log K_{oa}, log K_{aw}), and estimated half-lives in various environmental media (air, water, soil and sediment) (Wania and Dugani, 2003). The study showed that the various approaches to LRT potential gave similar results for the PCB references and the PBDEs. On the basis of the model predictions, tetrabrominated congeners showed the greatest potential for atmospheric transport and decabrominated congeners the lowest transport potential. The characteristic travel distance (CTD) predicted ranged from 1113 to 2483 km for tetrabrominated congeners, 608 to 1349 km for pentabrominated congeners, and 480 to 735 km for the decabrominated congener. The CTD was defined as the distance at which the concentration of a chemical present in a mobile media of air or water has dropped to 1/e (where e is the base of the natural logarithm) or 63% of its initial value due to degrading reactions in the mobile medium and irreversible transfers to immobile media it interacts with during transport (Beyer et al., 2000; Gouin and Mackay, 2002).

7 Environmental Exposure

PentaBDE can be released and distributed in the environment through many channels, including: release into the atmosphere or wastewater from its industrial uses and disposal; emission or dust formation from pentaBDE-containing articles; and leaching and emission from landfill.

The most significant environmental compartment for pentaBDE to partition to is predicted to be soil, except where release is all to water, in which case partitioning will be predominantly to sediments. Where release from a sewage treatment plant occurs with pentaBDE being in the effluent (most probably still associated with suspended particles), it is most likely to migrate to the sediment component. When sewage effluent or bio-solids are applied to land, pentaBDE would associate with the soil where it would remain tightly bound. Similarly, where disposal of articles containing pentaBDE occurs to landfill, it would be expected to remain associated with surrounding soil in the event it migrates out of articles, and would remain immobile.

PentaBDE was detected in marine and terrestrial birds, sea and terrestrial mammals, sediments, soil, seafood and fish found in different countries or regions in the world. High levels of pentaBDE were also detected in several species, having populations of concern protected by the Bonn Convention (Convention on the Conservation of Migratory Species of Wild Animals) (Covaci et al., 2002; Thron et al., 2004). A summary of BDE-99 levels found globally is presented in Table 7.1. (UNEP, 2006).

Table 7.1 Levels of BDE-99 in various compartments from different countries or regions in the world (Adopted from UNEP, 2006)

Country/Region	Organism/Compartment	Level of BDE-99	Comments	References
Europe	Atmosphere (gas phase)	10-120 pg/m^3	From 22 countries	(Jaward et al., 2004)
Japan	Atmosphere (particulate)	0.05-0.9 pg/m^3	Measured in summer	(Hayakawa et al., 2004)
Japan	Atmosphere (gas phase)	0.05-19 pg/m^3	Measured in summer	(Hayakawa et al., 2004)
United Kingdom	Soil	78-3200 pg/g DW	-	(Hassanin et al., 2004)
Sweden	Sediments	<0.7-51.4 ng/g DW	Rivers at point source	(Palm et al., 2002)
Western Europe	Sediments	<0.2-6.9 ng/g DW	Estuaries	(Palm et al., 2002)
Japan (Osaka)	Sediments	9-28 ng/g DW	-	(Palm et al., 2002)
North Pacific Ocean	Skipjack tuna	0.18-2.1 ng/g LW	-	(Ueno et al., 2004)
Japan	Skipjack tuna	1.1-1.7 ng/g LW	Offshore waters	(Ueno et al., 2004)
East China Sea	Skipjack tuna	2.4-4.7 ng/g LW	None	(Ueno et al., 2004)

Country/Region	Organism/Compartment	Level of BDE-99	Comments	References
Philippines	Skipjack tuna	2.1 ng/g LW	Offshore waters	(Ueno et al., 2004)
Brazil	Skipjack tuna	1.9 ng/g LW	Offshore waters	(Ueno et al., 2004)
Canada	Atlantic tomcod	77 ng/g LW	-	(Law et al., 2003)
India (Chilika Lake)	Irrawaddy dolphin	0.12-0.78 ng/g LW	Endangered species	(Kannan et al., 2005)
China (Hong Kong)	Info-pacific humpback dolphin	33.6-720 ng/g LW	Measured from coastal waters with 12% of ∑PBDEs	(Ramu et al., 2005)
United Kingdom	White beaked dolphin	1480 ng/g LW	Endangered species	(Law et al., 2003)
China (Hong Kong)	Finless porpoises	27.6-117.6 ng/g LW	Measured from coastal waters with 12% of ∑PBDEs	(Ramu et al., 2005)
Japan	Northern fur seal	2.64-4.56 ng/g LW	Measured from Pacific coast with 12% of ∑PBDEs	(Kajiwara et al., 2004)

DW – Dry weight

LW – Lipid weight

7.1 Australian data

No pentaBDE processing occurs in Australia and importation of articles containing pentaBDE is no longer expected to occur.

The majority of articles containing pentaBDE are not likely to cause significant environmental exposure during their service life. Release of PBDEs contained in the foam matrix may occur in the form of dust particles, but this release is more likely to be disposed of to landfill in the event of vacuuming up dust, or potentially released to the atmosphere with the dust particles where they would be subject to deposition to either water or land. While some release to the aquatic environment may occur from disposal of water used in washing floors and clothing, this is very difficult to quantify. The greatest exposure is to the soil compartment when articles are disposed of to landfill.

In the absence of sufficient data to adequately estimate environmental concentrations of PBDEs in various environmental media, monitoring studies have been conducted to estimate PBDE exposure from articles. Studies on PBDEs in the environment (indoor and outdoor, and sediment) were commissioned by the Australian Department of the Environment and Heritage (now the Department of Agriculture, Water and the Environment). The environmental monitoring studies are described below and focuses on the congeners contained in pentaBDE.

7.2 Air

Limited monitoring of indoor and outdoor air concentrations was conducted near some home and office sites in Brisbane (Toms et al., 2006c). Indoor air was sampled at 5 homes and 3 offices. Outdoor air was sampled in the grounds of the indoor air sites – Home 2 and Office 1. Overall, 21 out of 26 BDE congeners were detected. The concentration of the sum of PBDEs (ΣPBDEs) in outdoor air was less than in the indoor air. For the home, the indoor air concentration was approximately 89 times that of the outdoor air, while at the office site it was just over twice that of the outdoor air. The concentration of ΣPBDEs was higher in the office outdoor air than in the home outdoor air, which contrasts with the indoor air concentrations for these sites where the home was higher than the office. A summary of the outdoor and indoor air concentrations measured in Brisbane is presented in Table 7.2. Exposure from indoor or outdoor air are further discussed in Section 8.2 (Public Exposure – Exposure from indoor or outdoor air).

Table 7.2 Australian outdoor and indoor air concentrations (pg/m^3) – total PBDEs

Concentrations	Home 2	Office 1
Indoor air	179	18
Outdoor air	1.7	6.8

For outdoor air, the congener profile was similar for both sites, with dominance of decabrominated (BDE-209) followed by nonabrominated (BDE-207, BDE-206), then octabrominated (BDE-197 and -196) congeners. For Home 2, this was followed by heptabrominated (BDE-183) and tribrominated (BDE-17) congeners. For Office 1, this was followed by tetrabrominated (BDE-49), heptabrominated (BDE-183), tetrabrominated (BDE-66, BDE-71) and heptabrominated (BDE-184) congeners. The concentrations of decaBDE (BDE-209) in the home and office samples were 1.3 and 5.8 pg/m^3, respectively. These results should be treated with caution since a very insensitive limit of detection (LOD) was found for BDE-47 and BDE-99. Therefore, these results only refer to those congeners found above their LOD and may not truly represent all congeners likely to be present.

The outdoor air concentrations in the study are likely to be higher than other ambient levels in outdoor air as they were sampled in the grounds of indoor air monitoring sites where higher levels were detected indoors. They are comparable to some international data where outdoor air levels (total PBDEs, but dominated by BDE-47 and BDE-99) in rural areas of the UK are reported up to around 8.5 pg/m^3 (although other data presented in EC 2001 report levels up to 270 pg/m^3 in UK rural air)(European Communities, 2001b). A remote site in Ireland had reported air levels up to 5.0 pg/m^3, again dominated by BDE-47 and BDE-99. Further, total PBDE levels up to 8 pg/m^3 are reported from Swedish air monitoring. Rural data presented from the US also indicate BDE-47 and BDE-99 dominate the congeners present in air with total PBDE concentrations for three rural sites being in the area of 6-14 pg/m^3.

While international data show much higher levels in urban areas, it is difficult to draw correlations between these and expected air concentrations in urban Australian environments. Conversely, the very small sample size offered for Australian outdoor air makes it difficult to confidently rely on these values as being representative of Australian urban air levels.

Noting these uncertainties, information available is simply too limited to estimate a meaningful atmospheric concentration for pentaBDE (or the main congeners found in pentaBDE) in the Australian environment.

7.3 Water

No measured data for PBDE congeners present in pentaBDE in water are available for Australia and only limited data are available internationally. The data that are available suggest these congeners may be found in water in very low to sub ng/L level.

The physico-chemical properties of tetra- and pentabrominated congeners along with fugacity modelling suggest the chemicals should not be found in appreciable levels in water.

No processing of pentaBDE occurs in Australia. Therefore, any release to water will be on a regional level. Information available is too limited to estimate a meaningful aquatic concentration for pentaBDE in the Australian environment.

7.4 Sediment

A study was conducted to determine the concentrations of brominated flame retardants (BFRs) in sediment samples from the Australian aquatic environment (Müller et al., 2004).

The study involved the re-analysis (for BFRs) of sediment samples collected in 2002-2003 to determine background concentrations of persistent organic pollutants as part of the then Australian Government Department of Environment and Heritage National Dioxin Program. Sediment samples from up- and downstream of the outfall of sewage treatment plants were collected in 2005 to assess contamination from these potential point sources. Samples were analysed from 39 locations from all States and Territories of Australia. At 7 locations, 2 samples were analysed to represent similar sites within the same location. Hence in total, samples from 46 different sites were analysed. These sites were chosen to be representative of various land uses – remote (5), remote/agricultural (2), agricultural (7), urban (9), STPs (6) urban/industrial (9), industrial/urban/agricultural (1) and industrial (7) and a range of salinities – freshwater (19), marine (1) and estuarine (26). Results are available for 42 out of 46 sites.

Samples were analysed for 26 PBDE congeners. Quality control was undertaken including analytical reproducibility, inter-laboratory comparison and sampling replication.

PBDEs were detected at 31 of 42 sites. The sum concentration of PBDEs ranged from less than the LOD to 60.9 µg/kg dw with a median of 0.17 µg/kg dw. The results are summarised as follows:

- 29 sites with concentrations ranging from less than the LOD to 1 µg/kg dw. These sites included all remote, remote/agricultural, agricultural and agricultural/urban/industrial sites.
- 8 sites with sum PBDE concentrations ranging from 1 to 10 µg/kg dw and included most of the sites near STP outfalls and other urban/industrial and urban sites.
- The sites with the highest concentrations (>10 µg/kg dw) were Port Phillip Bay, Port Jackson West and Parramatta River 'A'.

The highest concentrations were found in expected locations, as these were the estuaries with the highest degree of urbanisation and industrialisation. Overall, there was a trend that showed the sum concentrations of PBDEs to be higher in the industrial/urban areas and followed in descending order by industrial, sewage treatment plants, urban, agricultural/urban/industrial, agricultural, agricultural/remote and finally remote areas. Table 7.3 summarises the results of the sum PBDE (ΣPBDEs) concentrations in Australian aquatic sediment.

Table 7.3 Summary of ΣPBDE concentrations (µg/kg dw, excluding LOD) detected in Australian aquatic sediments by land-use type

Area	Number of samples	Mean	Standard deviation	Median	Range
Remote	5	0.096	0.21	0	0.0013-0.48
Remote/agricultural	2	0.047	0.014	0.047	0.037-0.057
Agricultural	7	0.052	0.096	0.002	0-0.25
Agricultural/urban/industrial	1	n/a	n/a	n/a	0.033
Urban	7	0.65	0.77	0.21	0-1.9
STPs	6	2.8	2.9	1.9	0.36-7.7
Industrial	7	3.6	8.5	0.37	0-25
Industrial/urban	7	15	24	1.3	0-62

n/a = not applicable

The PBDE congener profile in sediment samples was dominated by BDE-209 in 84% of the samples. The sample from Port Phillip Bay had a different congener profile with the highest concentration being heptabrominated (BDE-183) congener at 31,000 pg/g dw. This may suggest that there is a nearby point source of the octaBDE technical product for which BDE-183 is a marker. The PBDE profile of the samples obtained near the outfall of STPs was also dominated by BDE-209. However, there was also some contribution by some lower brominated congeners (BDE-17, BDE-47, BDE-49 and BDE-99), as well as some highly brominated congeners such as nonabrominated congeners (BDE-206 and -207).

The results were compared with those from the international literature; however, it is difficult to make comparisons with other studies due to differing aims, collection methods and analytical techniques. Overall, the concentrations of PBDEs in Australian sediment were relatively low with the exception of BDE-183 in the Port Phillip Bay sample. The Australian results were considerably lower than those found in sediment from North America, Europe and Asia. The maximum Australian results were comparable with the minimum results from some European and Asian countries.

While BDE-209 generally dominated the congener profile, there are some interesting observations regarding the distribution of the lower BDEs. In the Lower Yarra, elevated levels (relative to other observations) for BDE-47 (2.05 µg/kg dw) and BDE-49 (1.07 µg/kg dw) were found compared to levels of pentabrominated congeners BDE-99 (1.8 µg/kg dw) and BDE-100 (0.5 µg/kg dw). This relatively high level of BDE-49 is unexpected and may be the result of degradation as it is not a major component of pentaBDE formulation (it is a minor contributor, at about 1% of BDE-47 level). A similar result in terms of distribution was found in the Parramatta River samples where BDE-47 and BDE-49 were found at 0.23 and 0.55

µg/kg dw, respectively compared to 0.71 and 0.17 µg/kg dw for BDE-99 and BDE-100, respectively.

In 2005, in samples taken downstream from the Molonglo STP (Canberra, ACT), the distribution of PBDEs seemed remarkably high compared to other sampling locations, given the lack of industrialisation in this region. While BDE-209 was the dominant congener (3.41 µg/kg dw) there were comparable levels of BDE-100 at 0.2 µg/kg dw and BDE-99 at 1.05 µg/kg dw, BDE-49 at 0.1 µg/kg dw and BDE-47 at 2.1 µg/kg dw) reported.

The levels described above for the ACT and lower Yarra samples represent the highest levels of penta- and tetrabrominated congeners found in this study. Generally, levels were below the detection limit values.

7.5 Soil

Soil is expected to be exposed to PBDEs through application of sewage sludge (amended soils), or regionally where deposition from the atmosphere (i.e. particle-bound PBDEs) occur. As there is no longer any processing of pentaBDE in Australia, theoretically the amount of these compounds being found in sewage sludge resulting from release from processing sites should be very low. However, the findings of elevated levels of PBDE congeners present in pentaBDE, downstream from a sewage treatment plant (STP) in Australia, (and not from a notable industrial area), indicates that these compounds can still occur in sludge, possibly from domestic sources.

International monitoring data for non-amended soils suggested levels in the low µg/kg dw range may be found, although it is difficult to relate such levels to those that may be found in Australian non-amended soils. A study measuring levels in grassland and woodland areas in the UK and Norway showed that forest soils tended to have higher concentrations with evidence of more long-range transport through the atmosphere for the lower brominated congeners. BDE-99 tended to dominate the congeners found in these soils with BDE-47 the second most abundant congener detected.

In the absence of good local monitoring data and a scarcity of such data internationally, it is not considered possible to derive any meaningful soil exposure levels. This remains an area of high uncertainty, and may be addressed by monitoring in this area. Implications are considered further in the risk characterisation.

8 Human Exposure

8.1 Occupational exposure

PentaBDE has never been manufactured in Australia, and the importation of pentaBDE into Australia ceased by the end of 2005. Therefore, occupational exposure to pentaBDE in Australia via manufacturing and importing of pentaBDE is not discussed in this report. However, occupational exposure from use of articles containing pentaBDE is discussed below.

Exposure at workplaces can be divided into direct and indirect sources. Occupational exposure to pentaBDE refers to direct exposure in the workplace. Australian workers are not expected to handle commercial grade pentaBDE due to the phasing-out of pentaBDE. After pentaBDE has been incorporated into the polymeric matrix, it is no longer considered bioavailable by dermal contact, and dermal exposure from handling end-use products is therefore considered to be negligible.

Particle generation from the day-to-day handling of end-use products within the workplace is expected to be negligible, with the exception of recycling facilities where plastic components containing pentaBDE are dismantled and shredded into small pieces

Workers may also be exposed to pentaBDE indirectly via the environment. Indirect exposure is often defined as an exposure involving the transport of agents via various media from initial sources to an exposed individual. Indirect exposure at workplaces is not considered to link to specific sources within the workplace. Dust particles containing pentaBDE can either arise from the breakdown (wearing) of articles containing pentaBDE (for example arising from shredding) or pentaBDE adsorbing to existing indoor dust particles. While exposure to pentaBDE in indoor dust may be directly related to the use of particular articles, the use of a range of such articles and the need to assess exposure through wide area dust monitoring, means that this route of exposure is more appropriately considered as an indirect exposure. Workplace exposure via this route is comparable to other environmental settings such as in the home. Therefore, assessment of occupational exposure will focus on direct exposure to pentaBDE in the workplace, and indirect exposure will be addressed within the public exposure section (Refer to Section 8.2).

8.1.1 Occupational exposure from end-use

No data are available on the types and quantities of articles containing pentaBDE that have been imported into Australia from overseas. Since the manufacture and use of pentaBDE has been phased out overseas, it is unlikely that new articles imported into Australia will contain pentaBDE.

A reasonable worst-case scenario would be exposure from a workplace environment (i.e. office) that is fully furnished with chairs, sofas, cushions and carpet underlays manufactured with polyurethane foams containing pentaBDE. Typically, office furniture is replaced regularly, and most new articles introduced into the workplace at present are free of pentaBDE. Occupational exposure to pentaBDE from end-use products is expected to decline to minimal levels with the phase-out of pentaBDE. However, if some articles in offices are not replaced for many years, the potential for wear, and therefore exposure to pentaBDE could be a source of exposure.

Dermal exposure to pentaBDE from end uses is expected to be low due to limited direct contact with polyurethane foams and elastomers. Inhalation exposure is also expected to be minimal based on limited data being available on indoor dust concentrations of PBDE congeners in offices. According to an Australian study where levels of PBDE congeners in indoor air were measured, the mean concentration of all combined PBDE congeners in office air was 173 pg/m^3 compared with a mean level in homes of 50 pg/m^3 (Toms et al., 2006c). Considering that only a portion of the combined congeners would have originated from pentaBDE in articles, these levels are considered to represent worst case exposure. This is a reasonable comparison considering the ubiquitous nature of PBDE congeners and the widespread use of commercial PBDE mixtures in finished articles. Furthermore, it is difficult to attribute individual PBDE congeners found within the environment to specific article release and hence back to commercial mixtures. The complex issue of exposure from article release is addressed further in the public exposure section.

8.1.2 Occupational exposure from recycling

Recycling of waste electronic equipment in Australia

Exposure to pentaBDE from the recycling of polyurethane foam is expected to be minimal as polyurethane foam is not commonly recycled in Australia. Exposure to pentaBDE from the recycling of rigid polyurethane plastic casings may occur, but since hard plastics of this sort only account for about 5% of pentaBDE use in articles, and the recycling of these plastics in Australia is limited, this exposure is also expected to be minimal.

Recycling of electronic equipment that has reached the end of its working life is not a large industry in Australia. For instance, it has been estimated that 3 out of every 4 computers ends up discarded to landfill.

There are very few facilities in Australia that recycle plastics from electronic waste. One specialist plastics recycler in Australia claims that any plastic that may contain flame retardants is separated and not granulated or re-extruded, but compacted into bales and exported for recycling.

During a trial recycling project for computer equipment conducted in 2002-2003, the former Department of Environment and Conservation (2004) reported that plastics from computers sent for recycling were estimated to comprise 12% by weight of the recycled equipment that was sent to landfill. The reasons were that no viable reuse or recycling alternatives were identified due to difficulties in recycling plastics containing brominated flame retardants and difficulties in identifying which plastics contained such chemicals. There appears to be a lack of a viable end-market of recycled plastics containing brominated flame retardants due to the toxicity of the chemicals.

In contrast to electronics recycling, there is a well-established metals recovery industry, estimated to recover approximately 60-70% of metal from major appliances. Whole appliances are shredded without dismantling as part of this process. Non-metal materials, which are not recovered during the shredding process such as plastics, rubber, textiles, glass, wood, and other substances, are discarded to landfill as "shredder flock". It is expected that shredder flock would include a degree of plastics containing brominated flame retardants. Metal is also recovered from automobiles in a similar process.

Since pentaBDE is incorporated into the solid matrix within rigid polyurethanes, dermal exposure from handling electronic equipment parts containing pentaBDE is expected to be negligible. However, inhalation exposure from dust containing pentaBDE may occur during the dismantling process. As there are no Australian measured data available for pentaBDE concentrations at recycling sites, overseas measured data are used for the estimation of inhalation exposure via this source.

Measured data from recycling electronic equipment overseas

In Sweden, 2 studies reported air concentrations of pentaBDE-related congeners during recycling processes. In a Swedish factory that recycles electronic equipment, static measurements were collected from both the dismantling hall and the shredder where plastics were processed (Sjödin et al., 2001). Air samples were collected over 2 days from 3 different workstations in the dismantling hall, where the dismantling process was performed manually. The measured levels for the relevant congeners at the dismantling hall are presented in Table 8.1.

Table 8.1 Air concentrations of pentaBDE-related congeners at a dismantling hall (Sjödin et al., 2001)

BDE congener	Sample number (n)	Mean concentration (ng/m^3)	Concentration range (ng/m^3)
BDE-47	12	1.2	0.35-2.1
BDE-85	12	0.17	0.1-0.24
BDE-99	12	2.6	0.54-5.5
BDE-100	12	0.25	0.063-0.52
BDE-153	12	3.9	0.88-11
BDE-154	12	0.57	0.13-1.0
Total mean concentration:		**8.69**	

In another study, Julander et al. (2005) reported concentrations of pentaBDE-related congeners in air samples from an electronics recycling facility. The samples were collected from 2 consecutive 8-hour shifts (total sampling time of 16 hours) where 6 dismantling stations were in operation. Each station had 1 worker dismantling TV sets, computers and small electronic products with pneumatic tools and there were 4 more workers transferring incoming and outgoing goods. The concentrations of pentaBDE related congeners in air samples at a dismantling hall are presented in Table 8.2.

Table 8.2 Air concentrations of pentaBDE related congeners at a dismantling hall (Julander, 2005)

BDE congener	Detection limit (ng/m^3)	Sample No.	Mean concentration (ng/m^3)	Standard deviation (SD)
BDE-47	<0.19	4	0.96	0.18
BDE-49	<0.01	4	1.03	0.75
BDE-66	<0.02	4	0.26	0.04
BDE-71	<0.1	4	0.25	0.04

BDE congener	Detection limit (ng/m^3)	Sample No.	Mean concentration (ng/m^3)	Standard deviation (SD)
BDE-85	<0.02	4	0.08	0.02
BDE-99	<0.41	4	1.48	0.30
BDE-100	<0.08	4	0.15	0.03
BDE-119	<0.02	4	0.02	0.00
BDE-138	<0.03	4	0.09	0.02
BDE-153	<0.04	4	1.29	0.31
BDE-154	<0.03	4	0.30	0.08
Total mean concentration:			**5.91**	

The total PBDE concentrations from the 2 Swedish studies are of the same magnitude. The higher concentration (8.69 ng/m^3) is selected for inhalation exposure estimation. Assuming a worker has a bodyweight of 70 kg and a respiratory rate of 1.2 m^3/h, and spends 8 hours per day for 5 days per week in a recycling workshop, the internal dose arising from inhalation is calculated to be 0.85 ng/kg bw/day.

8.1.4 Overseas biological monitoring studies

Several biological monitoring studies on brominated flame-retardants including pentaBDE have been published, and are summarised below:

Sjödin et al. (1999) & Thuresson et al. (2006)

Concentrations of PBDEs in blood from Swedish clerks working full-time at computer screens and personnel at an electronics-dismantling plant were determined in 1997. A group of hospital cleaners and a group of abattoir workers were used as a non-occupationally exposed control group. BDE-99 and BDE-100 were present in all samples but were below the limit of quantification by chromatography.

Table 8.3 Blood concentrations of pentaBDE related congeners (pmol/g lipid weight) in Swedish workers in 1997

BDE congener	Control group				Test groups			
	Abattoir workers (n=17)		Hospital cleaners (n=20)		Computer clerks (n=20)		Electronics dismantlers (n=19)	
	Median	Range	Median	Range	Median	Range	Median	Range
BDE-47	2.5	<1-13	3.2	<1-34	3.0	<-10	5.9	<-47
BDE-153	2.9	1.7-5.7	0.89	0.64-7.6	1.3	0.8-5.1	7.0	3.2-1.9
BDE-154	Not reported		0.59	0.25-1.4	0.79	0.43-1.5	1.9	0.74-7.4
Total median	**5.4**		**4.68**		**5.09**		**14.8**	

The highest levels of pentaBDE-related congeners were seen in the blood samples of recycling workers (electronic dismantlers). The total congener blood level in dismantlers was approximately 3-fold higher than that in the control group. Levels in the computer clerks were slightly higher than the control group. These results are consistent with the exposure assessment, where a higher exposure is estimated in dismantlers. The Sjodin study (1999) reported a median reduction value of 16% for BDE-47, 153 and 154 levels in the electronic dismantlers when measured during a summer vacation.

The Thuresson et al. (2006) study reported BDE-47 and BDE-153 levels of 1.2 and 1.3-pmol/g lipid weight, respectively, in workers who manufactured flame-retarded rubber compounds with occupational exposure primarily to decaBDE. Both levels were similar to those in the control groups. The recycling workers appear to have been exposed to octaBDE and decaBDE as well as to pentaBDE, based on the monitoring results for BDE-183 and BDE-209 in these workers. Accordingly the commercial octaBDE mixture may be the source of a large proportion of the BDE-153 and 154 levels seen in this group of workers.

From 1997 to 2000, the volumes of dismantled electronics goods at the factory approximately doubled, and the quantity of brominated plastic materials that was recycled in 1997 and 2000 was 75 and 195 tonnes, respectively. During that period, the company employed more workers and the factory also made some major industrial hygiene improvements in 1999. The shredder was placed outside, away from the operators. The ventilation system in the factory was upgraded with a specific process forcing airflow from the ceiling to the floor in order to reduce levels of airborne dust and particles. In addition, the cleaning routines of workbenches and workstations were revised.

In 2000, blood samples from 27 workers were collected and analysed by two laboratories (Laboratory A and B). The study also included white-collar office workers who worked within the same factory building, but the offices were separated from the large dismantling hall by walls.

Table 8.4 Blood concentrations of pentaBDE related congeners (pmol/g lipid weight) in Swedish workers in 2000 (Sjödin et al., 1999; Thuresson et al., 2006)

BDE congeners	Laboratory A				Laboratory B			
	Blue collar (n=11)		White collar (n=2)		Blue collar (n=8)		White collar (n=6)	
	Median	Range	Staff 1	Staff 2	Median	Range	Median	Range
BDE-47	7.3	3.6-110	8.0	4.5	4*	<4-16	4*	nd
BDE-99	3.0	1.1-23	2.1	1.0	3.1*	<0.7-6.6	0.7*	<0.7-1.2
BDE-100	2.7	1.1-18	2.2	1.5	1.9	0.57-4.6	1.0	0.6-2.3
BDE-153	7.9	4.6-19	4.3	12	5.5	3.0-17	2.1	0.9-5.6
Total	**20.9**	**nd**	**16.6**	**19.0**	**14.5**	**nd**	**7.8**	**nd**

nd = non-detectable

* The group contained samples below the limit of quantification

In addition to the PBDE congeners shown in Table 8.4, BDE-85 (median=0.6 pmol/g lipid weight, ranged <0.1-204) and BDE-154 (median=0.17 pmol/g lipid weight, ranged <0.05-0.57) were determined in workers from Laboratory A and B, respectively.

Results from Laboratory A are slightly higher than Laboratory B, and the levels from white-collar workers are lower than that of blue collar workers. When comparing the levels between 1997 and 2000, the concentrations of BDE-47 and BDE-153 did not significantly differ between the years.

Thomsen et al. (2001)

In this study, concentrations of PBDE congeners were determined in the blood samples of Norwegian workers from an electronics dismantling facility; workers producing printed circuit boards; and laboratory workers. The results presented in Table 8.5 are similar to those obtained from the Swedish studies discussed above.

Table 8.5 Concentrations of pentaBDE-related congeners (ng/g lipid weight, with pmol/g lipid weight in parentheses) in Norwegian workers (Thomsen et al., 2001)

BDE congener	Electronic dismantlers (n=5)		Circuit board producers (n=5)		Laboratory personnel (n=5)	
	Mean	Range	Mean	Range	Mean	Range
BDE-47	4.0 (8.2)	0.87-15	1.6 (3.3)	0.43-3.4	1.5 (3.1)	1.0-3.0
BDE-99	0.97 (1.7)	0.18-3.6	0.32 (0.57)	n.d.-0.77	0.4 (0.71)	0.17-0.73
BDE-100	0.71 (1.3)	0.16-2.8	0.38 (0.67)	0.17-0.99	0.23 (0.41)	0.15-0.41
BDE-153	1.7 (2.6)	1.2-2.3	0.95 (1.5)	0.5-1.8	0.54 (0.84)	0.43-0.63
BDE-154	0.44 (0.61)	0.21-0.86	0.21 (0.33)	nd -0.3	nd	nd
Total mean:	**7.82 (14.41)**		**3.46 (6.37)**		**2.67 (5.06)**	

nd = non-detectable

BDE-47 was the dominant PBDE congener in all blood samples from all 3 groups. BDE-154 was not detected in the laboratory personnel, but was detected in 4 out of 5 samples in the group producing electronic circuit boards. The mean concentrations of PBDE congeners were elevated in the group of electronic dismantlers. The authors suggest that the consumption of dietary products is expected to represent a major source of human exposure to the brominated pollutants.

8.2 Public exposure

Public exposure to pentaBDE includes direct exposure through products containing pentaBDE, and indirect exposure due to the presence of pentaBDE 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 pentaBDE in the different environmental compartments, and in food and drinking water. Exposure via dust released by pentaBDE-containing articles 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 industrial sources, or they have dietary habits or age-specific behaviours that may increase their exposure, such as inadvertent ingestion of treated articles among young children.

8.2.1 Direct consumer exposure

Based on both Australian and overseas information, pentaBDE was used mainly in flexible and rigid polyurethane foams and polyurethane elastomers. Concentration of pentaBDE in end-use products was in the range of 1.6-9.8%. Flexible polyurethane foam containing pentaBDE was used primarily in soft furnishings including sofas, chairs, mattresses and carpet underlays and in automotive applications like headrests, seating, steering wheels, acoustic systems, dashboards, door panels and carpeting. In most cases, a layer of textile, leather or PVC covers the polyurethane foam. When the flexible polyurethane foam is used as carpet underlay, a layer of carpet is laid on the top. Non-foamed polyurethane is used in the production of hard plastic casings.

Some flame retardants are physically incorporated into consumer products and are not chemically bound within the article matrix. Therefore, it is possible for pentaBDE to be released from the treated articles to some extent, and consumers who use these treated products may be exposed.

It is unlikely that pentaBDE detached from treated articles will be ingested directly. Most hard plastic casings made from pentaBDE-containing polymers are unlikely to be mouthed by young children. For toddlers less than 5 years old, mouthing activity on cushions with or without exposed flexible polyurethane foam treated with pentaBDE (i.e. through tears or holes in the fabric covering) was estimated to be below 0.01 ng/kg bw/day (ENVIRON International Corporation, 2003).

As almost all the flexible polyurethane foam pieces in sofas, chairs, mattresses and vehicles are covered by different surface materials, any dermal exposure through skin contact is considered negligible. Dermal contact with hard plastic casings containing pentaBDE, like some automobile parts, is possible. As pentaBDE is incorporated into the polymeric matrix, dermal exposure from handling these articles is also considered negligible.

Based on an in vitro human skin study with unspecified 'tetrabromodiphenyl oxide', the dermal absorption rate of pentaBDE is predicted to be low (ENVIRON International Corporation, 2003).

PentaBDE has a low vapour pressure and losses from flexible polyurethane foam due to volatilisation are expected to be minimal. As a worst-case, the predicted loss of pentaBDE during the lifetime of cushions and mattresses containing flexible polyurethane foam is less than 0.39% per year over the life cycle, which may be considered as trace levels (Danish EPA, 1999; ENVIRON International Corporation, 2003).

8.2.2 Indirect consumer exposure

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

PentaBDE can be released and distributed in the environment by a number of routes:

- release into the atmosphere or waste water from its industrial uses and disposal
- emission or dust formation from pentaBDE-treated articles and
- leaching and emission from landfill.

Exposure from indoor or outdoor air

In the Australian study conducted by Toms et al. (2006c), samples from indoor and outdoor air, dust and surface wipes were collected and analysed to determine concentrations of PBDEs in the environment. A total of 9 indoor air samples were collected from 5 homes and 3 offices in South East Queensland, while 2 outdoor air samples were obtained from outside 1 home site and 1 office site.

PBDEs were detected in all samples of air and dust, and 90% of surface wipes samples. Samples were analysed for 24 congeners including tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and decabrominated congeners. The concentrations of ∑PBDEs in indoor air are presented in Table 8.6.

Table 8.6 Concentration of total PBDEs ($\sum_{26}$BDE; pg/m^3) indoor air from homes and offices (Adopted from (Toms et al., 2006c))

Site	No of sites	Range	Mean ± SD	Median
Homes	5 + 1 replicate	0.5-179	50 ± 70	19
Offices	3	15-487	173 ± 272	18

Combined measured concentration of congeners BDE-47, -99, -100, -153 and -154 levels, or total PBDE ($\sum_{26}$BDE), is used to represent the indoor and outdoor exposure levels of pentaBDE, and presented in Table 8.7. It should be noted that pentaBDE may contain the congeners BDE-153 and -154, which are present in another commercial product, octaBDE.

Table 8.7 Concentrations of selected pentaBDE congeners in Australian indoor and outdoor air samples (pg/m^3) (Toms et al., 2006c)

Site	BDE 47	BDE-99	BDE-100	BDE-153	Total PBDE congeners*
Home 1A	<92.3	<41.6	<9.3	<2.4	**1.6**
Home 1B	<16.67	<10.42	<2.08	<0.52	**0.5**
Home 2	<26.11	<18	<3.9	7.85	**179**
Home 3	73	<34	<9	1.90	**83**
Home 4	<45	<8	<3	<0.7	**30**
Home 5	<14	<8	<2	<1.3	**17**
Office 1	<40	<10	<3	<1	**18**
Office 2	358.1	20.03[#]	4.6[#]	1.65[#]	**486**
Office 3	<23.2	<10.3	<2.7	0.75[#]	**15**
Outdoor 1	<3.2	<1.4	<0.4	<0.1	**7**
Outdoor 2	<2	<1	<0.03	<0.1	**1.7**

[#] not detected on XAD-2, value detected on filter included here

* excluding limit of detection (LOD) values

The mean level of BDE-47 in the office samples was significantly higher than in the home samples, which is caused by a high reading in one of the office samples. This office also had the highest concentrations in other PBDE congeners. The office was refurbished 2 years prior to sample collection and furnished with carpet and an air-conditioner. Overall, the concentrations of PBDEs were greater in indoor air than in outdoor air.

Exposure from dust

In the dust study, 9 settled dust samples were collected from the same home and office sites as for indoor air sampling. The results of dust samples from each of the homes and offices are presented in Table 8.8.

Table 8.8 Concentrations of selected pentaBDE congeners in Australian dust samples (ng/g dust) (Toms et al., 2006c)

Site	BDE 47	BDE-99	BDE-100	BDE-153	Total PBDE congeners*
Home 1	7.81	10.8	0.69	3.21	**86.8**
Home 2	21.4	25.1	5.05	7.31	**294**
Home 3	53.6	81.8	16.9	14	**591**
Home 4	17.7	19.4	4.31	2.91	**175**
Home 5	18.2	41.3	7.77	7.41	**733**
Office 1A	46.6	63	11.1	19.3	**836**
Office 1B	47.9	49.4	9.22	6.01	**583**
Office 2	210	294	61.2	33.8	**3070**
Office 3	64.2	110	18.8	26.2	**1700**

* Excluding LOD values

Surface wipes were obtained from two homes. The surface samples were obtained from televisions, refrigerators, stereos and DVD players. The study found ΣPBDE on surfaces to range from non-detectable to 23.5 ng/cm^2. Overall, the concentrations of ΣPBDE in the surface wipes from Australia were comparable to those reported in the US, ranging from 0.77 to 15.5 ng/cm^2 (Schecter et al., 2005).

In a study commissioned by NICNAS (Waller et al., 2007), the potential sources of human exposure to PBDEs through dust in Australian homes were investigated (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, such as:

a) decaBDE used in back casing of television sets

b) decaBDE used in flame retarded textiles

c) decaBDE in monitor back casings

d) pentaBDE in circuit boards in homes, offices and in furniture foams

The findings of the study indicated that the presence of foam 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 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; Sjödin et al., 2006). The highest level recorded by Harrad et al. (2008) was 520,000 ng/g dust (predominantly BDE-209); of the order of 100 times 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 (Sjödin et al., 2006), and that this is the only country within the EU that has a regulation specifying the level of flame retardancy for domestic upholstery.

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 limited use of pentaBDE in Australian furniture foam, although this cannot be independently confirmed. The annual demand worldwide for pentaBDE 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 populations in the US (43 homes) (Schecter et al., 2005; Stapleton et al., 2005) and Canada (68 homes) (Wilford et al., 2005), with individual home data being available from several studies in the US. Two studies with individual home data are also available from Kuwait (Gevao et al., 2006), and Singapore (Tan et al., 2007). A number of European studies have been restricted to pooled dust samples (Al Bitar, 2004; Knoth et al., 2002; Santillo et al., 2003a; Santillo et al., 2003b; Sjödin et al., 2006; Sjödin et al., 2004), allowing comparison only of mean values between these studies and the Australian data. Table 8.9 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).

The pool for Scotland reported by (Santillo et al., 2003a) was considered an outlier, as the results for BDE-47 and BDE-99 were reported by the author as indicating inclusion of or more highly contaminated households, and inclusion of this would give an average result that is not representative of the remaining 9 pools in this study. In this pool of 10 houses, BDE-47 was present at 1980 ng/g dw, and BDE-99 at 2100 ng/g dw.

These data relate to the concentration of PBDEs in the household dust (ng/g), rather than the surface loading of PBDEs (ng/m^2), which would be a more direct measure of potential for exposure. However, Allen et al. (2008) showed that these parameters were highly correlated.

Allen et al. (2008) measured the levels of PBDE in household dust and air in 20 US homes. Different PBDE levels in dust from different rooms were reported. Penta- and decaBDE concentrations were significantly higher in the main living area than in the bedroom, while there were no significant differences in octaBDE concentrations. This suggests that penta- and decaBDE have room-specific sources (i.e. televisions, curtains, 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 that used micro-X-ray analysis to characterise the distribution of bromine within household dust from Japan, the UK and the US (Webster et al., 2009) showed that bromine is largely present in scattered particles containing high bromine levels, 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 that was found in two dust samples from a single home in Boston, USA. These samples had very high BDE-209 concentrations of 530,000 and 260,000 ng/g. The bromine was associated with calcium, for example from calcium carbonate or kaolin fillers. The material was also examined by micro-Fourier Transform Infrared Spectroscopy and found to be consistent with an acrylic plastic. This further suggests that the use of textile back coating is associated with high levels of BDE-209 in dust, as textile back coating is the only major application of decaBDE that uses an acrylic matrix.

Table 8.9 International comparison of indoor dust concentrations of BDE-47, BDE-99 and BDE-209 in ng/g dw

Country	BDE-47		BDE-99		BDE-209	
	Median	Max	Median	Max	Median	Max
UK[a] (100 pooled)	27.2 (mean)	nd	79.8 (mean)	nd	10290 (mean)	nd
UK[b] (28 individual) (16 individual)	13	160	23	320	2800	520000
Other Europe[c] (259 pooled)	21.6 (mean)	nd	32.8 (mean)	nd	425 (mean)	nd
Kuwait[d] (17 individual)	2.7	65	3.4	36	83	338
Singapore[e] (31 individual)	20	1500	24	6300	1000	13000
New Zealand[b] (20 individual)	24	150	51	380	nd	nd
Canada[f] (64 individual)	300	33000	430	60000	630	10000
Canada[b] (10 individual) (7 individual)	140	720	330	1800	560	1100
USA[g] (43 individual)	674	10538	626	13841	1680	65777
USA[b] (20 individual) (17 individual)	410	3300	820	6000	1300	3300
USA[h] (10 pooled)	230 (mean)	nd	880 (mean)	nd	2000 (mean)	nd
Australia[i] (10 pooled)	60 (mean)	nd	106 (mean)	nd	732 (mean)	nd

Country	BDE-47		BDE-99		BDE-209	
	Median	Max	Median	Max	Median	Max
Australia[j] (9 individual)	34.3	210	48.8	294	401	2230
Australia[k] (10 individual)	56.5	434	87	862	291	1585

nd = not determined

Sources of data include:

a. (Santillo et al., 2003a) (Sjödin et al., 2006)
b. (Harrad et al., 2008); different sample numbers were used for lower and higher brominated BDEs
c. (Al Bitar, 2004; Knoth et al., 2002; Santillo et al., 2003b; Sjödin et al., 2004)
d. (Gevao et al., 2006)
e. (Tan et al., 2007)
f. (Wilford et al., 2005)
g. (Costner et al., 2005; Schecter et al., 2005; Sharp and Lunder, 2004; Stapleton et al., 2005)
h. (Sjödin et al., 2004)
i. (Sjödin et al., 2006)
j. (Toms et al., 2006c)
k. (Toms et al., 2009)

Information on indoor and outdoor air and dust concentrations of PBDEs was collected in various countries in Europe, North America, Asia and Australia (Besis and Samara, 2012). 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. Concentrations of PBDE in indoor dust were highest in workplaces, particularly in recycling facilities (Table 8.10). The concentrations vary largely among different locations depending on differences in emissions, the atmospheric phase (particle, vapour, or both) where PBDEs were measured and the sampling season. The concentrations are generally higher in the warmer months (Cetin and Odabasi, 2005).

The highest 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 the US; most likely due to high use of PBDE-based flame retardants, owing to particularly stringent UK fire regulations (Besis and Samara, 2012). 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 pg/m^{-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 (Besis and Samara, 2012). Very low outdoor PBDE levels, in the range 1.7-6.8 pg/m^{-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 US, 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 (La Guardia et al., 2006; Sjödin et al., 2001). The fact that BDE-209 is not among PBDEs with high concentrations in the USA samples is indicative of comparatively lower use of the decaBDE mixture in comparison to the use of the pentaBDE.

The outdoor air, indoor air and indoor dust concentrations of selected BDE congeners reported for various countries are presented in Table 8.10.

Table 8.10 Concentrations of PBDEs in indoor air (pg/m^3) and outdoor air (pg/m^3), and indoor dust (ng/g) in various countries (Adopted from Besis and Samara, 2012)

Country	Environment (total of PBDEs detected)	*Median concentration of PBDEs (range)	Comments
USA	Urban outdoor air($\sum_7$PBDEs)	52^a (33-77)	BDE-47 and -99 accounted for 94% of total PBDEs
	Rural outdoor air($\sum_7$PBDEs)	(5.5-15)	BDE-47 and -99 accounted for 91% of total PBDEs
	Home indoor air($\sum_{15}$PBDEs)	760 (210-3980)	BDE-47 and -99 accounted for 76% of total PBDEs
	Home indoor dust ($\sum_7$PBDEs)	4200 (520-29000)	BDE-209 accounted for 48% of total PBDEs
	Home indoor dust ($\sum_{13}$PBDEs)	3500 (920-17000)	BDE-47, -99, -209 accounted for 17%, 29% and 33% of total PBDEs, respectively.
	Office indoor air ($\sum_{21}$PBDEs)	1260 (21-17200)	BDE-17, -47 and -99 accounted for 72% of total PBDEs
Canada	Semi-urban outdoor air ($\sum_9$PBDEs)	(38.8-48)	Predominantly BDE-47
	Rural outdoor air ($\sum_{14}$PBDEs excluding BDE-209)	3.8 (1.2-55)	Samples collected from remote station Alert in the Canadian High Arctic. Predominantly BDE-47 and -99
	Home indoor air ($\sum_{10}$PBDEs)	100 (2-3600)	BDE-47 and -99 accounted for 78% of total PBDEs
	Home indoor dust ($\sum_{13}$PBDEs)	950 (750-3500)	BDE-47, -99, -209 accounted for 21%, 36% and 48% of total PBDEs, respectively
	Office indoor air ($\sum_{20}$PBDEs)	140 (25-350)	BDE-47 and -99 accounted for 69% of total PBDEs

Country	Environment (total of PBDEs detected)	*Median concentration of PBDEs (range)	Comments
UK	Urban outdoor air ($\sum_5$PBDEs)	18 (10-33)	BDE-47 and -99 accounted for 69% of total PBDEs
	Home indoor air ($\sum_5$PBDEs)	128 (60-1,622)	BDE-47 and -99 accounted for 94% of total PBDEs
	Home indoor dust ($\sum_{13}$PBDEs)	2900 (360-520,000)	BDE-209 accounted for almost 100% of total PBDEs
	Office indoor air ($\sum_5$PBDEs)	1082 (82-15,509)	BDE-47 and -99 accounted for 90% of total PBDEs
	Office indoor dust ($\sum_{13}$PBDEs)	7400 (790-280,000)	BDE-209 accounted for 97% of total PBDEs
Sweden	Urban outdoor air ($\sum_8$PBDEs)	6.3 (2.2-21)	Sampling site near a municipal solid waste and treatment plant. BDE-47 and -99 accounted for 67% of total PBDEs
	Home outdoor air ($\sum_{10}$PBDEs)	330 (72-1,400)	BDE-209 accounted for 80% of total PBDEs
	Apartment indoor dust ($\sum_{10}$PBDEs)	1,400 (13-100,000)	BDE-209 accounted for 80% of the total PBDEs
	Office indoor air ($\sum_{10}$PBDEs)	4,000 (140-7,300)	BDE-209 accounted for 72% of total PBDEs
	Office indoor dust ($\sum_{10}$PBDEs)	1,200 (800-13,000)	BDE-209 accounted for 76% of total PBDEs
Kuwait	Urban outdoor air ($\sum_7$PBDEs)	9.3[a] (2.5-32)	BDE-47 and -99 accounted for 85% of total PBDEs
	Home indoor air ($\sum_8$PBDEs)	8.2 (2.5-139)	BDE-47 and -99 accounted for 77% of total PBDEs
	Home indoor dust ($\sum_9$PBDEs)	90 (1-393)	BDE-209 accounted for 93% of total PBDEs
	Office indoor air ($\sum_8$PBDEs)	8.6 (2-385)	BDE-47 and -99 accounted for 80% of the total PBDEs
Greece	Urban outdoor ($\sum_{12}$PBDEs)	26[a] (21-30)	The particle bound fraction of ∑PBDEs varied from 21 to 76%

Country	Environment (total of PBDEs detected)	*Median concentration of PBDEs (range)	Comments
	Semi-urban outdoor ($\sum_{12}$PBDEs)	15^a (4-44)	BDE-47 and -99 accounted for 70% of total PBDEs
	Rural outdoor ($\sum_{15}$PBDEs)	3b (2-11)	BDE-47 and -99 accounted for 67% of total PBDEs
	Home indoor air ($\sum_{30}$PBDEs)	11 (3-15)	Predominantly BDE-47 and -99
	Office indoor air ($\sum_{19}$PBDEs)	115 (19-10,848)	Public building offices with various network servers and telecommunication infrastructures
Japan	Urban outdoor (diBDEs - decaBDE)	19 and 25	2 samples were collected. Individual congeners not provided. BDE-209 accounted for 52 and 76% of total PBDEs, respectively
	Urban outdoor (BDE congeners not identified)	4.5-65	Individual congeners not identified.
	Home indoor (monoBDEs - decaBDE)	17-55	Predominantly BDE-209 collected from 2 samples
	Home indoor dust ($\sum_{26}$PBDEs)	700 (140-3,000)	BDE-209 accounted for 82% of total PBDEs
	Office indoor dust ($\sum_{40}$PBDEs)	1,800 (260-20,000	BDE-209 accounted for 73% of total PBDEs
Thailand	Suburban outdoor air ($\sum_{10}$PBDEs)	45 (8-150)	Collected at e-waste storage facilities. BDE-47 and -99 accounted for 41-75% of total PBDEs
	Home indoor air ($\sum_{10}$PBDEs)	23 (23-72)	BDE-47 and -99 accounted for 61% of total PBDEs
	Home indoor dust ($\sum_{10}$PBDEs)	10 (0.6-257)	BDE-47 and -99 accounted for 22% and 39% of total PBDEs
	e-Waste storage facilities indoor air ($\sum_{14}$PBDEs)	52 (46-350)	BDE-47 and -99 accounted for 72% of total PBDEs

Country	Environment (total of PBDEs detected)	*Median concentration of PBDEs (range)	Comments
	e-Waste storage facilities indoor dust ($\sum_{10}$PBDEs)	28,000 (320-290,000)	BDE-209 accounted for 77% of total PBDEs
China	Urban outdoor air (Guangzhou) ($\sum_{10}$PBDEs)	88-1,941	BDE-47 and -99 accounted for >50% of total PBDEs
	Rural outdoor air (Shunde) ($\sum_{15}$PBDEs)	195-1,450	BDE-209 accounted for 85% of total PBDEs
	Home indoor air ($\sum_{10}$PBDEs)	628 (125-2,877)	BDE-47 and -99 accounted for 72% of total PBDEs
	Home indoor dust ($\sum_{13}$PBDEs)	696 (132-3,887)	BDE-209 accounted for 88% of total PBDEs
	Office indoor air ($\sum_{10}$PBDEs)	518 (181-8,315)	BDE-47 and -99 accounted for 80% of total PBDEs
	e-Waste recycling shop indoor dust ($\sum_{10}$PBDEs)	30,700 (6,300-82,200)	BDE-209 accounted for 97% of total PBDEs
Australia	Urban outdoor air ($\sum_{28}$PBDEs)	1.7	BDE-209 accounted for 82.8% of total PBDEs
	Urban outdoor air ($\sum_{28}$PBDEs)	6.8	BDE-209 accounted for 76.5% of total PBDEs
	Home indoor air ($\sum_{26}$PBDEs)	19 (0.5-179)	Lowest concentration was found in home with no carpet, no air conditioning, aged >5years. Predominantly BDE-47 and -209
	Home indoor dust ($\sum_{7}$PBDEs)	1,200 (500-13,000)	BDE-209 accounted for 61% of total PBDEs
	Home indoor dust ($\sum_{26}$PBDEs)	294 (87-733)	BDE-209 accounted for 65% total PBDEs
	Office indoor air ($\sum_{26}$PBDEs)	18 (15-487)	Highest concentration found in office with carpet, air conditioning and refurbished in the last 2 years. Predominantly BDE-47, and -209
	Office indoor dust ($\sum_{26}$PBDEs)	1,268 (583-3,070)	BDE-209 accounted for 70% of total PBDEs

[a] Mean

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

8.2.3 Exposure from food

Food Standards Australia New Zealand (FSANZ) conducted a survey of PBDEs in a limited range of Australian foods (FSANZ, 2007). A total of 35 foods in table-ready form were analysed. 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. Information on breast milk concentrations of PBDEs was taken from the Australian study by Harden et al (2005). No PBDEs were found in tap water at the limit of detection. Composite samples collected for the 22nd Australian Total Diet Survey (ATDS) were analysed for 26 PBDE congeners ranging from tribrominated to decabrominated congeners.

Calculations of probabilistic dietary exposure estimates were performed using the FSANZ DIAMOND (Dietary Modelling of Nutritional Data) model and the food intake data from the 1995 National Nutrition Survey (NNS) that surveyed 13,858 Australians aged 2 years and above using a 24-hour food recall methodology.

Results were reported for the concentration of each analysed congener in each foodstuff. An overall PBDE intake was determined for each range of age groups, and median and 95th percentile intakes were reported. Individual congener intakes were not reported.

Table 8.11 presents the median and 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.

Table 8.11 Estimated food intake for tri- to hexabrominated PBDE congeners (ng/kg bw/day)

Intake PBDEs from food (ng/kg bw/day)									
Gender and age group	Body Weight (kg)	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	[1]$\sum_6$ PBDE	Total
Median									
Male 2-5	18	0.18	1.15	0.99	0.19	0.15	0.09	2.76	2.82
Female 2-5	17	0.17	1.12	1.02	0.20	0.16	0.10	2.77	2.83
Male 6-12	33	0.14	0.97	0.89	0.17	0.14	0.08	2.39	2.45
Female 6-12	35	0.14	0.81	0.71	0.14	0.11	0.07	1.98	2.03
Male 13-18	65	0.10	0.70	0.65	0.12	0.10	0.06	1.73	1.77
Female 13-18	59	0.09	0.51	0.44	0.08	0.07	0.04	1.24	1.27
Male 19+	82	0.10	0.54	0.47	0.09	0.07	0.05	1.32	1.35
Female 19+	68	0.09	0.41	0.36	0.07	0.06	0.04	1.03	1.05
95th percentile									
Male 2-5	18	0.36	2.33	2.02	0.39	0.31	0.18	5.60	5.73
Female 2-5	17	0.36	2.40	2.17	0.43	0.34	0.21	5.90	6.05
Male 6-12	33	0.28	1.96	1.80	0.35	0.28	0.17	4.83	4.95
Female 6-12	35	0.29	1.66	1.46	0.28	0.23	0.14	4.05	4.15
Male 13-18	65	0.20	1.32	1.23	0.23	0.19	0.12	3.28	3.36
Female 13-18	59	0.18	1.00	0.87	0.17	0.14	0.08	2.44	2.50
Male 19+	82	0.21	1.13	1.00	0.20	0.16	0.10	2.79	2.86

Intake PBDEs from food (ng/kg bw/day)									
Female 19+	68	0.18	0.86	0.75	0.15	0.12	0.07	2.15	2.20

[1] Sum of PBDE congeners BDE-28, -47, -99, -100, -153, -154

8.2.4 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, 2 studies on concentrations of PBDE in pooled human serum and breast milk samples across Australia (Harden et al., 2005; Toms et al., 2006a) provide information on the actual absorbed dose of PBDEs in the Australian population. The pooled serum data show that there are significantly higher levels of total PBDEs in children compared to adults.

Exposure of infants from breast milk

A review of the Polychlorinated Biphenyl (PCB) Management Plan in 2002 resulted in the collection of data on the levels of organochlorine pesticides (OCPs) and PBDEs in the Australian population (Harden et al., 2005). Breast milk samples were collected between March 2002 and September 2003, 2-8 weeks postpartum from primiparous mothers from 12 regions throughout Australia. A total of 157 samples were collected and pooled into 17 samples for analysis, based on the regions. The PBDE congeners that were analysed included BDE-17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154 and -183. The percentage of lipid weight in breast milk samples were determined to be 3.7% (n=17, SD=0.5). The average PBDE concentration was 11 ng/g lipid weight, ranging from 6 ng/g lipid weight in the Tasmanian samples to 18 ng/g lipid weight in the rural NSW samples.

In addition, 3 pools of 8 'historical' breast milk samples collected by the Key Centre for Applied and Nutritional Toxicology in Melbourne in 1993 were also analysed. The mean concentration of total PBDE was 13 ng/g lipid weight.

Breast milk samples collected were dominated by pentaBDE-related congeners, BDE-47, -99, -100, -153 and -154. The results showed similar congener distribution patterns and concentrations between 1993 and 2002-03. The total concentration for each pooled sample for the pentaBDE congeners are presented in Table 8.12.

Table 8.12 Concentrations of pentaBDE related congeners in lipid component of breast milk from the Australian studies (ng/g lipid wt) (Harden et al., 2005)

Congeners	No of samples	Range	Mean	SD
2002-03 samples				
BDE-47	17	2.8-9.6	5.6	1.9
BDE-99	17	1-3.5	1.9	0.6
BDE-100	17	0.7-2.3	1.3	0.4
BDE-153	17	0.6-1.6	1.1	0.2
BDE-154	17	0.1-0.2	0.1	0.03
Σ_5BDE*	17	5.3-17.3	10.0	2.9
1993 samples				

Congeners	No of samples	Range	Mean	SD
BDE-47	3	4.1-5.2	5.4	1.5
BDE-99	3	2.9-3.7	3.2	0.4
BDE-100	3	1.3-1.7	1.5	0.2
BDE-153	3	0.9-1.2	1.0	0.2
BDE-154	3	0.3	0.3	-
$\sum_5$BDE*	3	9.8-13.7	11.4	2.0

* $\sum_5$BDE is the total concentration of BDE-47, -99, -100, -153 and -154.

Some regional variability was reported, although the small sizes of the pool may mean that inter-individual variability in results accounted for most of the observed variations. The 5 major congeners accounted for approximately 91% of the total of congeners analysed. Mean values of 10 and 11.4 ng/g lipid weight were reported in the 2002-03 and 1993 samples, respectively, with BDE-47 as the dominant congener in all pools (approximately 50% of total PBDEs).

A published Australian study reported the levels of pentaBDE 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. Analysis was done on 10 matched samples of human milk, indoor air and dust collected in 2007-2008 in Brisbane, Australia. PBDEs were detected in all matrices (human milk, dust and air) and the median concentrations of BDE-47 and BDE-209 in human milk, air and dust were: 4.2 and 0.3 ng/g lipid; 25 and 7.8 pg/m^3 air; and 56 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 2002-03 to 2007-08 but this may be due to sampling and analytical differences (Toms et al., 2009). Overall, average PBDE concentrations from these individual samples were similar to results from pooled human milk collected in 2002-03 (Harden et al., 2005), indicating that this may be an efficient, cost-effective strategy of assessing PBDE concentrations on a population basis.

Concentrations of PBDEs in breast milk, covering a range of congeners, have been reported for various countries covering large areas of the world, including Asian countries. These are tabulated in Appendix 4. The general findings are consistent, with North American countries having much higher levels of tetra- to hexabrominated PBDEs than elsewhere in the world, and Asian countries generally showing comparatively low levels. In general, the levels of pentaBDE-related congeners detected in breast milk in Australia were higher than those levels found in Europe and Japan but lower than those reported for North America and Canada. The data from Japan was based on low number of samples and in some cases from a single sample. The levels of PBDEs in breast milk reported for North America and Canada are the likely consequence of lactating mother's high utilisation of products and articles containing pentaBDE.

PBDE in blood

In Australia, Toms et al. (2006b) conducted a study to determine the concentration of PBDEs using pooled blood sera samples collected in 2002-03 as part of the (then) Department of the Environment and Heritage National Dioxins Program (NDP). Additional blood serum samples were collected and pooled in 2004-05. All Australian regions were sampled in 2002-

03, while only the Northeast region was sampled in 2004-05. The age range varied from 0-4 to >60 years old. A total of 85 blood sera samples from 8132 individuals were examined.

The concentrations of PBDEs were slightly higher in males than females and were similar across all regions of Australia within each of the designated age ranges, although age was the major influencing factor reported. High correlation is seen between the total PBDE levels and the levels of the 5 major pentaBDE congeners. The data for the pentaBDE-related congeners show no indication of an increase between the first sample collection, 2002-03, and the later collection, 2004-05. Overall, a slight decrease in the concentration of these congeners in adults is seen when comparing the results for the 2 collection times in the Northeast. The total concentrations of pentaBDE-related congeners (BDE-47, -99, -100, -153 and -154) from different regions and age groups are presented in Table 8.13.

Table 8.13 Levels of pentaBDE (sum of BDE-47, -99, -100, -153 and -154) in Australian pooled blood sera from different regions and age groups (ng/g lipid wt)

Gender	Age Group	Region					
		Northeast	Northeast*	Southeast	Rural	West	South
Female	0-4	nd	44.6	nd	nd	nd	nd
	5-15 (<16)	26.3	16.4	17.5	31.0	9.7	nd
	16-30	10.8	8.6	15.3	9.3	12.5	6.9
	31-45	14.7	7.3	7.2	8.8	8.3	6.2
	46-60	5.2	7.7	6.1	6.2	6.5	8.0
	>60	8.2	4.7	4.8	10.9	5.7	6.5
Male	0-4	nd	48.3	nd	nd	nd	nd
	5-15	23.5	19.8	23.2	20.3	20.7	21.5
	16-30	16.7	11.3	17.9	13.1	12.1	12.2
	31-45	13.3	9.7	11.3	12.7	14.4	10.0
	46-60	10.8	8.8	12.1	8.7	9.7	8.0
	>60	6.6	7.6	6.5	20.4	5.9	4.7

* samples collected in 2004-2005

nd = not determined

Table 8.14 presents the mean concentration of individual pentaBDE congeners across all Australian regions from different age groups. The group ‘adults’ include pooled samples from ages 13 to >60 and the group ‘child bearing’ include ages from 16 to 45.

Table 8.14 Mean levels of individual pentaBDE congeners in Australian pooled sera from various age groups

Gender	Age Group	Congener					Sum
		BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	
Female	0-4	25.0	9.0	7.2	6.3	0.9	48.3
	5-15	9.6	4.0	2.5	3.6	0.4	20.2
	16-30	5.1	2.2	1.3	1.7	0.2	10.6
	31-45	4.2	1.7	1.0	1.6	0.2	8.7
	46-60	3.1	1.0	0.8	1.5	0.2	6.6
	>60	3.2	1.2	0.8	1.3	0.2	6.8
	Adult	3.9	1.5	1.0	1.5	0.2	8.2
	Childbearing age	4.6	1.9	1.1	1.6	0.2	9.5
Male	0-4	23.0	7.9	6.5	6.4	0.9	44.6
	5-15	9.1	4.3	2.5	5.0	0.5	21.5
	16-30	6.3	2.5	1.6	3.2	0.3	13.9
	31-45	5.3	2.3	1.5	2.6	0.3	11.9
	46-60	4.5	1.6	1.1	2.2	0.3	9.7
	>60	4.1	1.4	1.0	1.9	0.3	8.6
	Adult	5.0	1.9	1.3	2.5	0.3	11.0
Both	Adult	4.5	1.7	1.2	2.0	0.3	9.6

Overall, the Australian study results indicate that the dominant pentaBDE congener in all the matrices was BDE-47. BDE-99, which is the dominant congener in commercial pentaBDE, is normally present at lower concentrations than BDE-47 and comparatively similar concentrations to BDE-100, while BDE-154 is commonly seen at much lower levels than the other 4 major congeners. This is likely to be due to toxicokinetic differences, whether differences in metabolism or in excretion of the unmetabolised congener. Stapleton (2004) demonstrated a specific reduction of BDE-99 to BDE-47 in the intestines of common carp.

Therefore, the relative congener concentrations in serum are expected to vary with time after exposure, and also with the exposure route, as relative dust levels of BDE-47 and BDE-99 are reflective of the dominance of BDE-99 in pentaBDE formulations, while many foods show a dominance of BDE-47 over BDE-99 (FSANZ, 2007), consistent with environmental biomonitoring results. A further possibility is that the levels of the hexabrominated congeners, particularly BDE-153, are supplemented by exposure to the commercial octaBDE, which also contains these congeners, particularly as the marker congener for this commercial mixture, BDE-183, was found in house dust in Australia.

9 Hazard Classification

Based on the available data, pentaBDE meets the criteria for classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (UNECE, 2009). PentaBDE is classified as hazardous, with the following hazard categories and hazard statements for human health in the Hazardous Chemical Information System (HCIS) (Safe Work Australia):

- Specific target organ toxicity (repeated exposure) – Category 2; H373 (May cause damage to organs through prolonged or repeated exposure) and
- Reproductive toxicity (effects on or via lactation) – Category H362 (May cause harm to breast-fed children).

The HCIS also includes the following hazard categories and hazard statements for the environment:

- Hazardous to the aquatic environment (acute) – Category 1; H400 (Very toxic to aquatic life) and
- Hazardous to the aquatic environment (chronic) – Category 1; H410 (Very toxic to aquatic life with long lasting effects).

The following information summarises the overall health hazards of pentaBDE, which is also representative of the toxicity of tetra- to hexabrominated congeners.

9.1 Absorption, distribution, metabolism and excretion

The individual PBDE congeners in the tetrabrominated and pentabrominated range are readily absorbed orally and by inhalation; dermal absorption has been observed to a lesser extent. In the body, there is a large degree of localisation to adipose tissue, particularly for the lower brominated congeners. These also readily partition to breast milk. Excretion in rats is mainly faecal, although adult mice have shown to readily excrete the tetrabrominated congener BDE-47 in urine. The excretion difference results in different half lives in rats and in mice. The human half life has been estimated to be 1,040 days for BDE-99 and 573 days for BDE-100 (Geyer et al., 2004).

In fish, there is evidence of specific reductive debromination of BDE-99 to BDE-47. This may contribute to the different bioaccumulation behaviour of these 2 major congeners. Metabolism of pentabrominated and tetrabrominated congeners has been demonstrated to result in small amounts of conversion to hydroxylated metabolites.

9.2 Acute toxicity

PentaBDE has low acute toxicity by oral route with reported LD50 values in rats ranging from 2,640 – 6,200 mg/kg bw. For dermal toxicity, no mortality was seen up to 11,000 mg/kg bw, with LD 50 values in rats reported as >2000 mg/kg. In an acute inhalation toxicity study in rats, mortality was not seen up to 200 mg/L, although the fraction of the aerosol in the respirable size range was not clearly identified (European Communities, 2001b).

9.3 Irritation and skin sensitisation effects

PentaBDE was slightly irritating to rabbit skin, producing slight erythema and oedema which resolved within 72 hours in some animals. In eye irritation studies, conjunctival irritation which resolved within 7 days was reported. Slight respiratory irritation was observed at high exposure concentrations in rat inhalation toxicity studies (European Communities, 2001b).

No evidence of skin sensitisation in guinea pigs was reported in various maximisation tests (European Communities, 2001b).

9.4 Repeat dose toxicity

A number of repeat dose toxicity studies (28-90 days) in rodents have been conducted using pentaBDE by dietary administration. A number of studies using repeated dose administration of pentaBDE, or individual pentaBDE congeners (for study of more specific endpoints) in rats have also been reported. A similar pattern of effects was reported across the repeat dose studies. The major effects were seen in the liver and the thyroid.

In rats and mice, increases in absolute and relative liver weights and histopathological changes including enlarged centrilobular and midzonal liver parenchymal cells in which the cytoplasm had large areas of finely granular ‘ground glass’ structures containing eosinophilic ‘round bodies’ and/or vacuolisation were reported. Histopathological changes in the thyroid occurred at 100 mg/kg bw/day. The studies reported changes in T_4 levels at the end of 90 days. The LOAEL in a 90 day study was set at 2 mg/kg bw/day due to histopathological effects in the liver (European Communities, 2001b; Fowles et al., 1994; Great Lakes Chemical Corporation, 1976; Rowsell et al., 2004.).

In addition, the results of the in vitro and in vivo studies on the thyroid hormones and related systems of rats indicate that there is a clear reduction in T_4 levels associated with exposure to the lower brominated PBDEs (Darnerud et al., 2004; Stoker et al., 2004; Zhou et al., 2001; Zhou et al., 2002). T_3 levels were less affected. It is likely that at least part of the reduction in T_4 levels is associated with the upregulation of uridine diphosphate glucuronosyltransferase (UDPGT), which is involved in the elimination of T_4 from the body by Phase II conjugation. Some hydroxylated metabolites show binding to transthyretin (TTR), but this may be a more significant effect in rodents, where TTR is the major thyroxine binding protein, than in humans.

9.5 Reproductive toxicity

The reproductive endocrine effects following PBDE exposure to rats included some subtle effects to treated dams (Stoker et al, 2004). The reported effects in the offspring of treated dams induced at a very low dose included:

- ultrastructural changes in the ovaries
- reduced relative weights of testes and epididymis
- reduced sperm production.

These abnormalities were similar to effects produced by 6-n-propyl-2-thiouracil (PTU), which is believed to act through a thyroid hormone mediated mechanism (Kuriyama et al., 2004a; Kuriyama et al., 2004b; Kuriyama et al., 2005; Talsness et al., 2003). Other possible mechanisms for reproductive endocrine effects include:

- direct effects at receptors
- regulation of receptor gene expression or

- induction of aromatase (CYP19) which directly affect synthesis of sex hormones or CYP17.

9.6 Neurodevelopmental toxicity

Comparison of the in vitro neurotoxicity results for the individual congeners indicates decrease in neurotoxic effects as the bromination level increases above 6. Therefore, the pentaBDE formulation is expected to show the greatest effects among the PBDE mixtures that are commercially available. Neurodevelopmental effects of PCBs such as Aroclor 1254 have also been demonstrated, and the effects seen for the lower brominated PBDEs may be compared with the known effects of PCBs (hyperactivity and reduced habituation) (Branchi et al., 2005). In utero exposure to a single low dose of BDE-99 was also reported to disrupt neurobehavioural development and cause permanent abnormality in the male reproductive systems in rats, apparent in adulthood (Kuriyama et al., 2005).

A number of observations on endocrine effects following gestational or neonatal exposure to lower brominated PBDEs are relevant to neurodevelopment. Importantly, hypothyroidism is an observed effect of lower brominated PBDE exposure, and is a known cause of neurodevelopmental effects in rats (Bonet and Herrera, 1988; Widholm et al., 2001). Bonet and Herrera (1988) demonstrated that the effect of maternal hypothyroidism on neurodevelopment of rat pups was much greater when the thyroid hormone deficiency occurred during the first half of gestation, in a study using thyroxine supplemented thyroidectomised dams. This provides an indication of the importance of timing on the dosing of rat dams during gestation with thyroid-depleting agents such as PBDE congeners. In addition, several studies have indicated possible effects on sex hormone dependent neurological function, and effects on androgen, oestrogen and progesterone receptors may also affect neurodevelopment (Widholm et al., 2001).

Health assessments were conducted for a group of 35 workers exposed for at least 6 weeks to polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers during manufacture. In 4 workers, the study reported:

- higher than normal prevalence of primary hypothyroidism with elevated serum concentrations of thyrotropin
- low, or borderline-low, total serum T4 and free thyroxine indices (Bahn et al., 1980b).

The study also observed a significant reduction in sensory and fibular motor nerve velocities. Three of these workers were re-evaluated one year after the initial study. Partial reversibility was seen in 1 worker (Bahn et al., 1980a).

The NOEL and LOEL determined from various oral studies on pentaBDE are presented in Table 9.1 (UNEP, 2006)

Table 9.1 NOEL and LOEL after oral administration of BDE-99 congener or PentaBDE formulation (Adopted from the Risk profile on commercial pentabromodiphenyl ether)

Chemical	Duration	Dose mg/kg	NOEL mg/kg/day	LOEL mg/kg/day	Effects	Species	Reference
BDE-99	Single dose	0.8 or 12.0	Not available	0.8	Neurotoxicity behaviour – motor activity level and learning	Mouse	(Eriksson et al., 2001)
BDE-99	Single dose	0.6, 6, or 30	Not available	0.6	Developmental and neurotoxicity behaviour – hypoactive	Mouse	(Branchi et al., 2002)
BDE-99	Single dose	0.4, 0.8, 4.0, 8.0, or 16	0.4	0.8	Developmental and neurotoxicity behaviour	Mouse	(Sand et al., 2004; Viberg et al., 2004)
BDE-99	Single dose	0.06 and 0.3	Not available	0.06	Developmental and neurotoxicity behaviour – increased activity	Pregnant rat, F1	(Kuriyama et al., 2005)
BDE-99	Single dose	0.06 and 0 .3 pregnant animals	0.06	0.3	Reduced testis size and number of sperms	Rat, F1	(Kuriyama et al., 2005)
pentaBDE (DE-71)	30 days	0.01, 0.05, 0.1, 0.5, or 1	1	Not available	Growth, food intake, haematology, histopathology, clinical chemistry	Rat	(Great Lakes Chemical Corporation, 1985)
pentaBDE (DE-71)	30 days	0, 3, 30 or 60	3	30	Liver weight, puberty, reproduction, liver enzymes, T_4 reduction	Male rat	(Stoker et al., 2004)
pentaBDE (DE-71)	30 days	0, 3, 30 or 60	Not available	3	T_4 reduction	Female rat	(Stoker et al., 2004)
pentaBDE (DE-71)	35 days	0, 1, 10 or 30	1	10	T_4 reduction, Liver enzyme	Pregnant rat	(Zhou et al., 2001; Zhou et al., 2002)

Chemical	Duration	Dose mg/kg	NOEL mg/kg/day	LOEL mg/kg/day	Effects	Species	Reference
pentaBDE (DE-71)	90 days	0-0.44	Not available	0.44	Liver enzymes	Rat	(Carlson, 1980)
pentaBDE (DE-71)	90 days	0, 2, 10 or 100	0-2	2-10	Hepatocytomegally, thyroid hyperplasia	Rat	(Great Lakes Chemical Corporation, 1984)

9.7 Genotoxicity

A number of in vitro genotoxicity studies have been undertaken using commercial pentaBDE (European Communities, 2001b). These included point mutation and chromosomal aberration studies. The majority of the studies showed negative results, and the overall conclusion based on the total group of studies is that pentaBDE is not genotoxic.

9.8 Carcinogenicity

There is inadequate information to assess the carcinogenic potential of pentaBDE. Animal chronic toxicity or carcinogenicity studies are not available for pentaBDE.

10 Discussion and Conclusions

10.1 Environmental hazard and risk

The main components of commercial pentaBDE (tetra-, penta- and hexabrominated congeners) have low water solubility and vapour pressure along with high octanol-water partition coefficients. These factors indicate they will partition strongly to organic carbon and be unlikely to volatilise to the atmosphere.

Rates of photodegradation of PBDEs have been shown to decrease as the levels of bromination decreases. In the environment, pentaBDE will be initially found in bulk matrices, hence exposure to light would only occur for a very small proportion of the available compounds.

The breakdown of tetra- and pentabrominated congeners through reaction with hydroxyl radicals is likely to be very slow with a calculated half-lives by this mechanism of 7.1 days and 19.4 days respectively.

The main congeners found in the pentaBDE are expected to be hydrolytically stable. There is evidence that PBDEs are debrominated in water using a variety of reducing agents. Some of these included sulfides found in anaerobic sediment. Lower brominated congeners were formed under the same conditions from highly brominated BDEs, including those of particular environmental concern such as BDE-47, -99 and -100. However, the reaction rate constants of lower BDEs were shown to decrease as the number of bromines decreased.

The congeners found in pentaBDE are generally expected to be biotically stable under aerobic and anaerobic conditions. Biotransformation is a possible route of degradation of pentaBDE and there is evidence that organisms can metabolise pentaBDE to lower brominated congeners, particularly BDE-47.

Data generated from laboratory and field studies, along with a large volume of data monitoring levels of PBDEs in biota show that the components of pentaBDE are readily bioavailable, and can accumulate through the food chain. Generally, congeners contained in pentaBDE (BDE-47 and BDE-99) dominated PBDE levels found in biota. The dominance of the BDE-47 congener (often found at >40% total PBDEs in biotic samples) indicates that organisms either have a preferential uptake of this congener, or there is debromination of penta- and hexabrominated congeners to BDE-47 within the organisms, thereby increasing its concentration relative to that found in the commercial mixture.

BDE-47, BDE-99 and BDE-100 have very high bioconcentration and bioaccumulation factors and are generally the most dominant congeners measured in biota. Levels of these substances have been measured in marine predators including dolphins, seals, polar bears and birds. In addition to bioaccumulation within organisms, evidence shows a strong biomagnification tendency for these congeners.

The combination of the modelled and measured levels of individual congeners in remote environments indicates that pentaBDE is capable of undergoing long-range transport.

Calculating 'safe' concentrations for very persistent and very bioaccumulative substances such as pentaBDE is difficult because potential adverse effects from exposure to these chemicals may not manifest themselves for very long periods of time, much longer than can be captured by standard toxicity testing.

Test data for effects of pentaBDE, either in its commercial product or individual congeners, are available for fish, aquatic invertebrates, algae, sediment organisms, soil microorganisms, earthworms and 6 plant species in the form a seedling emergence study.

For aquatic species, chronic and sub-chronic NOECs (no observed effect concentrations) are available for fish and aquatic invertebrates with long-term NOECs available for algae. The most sensitive species tested was the marine copepod *Acartia tonsa*. This species was less sensitive to acute exposure (48 hours EC_{50} for pentaBDE-related congeners of 520-702 µg/L) than sub-chronic exposure where the 5 day EC_{50} for larval development rates for BDE-99 and BDE-100 were 4.2 and 1.2 µg/L respectively. While no NOEC was identified for the sub-chronic part of the test, 5-day EC10 values of 0.039 and 0.023 µg/L for BDE-99 and BDE-100, respectively were calculated and used as approximate NOECs.

There were 3 prolonged sediment toxicity studies available in different test species. In all tests, exposure was through spiked sediment and the lowest NOEC derived was 3.1 mg/kg sediment.

For the terrestrial compartment, test data are available for soil microorganisms (nitrogen transformation test only), plants (seedling emergence study only) and earthworms (acute test only). The soil microorganism study was only performed up to a concentration of 1 mg/kg soil dw and no effects were observed. The seedling emergence test was performed on 3 monocots and 3 dicots. The lowest NOEC from this test was 16 mg/kg dw for corn.

The earthworm test was a 14-day acute study where the NOEC was 500 mg pentaBDE/kg dw, the highest concentration tested. Based on experience it is becoming widely accepted that earthworms are much more sensitive to longer term testing than to the acute 14-day test, and the study provided may not be sufficient to determine toxicity of pentaBDE to earthworms.

While sufficient information exists from available ecotoxicity data to derive screening level PNECs (predicted no effect concentrations) for water, sediment and soil, the data required to determine PECs (predicted environmental concentrations) for these media were inadequate. Consequently, no standard risk assessment (PEC/PNEC approach) could be performed.

Nevertheless, there is ample evidence to conclude that under environmental conditions, pentaBDE is very persistent and very bioaccumulative, and is very toxic to aquatic organisms. In addition, pentaBDE may undergo long-range transport in the environment. Thus, it has been detected in remote regions that are far removed from major sources of emissions. This combination of characteristics means that there are very significant long-term risks to the environment from the manufacture, import and use of the chemical. PentaBDE is of international concern and has been listed on Annex A of the Stockholm Convention on Persistent Organic Pollutants, for global elimination. PentaBDE is also listed in Annex III of the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade under which importation of the mixture of the chemicals is subject to the prior informed consent (PIC) procedure).

10.2 Human health risk

Health effects

Based on the available information, pentaBDE has very low acute toxicity, with no irritant or sensitising effects. The critical effects seen on single or repeat dosing with pentaBDE or pentaBDE congeners have been observed in the liver, the thyroid hormone system, neurobehavioural development, and development of sex organs. PentaBDE is classified as hazardous for human health in the Hazardous Chemical Information System (HCIS) (Safe Work Australia). Refer to Section 9 for the human health classification, hazard categories and hazards of pentaBDE in accordance with the GHS.

The liver effects and enzyme induction in rats may be considered to be an adaptive change. However, a number of studies have shown that the enzyme induction may have further systemic effects, particularly at sensitive life stages, for example via mechanisms controlled by the thyroid hormones. The results of the in vitro and in vivo studies on the effect of pentaBDE or individual congeners on the thyroid hormones and related systems indicate that there is a clear reduction in T_4 levels associated with exposure to the lower brominated PBDEs. Following oral dosing of rat dams during gestation with a single dose of 60 µg BDE-99/kg maternal bw, adverse effects were seen on neurobehavioural development, sperm counts and ovarian microstructure in offspring. There are a wide range of studies that suggest that the neurodevelopment and sexual development effects are likely to be related to hypothyroidism following enzyme induction occurring at critical foetal development periods.

Routes of exposure

While pentaBDE is no longer imported into Australia as a raw material, pentaBDE is likely to be present in Australia in articles manufactured or imported in the past. Therefore, occupational exposures to pentaBDE in the form of pure chemical or chemical mixtures is not expected to occur. However, controls should be in place to ensure that importation and use of pentaBDE continues to be prohibited in the future.

The major route of occupational exposure is expected to be due to release from articles in use, and particularly foam furnishings manufactured or imported in the past. This is likely to be widespread, particularly among office workers. These exposures are expected to be similar to those for the general public using articles of a similar type. Biomonitoring results used for determination of the public health risk will include the contribution from incidental occupational exposure (considered as indirect exposure in this report).

Another potential route of occupational exposure will arise for workers involved in disposal and dismantling of articles that have been flame-retarded using pentaBDE. Electronics dismantling has been shown in several Scandinavian studies to give rise to greater exposure to PBDEs than in the general public; however, the major exposure was to octaBDE and decaBDE. It is not clear that electronics dismantling involving shredding of the components is carried out in Australia; therefore, it is not possible to derive a suitable worst case estimate of exposure.

For a number of persistent and bioaccumulative chemicals, such as polychlorinated biphenyls (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).

Recent work has indicated that there are large differences in exposure, particularly to pentaBDE-related congeners in household dust (Jones-Otazo et al., 2005; Sjödin et al., 2004). There is also evidence that human serum and breast milk levels of PBDEs, particularly the pentaBDE congeners, are greatly affected by levels of PBDEs in indoor dust (Wu et al., 2007).

North America has much higher levels of pentaBDE congeners in household dust compared to anywhere else in the world; and higher levels of these congeners were also found in human serum and breast milk in Americans (Sharp and Lunder, 2004; Wu et al., 2007). However, a link between dietary habits and PBDE levels in humans has not been clearly established. The age variation of PBDE levels in humans (NICNAS, 2007c) is unlike that for PCBs, which are largely taken in through food, and reach higher levels in older individuals.

Similar results from the UK are particularly 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. These results from the UK 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 (Sjödin et al., 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 plasma was found to be the best matrix for the detection of higher brominated congeners.

Articles as sources of PBDEs

Scientific literature on the release of PBDEs from articles is limited. One 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 (Toms et al., 2006c) is difficult to interpret because it does not include control dust wipes to examine if the measured PBDEs are from the presumed source or from more remote sources.

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 the 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 throughout 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 may contain alternative flame retardants) or the presence of other major determinants that were not taken into account in the analyses may also contribute to correlation difficulties. The study reported in Appendix 3 demonstrates this spatial inhomogeneity. A study conducted in 20 homes in the US showed that:

- there was inter-room variability, although not large temporal variability and
- the contents of the household vacuum bag did not correlate well with researcher-collected dust (Allen et al., 2008).

These issues support the use of biomonitoring data as the key measure for human health risk assessment. A relevant risk assessment with the focus on certain PBDE congeners was undertaken by NICNAS (NICNAS, 2007c). This report recommended a full risk assessment when data becomes available from international assessments. A precautionary approach, which prohibits the importation and/or manufacture of pentaBDE while it remains as a priority existing chemical was adopted to ensure that human exposure to pentabrominated congeners was minimised.

Overall, the neurobehavioural, developmental and reproductive effects in the offspring of experimental animals exposed to pentaBDE, and the potential for these effects to occur in humans cannot be completely ruled out. Repeated exposure to pentaBDE also resulted in perturbation of the thyroid hormone homeostasis. The biomonitoring studies, although not robust, indicate exposure to pentaBDE. Considering the available range of studies (animals, humans and biomonitoring studies) and the routes of exposure, there is potential for human health risk to pentaBDE.

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
BDE-28	2,4,4′-tribromodiphenyl ether
BDE-29	2,4,5-tribromodiphenyl ether

Tribrominated	
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
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

Tetrabrominated	
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
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

Pentabrominated	
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
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

Hexabrominated	
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
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

Hexabrominated	
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
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

Octabrominated	
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

Octabrominated	
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 gives 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 that 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

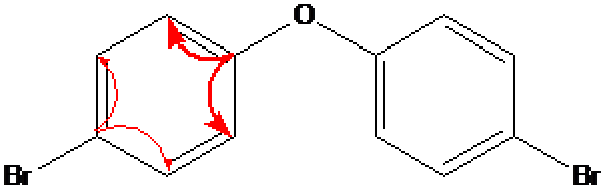
The production of PBDEs utilises electrophilic aromatic substitution starting with diphenyl ether, and using Br_2 and a Lewis acid catalytic species such as $FeBr_3$. The isomer selectivity of the aromatic substitution reactions is very widely known Substituents on a benzene ring are categorised according 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 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 initial substituent, but also 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 para-substituted reaction product, due to the steric crowding at the ortho position.

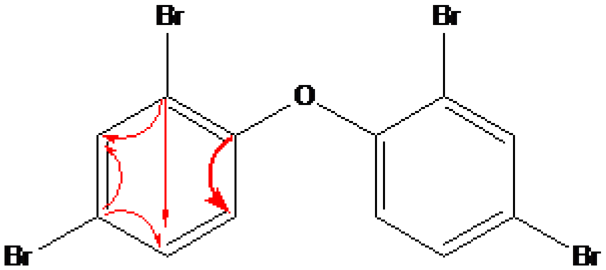
In the case of diphenyl ether, the ether group is categorised as moderately activating and (ortho, para) directing. The phenyl ether substituent is quite bulky; therefore, the most probable substitution reaction will occur at the para (4-) position, with ortho substitution (2-) occurring at a much lower 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 3 tetrabrominated congeners at above their limits of quantification in the 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 the bromine atoms. The 2 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 3 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 2 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 2 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 1 major starting substitution pattern. However, there are only 3 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 2 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 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 (i.e. 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 (Grabda et al., 2007; Hu et al., 2005).

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 gas chromatography (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.

An example of such a congener is the octabrominated BDE-202, which has been identified in studies in 2 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 (Grabda et al., 2007; Hu et al., 2005), 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 sulfides 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 (Bezares-Cruz et al., 2004; Keum and Li, 2005; Konstantinov et al., 2008), 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 3 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 (Söderström et al., 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. The objective was to see if there was a correlation between the concentrations of the PBDEs in dust to the proximity of PBDE containing sources.

In this study (CSIRO, 2007) 4 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, whether 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 semi quantitative 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 >100,000 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, i.e. 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 cathode ray tube (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 back coatings, 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 liquid crystal display (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 power boards, 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 US 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 US, 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 m^2 to 2 m^2, 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 8 congeners BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209. The first 6 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 four Australian homes

Location		BDE -28	BDE -47	BDE -99	BDE - 100	BDE - 153	BDE - 154	Sum pentaBDE	BDE - 183	BDE - 209	Total	Source
House 10												
Bedroom 2	Near TV	6.8	760	1,450	270	180	140	2,800	24	230	3,270	TV back
Bedroom 2	Away from TV	2.8	300	650	120	140	77	1,287	310	1,330	3,640	-
Bedroom 1	Away from foam underlay	74	9,050	16,900	2,430	1,710	1,200	31,290	200	4,100	38,200	Underlay
Study	Near computer	<10	220	360	63	110	54	807	55	1,760	3,380	Monitor
Study	Away from computer	8.3	200	330	59	58	42	689	28	450	1,290	-
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	1,127	18	1,040	2,340	-
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	1,100	-
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	4,540	5,770	TV back
Lounge	Away from TV	10	370	410	83	45	37	945	5.9	510	1,580	-

Location		BDE -28	BDE -47	BDE -99	BDE -100	BDE -153	BDE -154	Sum pentaBDE	BDE -183	BDE -209	Total	Source
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	1,810	-
Study	Near desk chair	20	5,340	13,700	2,230	2,290	1,520	25,080	120	5,790	32,900	Desk Chair
Study	Away from desk chair	12	3,070	6,030	1,060	770	630	11,560	37	1,030	13,500	-
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	1,340	Sofa
Upstairs Living	Away from Sofa	<9	79	120	18	36	10	263	92	1,600	2,280	-
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, House 10, 2 other foam scenarios were examined. One related to mattresses in Bedroom 2 and Bedroom 3 of House 12. In this case, the 2 bedrooms were similarly furnished, with identical mattresses, both containing bromine. However XRF analysis of the dust from the 2 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 US 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 (Sjodin et 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 US (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 US 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 et al., 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 US, 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 US would be in the prevalence of such 'hot spots' around pentaBDE-containing foam in furniture. In the case of decaBDE, the maximum international dust levels have generally been seen in the UK (Harrad et al., 2008; Santillo et al., 2003a; Sjödin et al., 2006). The highest level recorded by Harrad et al was 520,000 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 EU 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 back coatings are reported to be composed of a latex material, with a high content of around 30% decaBDE. Specifications for performance of the back coatings 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 back coating 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 back coating had not commenced to break down, or that the back coating 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.

Appendix 4 – Summary of human biomonitoring studies

A wide range of results from many countries have been reported for breast milk. Results below are standardised to ng/g/lipid weight. The different studies have often quantified different suites of PBDE congeners, and these may include pentaBDE-related congeners apart from those given in the Tables. However, for consistency of reporting, only the five congeners, BDE-47, -99, -100, -153 and -154 are reported. The majority of studies have quantified all these congeners.

Results expressed as median or geometric mean are preferred given that the distributions of PBDE concentrations are expected to be log normal. Pooled studies or results expressed as means give much higher results as the effects of the high concentration outliers on the measure of central tendency are more pronounced. For example, Schecter et al (2003) found a mean value for BDE-47, for 47 participants, of 40.8 ng/g lw, while the median was 18.4 ng/g lw. The tables have been separated according to whether median or mean results are presented. The Australian pooled data should only be compared with mean values.

A sum of the concentrations of the 5 congeners is presented for the mean data. This sum cannot be calculated for median data. While a combined median is reported in the majority of the studies, the differences in the congeners determined does not allow these to be directly compared.

Table A3-1 Human breast milk monitoring results: Results reported as median or geometric mean

Country	No. Participants	Year	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Europe								
Finland	11	1996	0.85	0.35	-	0.29	-	(Strandman et al., 2000)
Sweden	39	1997	1.83	0.44	0.34	0.48	0.06	(Darnerud et al., 1998)
Sweden	39	1999	2.52	0.72	0.48	0.65	0.07	(Atuma et al., 2001)
Sweden	15	2000	1.15	0.21	0.14	0.32	0.02	(Guvenius-Meironyté et al., 2003)

Country	No. Participants	Year	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Germany	62	2001-03	0.54	0.17	0.17	0.53	0.02	(Vieth et al., 2004)
UK	54	2001-03	*2.7*	0.8	0.5	1.3	0.4	(Kotz et al., 2005)
North America								
Canada	10	1991	1.75	0.65	0.21	0.29	-	(Ryan and Patry, 2000)
Canada	72	1992	1.4	0.5	0.2	0.3	0.05	(Ryan and Patry, 2001)
USA	4	2000	126	27	23.5	14.8	1.66	(Päpke et al., 2001)
Canada	20	2001	13.3	3	2.3	3	0.6	(Ryan and Patry, 2002)
USA	47	2002	18.4	5.7	2.9	2	0.22	(Schecter et al., 2003)
USA	20	2002-03	24.8	4.47	4.91	10.06	0.32	(Sharp and Lunder, 2004)
USA	40	2003	27.8	5.36	5.25	4.79	0.4	(She et al., 2005)
Other								
Japan	13	1999	0.58	0.14	0.12	0.28	0.03	(Akatsu et al., 2003)
China	27	-	1.3	0.23	0.19	0.8	0.11	(Bi et al., 2006)

Country	No. Participants	Year	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Japan	105	2004	0.68	0.41	0.38	0.31	0.23	(Eslami et al., 2006)

Table A3-2 Human breast milk monitoring results: Results reported as mean or pooled studies

Country	No. Participants	Year	Sum	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Europe									
Sweden	Pool	1972	0.07	0.06	-	-	0.01	-	(Meironyté et al., 1999)
Sweden	Pool	1976	0.3	0.18	0.04	0.05	0.02	0.01	(Meironyté et al., 1999)
Sweden	Pool	1980	0.45	0.28	0.09	0.04	0.03	0.01	(Meironyté et al., 1999)
Sweden	Pool	1980	0.261	0.12	0.06	0.044	0.037	-	(Fängström et al., 2008)
Sweden	Pool	1984	0.7	0.49	0.08	0.06	0.05	0.02	(Meironyté et al., 1999)
Sweden	Pool	1984	0.458	0.26	0.043	0.073	0.082	-	(Fängström et al., 2008)
Sweden	Pool	1988	1.23	0.57	0.26	0.16	0.24	-	(Fängström et al., 2008)
Sweden	Pool a (n=20)	1990	1.13	0.55	0.24	0.17	0.17	-	(Fängström et al., 2008)

Country	No. Participants	Year	Sum	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Sweden	Pool b (n=20)	1990	2.18	1	0.62	0.28	0.28	-	(Fängström et al., 2008)
Sweden	Pool	1992	2.67	1.4	0.48	0.31	0.48	-	(Fängström et al., 2008)
Sweden	Pool	1994	2	1.48	0.26	0.09	0.15	0.02	(Meironyté et al., 1999)
Sweden	Pool	1996	2.89	2.08	0.41	0.15	0.24	0.01	(Meironyté et al., 1999)
Sweden	Pool	1994	3.3	1.7	0.84	0.31	0.45	-	(Fängström et al., 2008)
Sweden	Pool	1995	4.03	2.1	0.75	0.51	0.67	-	(Fängström et al., 2008)
Sweden	Pool	1996	3.7	2	0.74	0.43	0.53	-	(Fängström et al., 2008)
Sweden	Pool	1997	3.69	2.28	0.48	0.42	0.46	0.05	(Meironyté et al., 1999)
Sweden	Pool	1997	3.3	1.6	0.69	0.36	0.65	-	(Fängström et al., 2005)
Sweden	124	1999	2.98	1.77	0.37	0.27	0.51	0.06	(Darnerud et al., 1998)
Sweden	Pool	1999	3.74	2.1	0.53	0.29	0.82	-	(Fängström et al., 2008)
Italy	10	2000-01	3.89	1.9	0.97	0.48	0.47	0.07	(Ingelido et al., 2007)
	10	1998-2000	2.625	1.5	0.41	0.28	0.41	0.025	

Country	No. Participants	Year	Sum	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
	13	1998-2000	2.117	0.9	0.51	0.19	0.47	0.047	
	6	1998-2000	1.46	0.55	0.14	0.15	0.6	0.02	
Sweden	Pool	2001	4.3	1.8	0.57	0.63	1.3	-	(Fängström et al., 2008)
Sweden	Pool	2002	2.72	1.4	0.33	0.27	0.72	-	(Fängström et al., 2008)
Germany	62	2001-03	1.93	0.82	0.25	0.21	0.63	0.02	(Vieth et al., 2004)
Belgium	Pooled	2001-03	1.93	0.89	0.2	0.2	0.62	0.02	(Kotz et al., 2005)
Bulgaria	Pooled	2001-03	0.61	0.27	0.11	0.05	0.15	0.03	(Kotz et al., 2005)
Croatia	pool	2001-03	1.85	0.99	0.31	0.2	0.3	0.05	(Kotz et al., 2005)
Czech Republic	pool	2001-03	0.68	0.4	0.09	0.08	0.1	0.01	(Kotz et al., 2005)
Finland	Pooled	2001-03	4.568	3.01	0.49	0.408	0.61	0.05	(Kotz et al., 2005)
Germany	Pooled	2001-03	5.43	3.1	1.23	0.47	0.58	0.05	(Kotz et al., 2005)
Hungary	Pooled	2001-03	0.62	0.29	0.09	0.06	0.17	0.01	(Kotz et al., 2005)
Ireland	Pooled	2001-03	9.75	6.14	1.51	1.02	0.99	0.09	(Kotz et al., 2005)

Country	No. Participants	Year	Sum	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Italy	Pooled	2001-03	2.64	1.14	0.5	0.26	0.66	0.08	(Kotz et al., 2005)
Luxembourg	Pooled	2001-03	2.77	1.51	0.28	0.29	0.66	0.03	(Kotz et al., 2005)
Romania	Pooled	2001-03	1	0.5	0.16	0.09	0.21	0.04	(Kotz et al., 2005)
Slovakia	Pooled	2001-03	0.81	0.37	0.12	0.09	0.19	0.04	(Kotz et al., 2005)
Spain	Pooled	2001-03	2.52	1.24	0.42	0.27	0.56	0.03	(Kotz et al., 2005)
Ukraine	pool	2001-03	1	0.56	0.14	0.11	0.16	0.03	(Kotz et al., 2005)
Sweden	Pool	2003	2.9	1.2	0.29	0.31	1.1	-	(Fängström et al., 2005)
Russia	10	2003/04	0.503	0.14	-	0.043	0.32	-	(Tsydenova et al., 2007)
Poland	22	2004	0	1.07 (SD 1.03)	0.47 (SD 0.13)	0.15 (SD 0.13)	0.53 (SD 0.27)	No data	(Jaraczewska et al., 2006)
Sweden	Pool	2004	2.4	0.93	0.26	0.29	0.92	-	(Fängström et al., 2008)
Sweden	5	-	4.8	1.5	0.5	0.6	1.7	0.5	(Lopez et al., 2004)
North America									

Country	No. Participants	Year	Sum	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
USA	47	2002	69.06	40.8	14	8.2	5.3	0.76	(Schecter et al., 2003)
USA	Pool	2001-03	352.29	233.87	58.65	39.23	17.56	2.98	(Kotz et al., 2005)
USA	20	2002-03	145.55	84.94	20.93	18.43	19.79	1.46	(Sharp and Lunder, 2004)
USA	40	2003	89.21	50.1	10.3	11.7	16.3	0.81	(She et al., 2005)
Mexico	7	2004?	4.1	1.7	0.6	0.8	0.8	0.2	(Lopez et al., 2004)
Other									
Japan	Pool (n=19)	1983	0.4	0.26	0.04	0.02	0.07	0.01	(Akatsu et al., 2003)
Japan	Pool (n=24)	1988	1	0.67	0.08	0.05	0.18	0.02	(Akatsu et al., 2003)
Japan	Pool (n=30)	1993	0.69	0.32	0.06	0.07	0.21	0.03	(Akatsu et al., 2003)
Australia	Pool (n=24)	1993	11.5	5.4	3.3	1.5	1	0.3	(Harden et al., 2005)
Japan	Pool (n=35)	1998	2.12	1.03	0.53	0.22	0.29	0.05	(Akatsu et al., 2003)
Japan	Pool (n=30)	1999	1.28	0.62	0.16	0.18	0.29	0.03	(Akatsu et al., 2003)

Country	No. Participants	Year	Sum	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Japan	6	1999	0.92	0.34	0.1	0.13	0.32	0.03	(Ohta et al., 2002)
Japan	13	1999	20.38	15.17	1.81	2.23	1.04	0.13	(Akatsu et al., 2003)
Japan	Pool (n=27)	2000	1.22	0.53	0.15	0.17	0.34	0.03	(Akatsu et al., 2003)
Vietnam	5	2000	0.69	0.31	0.1	0.08	0.17	0.03	(Sudaryanto et al., 2005a)
Cambodia	6	2000	1.43	0.83	0.22	0.17	0.18	0.03	(Sudaryanto et al., 2005a)
Philippines	4	2000	2.35	1.1	0.47	0.3	0.39	0.09	(Sudaryanto et al., 2005a)
India	5	2000	0.56	0.27	0.11	0.06	0.1	0.02	(Sudaryanto et al., 2005a)
Australia	157	2002/03	10.04	5.6	1.9	1.3	1.1	0.14	(Harden et al., 2005)
Japan	10	2000	3.55	1.5	0.38	0.41	1.2	0.06	(Sudaryanto et al., 2005a)
Japan	105	2004	4.24	1.24	1.07	1.12	0.54	0.27	(Eslami et al., 2006)
Indonesia	30	2001-2003	1.07	0.39	0.18	0.15	0.32	0.03	(Sudaryanto et al., 2008)
Malaysia	5	2003	2.996	1.6	0.42	0.32	0.65	0.006	(Sudaryanto et al., 2005b)

Country	No. Participants	Year	Sum	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	Reference
Taiwan	20	2000-01	3.428	1.52	0.512	0.374	0.871	0.151	(Chao et al., 2006)
Brazil	pool	2001-03	0.72	0.34	0.13	0.11	0.12	0.02	(Kotz et al., 2005)
Philippines	pool	2001-03	2.94	1.36	0.31	0.29	0.78	0.2	(Kotz et al., 2005)
Korea	9	2004	2.2	0.81	0.2	0.34	0.79	0.06	(Sudaryanto et al., 2005a)
China	9	2004	2.08	0.66	0.17	0.17	1	0.08	(Sudaryanto et al., 2005a)
Japan	89	2005	0	-	-	-	-	-	(Inoue et al., 2006)

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