Australian Government

Department of the Environment and Heritage

Assessment of concentrations of polybrominated diphenyl ether flame retardants in indoor environments in Australia

A consultancy funded by the Australian Government
Department of the Environment and Heritage

Prepared by Leisa Toms, Jochen Mueller, Michael Bartkow, Robert Symons
National Research Centre for Environmental Toxicology

ISBN 0 642 55313 0

Disclaimer:
The views and opinions expressed in this publication do not necessarily reflect those of the Australian Government for the Minister for the Environment and Heritage.

While reasonable efforts have been made to ensure that the contents of this publication are factually correct, the Commonwealth does not accept responsibility for the accuracy or completeness of the contents, and shall not be liable for any loss or damage that may be occasioned directly or indirectly through the use of, or reliance on, the contents of this publication.

This document is one of three reports:

1. *Assessment of concentrations of polybrominated diphenyl ether flame retardants in aquatic environments in Australia*
2. **Assessment of concentrations of polybrominated diphenyl ether flame retardants in indoor environments in Australia**
3. *Assessment of concentrations of polybrominated diphenyl ether flame retardants in the Australian population: levels in blood*

To obtain further copies of these documents:
Phone: 1800 803 772
Fax: 02 6274 1970
Email: ciu@deh.gov.au
Mail:
c/- Chemical Policy Section
Department of the Environment and Heritage
GPO Box 787
CANBERRA ACT 2601
AUSTRALIA
This document may be accessed electronically from:
http://www.deh.gov.au/settlements/publications/chemicals/bfr/indoor.html

Citation
This report should be cited as follows:
Toms L, Mueller J, Bartkow M and Symons R 2006, *Assessment of concentrations of polybrominated diphenyl ether flame retardants in indoor environments in Australia*, Australian Government Department of the Environment and Heritage, Canberra.

Foreword

Polybrominated diphenyl ethers (PBDEs), a common class of brominated flame retardants, are a ubiquitous part of our built environment, and for many years have contributed to improved public safety by reducing the flammability of everyday goods.

Recently, PBDEs have come under increased international attention because of their potential to impact upon the environment and human health. Some PBDE compounds have been nominated for possible inclusion on the Stockholm Convention on Persistent Organic Pollutants, to which Australia is a Party. Work under the Stockholm Convention has demonstrated the capacity of some PBDEs to persist and accumulate in the environment and to be carried long distances. Much is unknown about the impact of PBDEs on living organisms, however recent studies show that some PBDEs can inhibit growth in colonies of plankton and algae and depress the reproduction of zooplankton. Laboratory mice and rats have also shown liver disturbances and damage to developing nervous systems as a result of exposure to PBDEs.

In 2004, the Australian Government Department of the Environment and Heritage began three studies to examine levels of PBDEs in aquatic sediments, indoor environments and human blood, as knowledge about PBDEs in Australia was very limited. The aim of these studies was to improve this knowledge base so that governments were in a better position to consider appropriate management actions.

Due to the high costs for laboratory analysis of PBDEs, the number of samples collected for each study was limited and so caution is required when interpreting the findings. Nevertheless, these studies will provide governments with an indication of how prevalent PBDEs are in the Australian population and the environment and will also contribute to international knowledge about these chemicals.

The Department of the Environment and Heritage will be working closely with other government agencies, industry and the community to investigate any further action that may be required to address PBDEs in Australia.

Department of the Environment and Heritage
November 2006

Glossary/Abbreviations

BDE	Brominated diphenyl ethers (used when specifying the congener or degree of bromination)
BFR(s)	Brominated flame retardant (s)
BSEF	Bromine Science and Environmental Forum
Congeners	Closely related chemicals derived from the same parent compound
DEH	Department of the Environment and Heritage
EnTox	National Research Centre for Environmental Toxicology
HRGC	High Resolution Gas Chromatograph
HRMS	High Resolution Mass Spectrometer
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of detection, the lowest level at which a chemical can be measured in a sample by the analytical method used.
LOD (excluding LOD)	The LOD is assumed to be zero when used to calculate the sum of PBDEs
LOD (including half LOD)	The LOD is assumed to be 50% of the reported LOD when used to calculate the sum of PBDEs.
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
ng	Nanogram 10^{-9} g
NMI	National Measurement Institute
PBDE	Polybrominated diphenyl ether (used to describe all PBDEs when not necessarily specifying which congener or degree of bromination)
pg	Picogram 10^{-12} g
POP	Persistent organic pollutant
QC/QA	Quality Control/Quality Assurance
SEQ	South East Queensland
SOC	Semi-volatile organic compound
UK	United Kingdom
US	United States of America
XAD-2	Resin used as part of the gas sampling system

Contents

Foreword i
Glossary/Abbreviations ii
Acknowledgements 1
Executive summary 2
1. Introduction 4
1.1 Background 4
1.1.1 Air 5
1.1.2 Dust 5
1.1.3 Surface wipes 5
1.2 Objectives 6
1.3 Project scope 6
2. Project design 8
2.1 Sampling programme 8
2.1.1 Access to sampling sites 9
2.2 Sample collection 9
2.2.1 Active air samples 9
2.2.2 Dust samples 11
2.2.3 Surface wipes 11
2.3 Ethics 12
2.4 Sample storage and shipping 12
3. Sample analysis 13
3.1 Analytical methodology 13
3.2 Quality Control/Quality Assurance 14
3.2.1 Inter-laboratory comparison 14
3.2.2 Sampling reproducibility 15
3.2.3 Field blanks 16
3.3. Statistical analysis 16
4. Polybrominated diphenyl ether concentrations in indoor environments 17
4.1 Air 17
4.1.1 Indoor air 17
4.1.2 Outdoor air 18
4.2 Dust 20
4.3 Surface wipes 21
4.4 Comparison of PBDEs in indoor environments 23
5. Comparison of Australian polybrominated diphenyl ether concentrations with other countries 24
5.1 Air 24
5.2 Dust 26
5.3 Surface wipes 27
6. Summary of findings 28
7. References 29
Appendix A Ethics Approval 31
Appendix B Analytical methodology 34
Appendix C results 41
Appendix D Quality Control/Quality Assurance 45
Appendix E filter and XAD-2 concentrations 52
Appendix F international data 53

List of Figures

Figure 2.1 Map of sampling locations. 8
Figure 2.2 Photos of indoor (left) and outdoor (right) active air sampling equipment. 10
Figure 2.3 Photo of dust collection equipment – vacuum cleaner (left) and plastic hosing (right) 11
Figure 2.4. Photo of surface wipe equipment 12
Figure 4.1 Concentrations of ΣPBDEs in air (pg/m^3) by age of building for homes and offices 18
Figure 4.2 Results of dust samples (ng/g dust) by site. 20

Figure 4.3 Comparison of mean surface wipe concentrations and air (left) and mean surface wipe concentration and dust (right) for Home 1 and Home 2. 23
Figure 4.4 Comparison of ΣPBDE concentrations in air and dust for all homes and offices. 23

List of Tables

Table 2.1 Programme for sample collection. 9
Table 3.1 BDE congeners analysed by NMI. 13
Table 4.1 Summary results for concentration of ΣPBDEs (pg/m^3) in indoor air 17
Table 4.2 Mean ± standard deviation concentrations of selected congeners (pg/m^3) to ΣPBDE (%) in indoor air from homes and offices. 17
Table 4.3 Concentration of ΣPBDEs (pg/m^3) in indoor and outdoor air from Home 2 and Office 1. ...19
Table 4.4 Mean contributions (%) of dominant congeners to the ΣPBDE concentration. 21
Table 4.5 Concentration of mean ΣPBDEs by surfaces (pg/cm^2) 22

List of Boxes

Box 1 Normalised Difference ……..……..…… 14

Acknowledgements

The Department of the Environment and Heritage (DEH) would like to acknowledge the following individuals and organisations that contributed to this study:

- the project teams from the National Research Centre for Environmental Toxicology, the National Measurement Institute (NMI) and Eurofins/ERGO who undertook this study.

- Professor Ian Rae from the University of Melbourne and Dr Arnold Schecter from the University of Texas for their valuable review of this report.

Project Team:
Leisa Toms, Jochen Mueller and Michael Bartkow – National Research Centre for Environmental Toxicology (EnTox)

Robert Symons– The National Measurement Institute

The National Research Centre for Environmental Toxicology is co-funded by Queensland Health.

The research team would like to thank the residents who allowed sampling in their homes and offices; the staff at the National Measurement Institute (NMI) Dioxins Analysis Unit; the staff at eurofins/ERGO; and Ryan Allsopp for assisting with laboratory and field work.

Executive summary

This study was conducted to determine the concentration of brominated flame retardants (BFRs) in indoor environments in Australia using samples of air, dust and surfaces. To date, there are no published data on the concentrations of BFRs in air or surfaces in Australia and only one study of BFRs in dust from Australian households (Sjodin et al 2004).

The current study involved the collection, processing and analysis of nine indoor air samples, two outdoor air samples, nine dust samples and ten surface wipes from South East Queensland (SEQ). The aim of the project was to determine the background concentrations of BFRs from buildings with different characteristics which may influence these concentrations. The main building characteristics of interest were age of the building, type of floor covering and presence or absence of air-conditioning. Indoor air samples were obtained from five homes and three offices. Outdoor air samples were obtained from outside one home site and one office site. Dust samples were obtained from each of the homes and offices. Surface wipes were obtained from two homes. Ethics approval was granted for the study by the University of Queensland Medical Research Ethics Committee.

The samples were collected by EnTox staff and risk of sample contamination was minimised at all stages of collection, processing and analysis by maintaining consistent Quality Control/Quality Assurance (QC/QA) techniques. Samples were sent to the National Measurement Institute (NMI), Sydney, Australia for chemical analysis of 26 polybrominated diphenyl ether (PBDE) congeners. The QC/QA included analysis of sampling replicates as well as an inter-laboratory calibration. For active air samples field blanks consisting of the sampling matrices (XAD-2 sorbent for vapour phase PBDEs and glass fibre filter for particle associated PBDEs) were analysed.

PBDEs were detected in all samples of air and dust and 90% of surface wipe samples.

Air

PBDEs were detected in all air samples. Concentrations of PBDEs were greater in indoor air than in outdoor air. For indoor air, the concentration of ΣPBDEs ranged from 0.5 -179 pg/m^3 for homes and 15 - 487 pg/m^3 for offices. The mean (± standard deviation) and median concentrations of ΣPBDEs in homes were 50 ± 70 and 19 pg/m^3 and in offices 173 ± 272 and 18 pg/m^3, respectively (excluding LOD). The lowest ΣPBDE concentration (0.5 pg/m^3) was found in Home 1, a house with no carpet, no air-conditioning and aged greater than five years. The highest ΣPBDE concentration (487 pg/m^3) was found in Office 2, an office with carpet, air-conditioning and refurbished in the last two years. Notably in locations with relatively low PBDE concentration in air the interpretation was affected by relatively high levels of PBDEs in the sorbent blanks and as a result of this in some cases only few of the PBDEs were above the LOD. For outdoor air, the concentration of ΣPBDEs (excluding LOD) was 1.7 pg/m^3 in the backyard of Home 2 and 6.8 pg/m^3 in the grounds outside Office 1.

Dust

PBDEs were detected in all dust samples and the ΣPBDE concentration ranged from 87 - 3070 ng/g dust. For all dust samples, the mean (± standard deviation) and median concentrations were 897 ± 944 and 591 ng/g dust, respectively (excluding LOD). The mean PBDE concentration in dust is included with the median and range for completeness only and should be treated with caution due to the large range of PBDE results and the influence of outliers on averaging the results of these dust samples. The site with the lowest concentration of ΣPBDEs (87 ng/g dust) in dust was Home 1, a home with no carpet or air-conditioning

which was greater than five years old. The site with the highest concentration of ΣPBDEs (3070 ng/g dust) was Office 2, an office with carpet, air-conditioning and refurbished in the last two years.

The sites with the lowest and highest dust concentrations also had the corresponding lowest and highest air concentrations for ΣPBDEs. However, for the other sites no correlation was apparent between dust and air concentrations.

Surface wipes

PBDEs were detected on 9 out of 10 surfaces sampled. The surfaces sampled represented televisions, refrigerators, stereos and DVD players. A stereo from Home 2 was the only surface where PBDEs were not detected. This surface was made of metal and was housed in a cabinet with a closed glass door. This could have slowed the accumulation of dust from the household environment on this surface. Hence for this surface wipe both leaching of PBDE from the material (metal) and dust deposition was minimal and thus this result is not surprising. The surface with the highest concentration of ΣPBDEs was a television from Home 2 'A' with 23 500 pg ΣPBDEs/cm^2 (excluding LOD).

In comparison to the few other study that investigated indoor environments, the results of this study found BFRs in indoor and outdoor air, dust and on surfaces were generally lower or similar to other studies. The outdoor air results were lower than or similar to those observed in North America and the UK (eg Wilford et al 2004, Harrad et al 2004). The domestic indoor air results were lower than two Canadian studies (Shoeib et al 2004, Wilford et al 2004) and one British study (Harrad et al 2004) but slightly higher than another Canadian study (Butt et al 2004a). For workplace indoor air, the results were lower than results from offices in Canada and the UK (Shoeib et al 2004, Harrad et al 2004). The dust results were lower than observed in a previous Australian study although different collection techniques could account for some of this variance. Compared to international data, the household dust results were lower than those found in North America but higher than in Germany (eg Schecter et al 2005, Knoth et al 2003). For office dust, the Australian data was higher than that found in Europe and no data was available from North America (Leonard et al 2001). There were limited data on surfaces with which to make comparisons and the current study results were lower than the results from computers and monitors analysed in the US (Schecter et al 2005), with the exception of the sample Home 2 – television 'A'.

It should be noted that due to the small sample size used in this study, the results cannot be assumed to be representative of all indoor environments in Australia with further work required to validate these results. However, this study demonstrated that BFRs are ubiquitous; and air conditioning, age and carpets may be potential sources for exposure to these chemicals in Australian indoor environments. The study provides very important results for the evaluation of BFRs in indoor environments in Australia; however it remains difficult to identify the specific pathways that result in exposure and the particular contribution of the indoor environment to the overall exposure of Australians.

1. Introduction

1.1 Background

Brominated flame retardants (BFRs) are compounds that are used to reduce the flammable nature of a multiplicity of commercial and household items. They are incorporated into plastics, rubbers and textiles and as such are found in electronic and electrical equipment, appliances, furniture, construction materials, vehicles and clothing. They are relatively persistent, lipophilic chemicals which have the tendency to bioaccumulate (ie accumulate in biota including humans). This study focused on the BFRs - polybrominated diphenyl ethers (PBDEs). To date, there are no published data on the concentrations of BFRs in indoor or outdoor air or surface wipes in Australia. There is one study which reported the concentration of PBDEs in dust from Australian homes (Sjodin et al 2004).

PBDEs have been used in three major commercial products: penta-BDE, octa-BDE and deca-BDE. The penta-BDE product mainly consists of the tetra, penta and hexa-BDEs including BDE -47, -99, -100, -153 and -154; the octa-BDE product consists of hexa, hepta, octa and nona-BDEs including BDE -153, -154, -183, -196, -197, -206 and -207; and the deca-BDE product consists primarily of BDE-209. Both penta and octa-BDE formulations contain the hexa-BDEs -153 and -154. The penta-BDE product was used mainly in flexible polyurethane foam for mattresses and cushioning, octa-BDE was used in the plastics industry in, for example, computer casings and monitors and deca-BDE is used in high impact polystyrenes and other materials used in electronic and electrical appliances, the automotive industry, construction and building applications as well as textiles (Department of Health and Human Services, 2004).

PBDEs are imported into Australia in raw chemical form and already incorporated into manufactured products. In 2003-04, it was estimated that 180 tonnes of deca-BDE product, 20 tonnes of penta-BDE product and less than 10 tonnes of octa-BDE product were imported into Australia. A decrease in the use of octa-BDE by approximately 90% and of penta-BDE by approximately 70% was seen in 2003-2004 compared to 1998-1999 (NICNAS, 2005). The amount of BFRs in manufactured products imported into Australia remains unknown. There are currently no restrictions on the use of PBDEs in Australia, although Australian industry indicated that importation and sales of the penta and octa-BDE products will cease towards the end of 2005, coinciding with the worldwide cessation of penta and octa-BDE product manufacture (NICNAS, 2005). The approximate composition of PBDE commercial products is listed in Table 1.1.

Table 1.1 General composition of PBDE based commercial products (de Wit 2002)

	Congener (%)						
Technical Product	**Tetra-BDEs**	**Penta-BDEs**	**Hexa-BDEs**	**Hepta-BDEs**	**Octa-BDEs**	**Nona-BDEs**	**Deca-BDEs**
Penta-BDE	24-38	50-60	4-8				
Octa-BDE			10-12	44	31-35	10-11	<1
Deca-BDE						<3	97-98

International studies on concentrations of BFRs in human samples have shown that levels have been increasing over time (Meironyte et al 1999). In addition, studies thus far have shown the BFR concentrations in Australian human samples to be lower than the concentrations in North America and higher than the concentrations reported from Europe and

Asia (Harden et al 2005). Worldwide the pathways of exposure for BFRs are unclear. This study of BFRs in indoor environments includes air, dust and surfaces in Australia.

1.1.1 Air

The atmosphere is an important medium for the distribution of persistent organic pollutants (POPs) including emerging POPs such as PBDEs. Furthermore, the atmosphere-plant-animal pathway is a major route through which POPs can contaminate the human food chain (McLachlan 1996). Recent studies in the United Kingdom, Western Europe and Canada have detected concentrations of BFRs in indoor and outdoor air with the indoor air concentrations generally exceeding those of outdoor air substantially (eg Harrad et al 2004, Lee et al 2004, Wilford et al 2004).

On average, humans spend a significant amount of time indoors and therefore, indoor air is potentially an important source of PBDE exposure to humans. The relatively high concentration of PBDEs indoors compared to outdoors is likely to be related to the usage and slow release of these chemicals from consumer products and building materials (Kemmlein et al, 2003). Recently Harrad et al (2004) found that indoor air concentrations in UK homes and workplaces could be correlated to some degree, with the number of foam chairs and electrical appliances in use.

To our knowledge, no PBDE concentrations in air samples collected in Australia have been published to date.

1.1.2 Dust

Researchers have used the collection of household dust in Germany and the US to evaluate PBDE levels in homes (eg Knoth et al 2003, Sjodin et al 2004, Stapleton et al 2005). Results showed that the concentrations of specific PBDEs were sometimes an order of magnitude higher in house dust collected from homes in the US compared with homes in Germany (Sjodin et al 2004). A study was conducted that included dust samples from 10 houses and apartments in Queensland, Australia and from the UK, Germany, and the US. This study showed that PBDE concentrations and congener profile in Australian dust were highly variable but results were generally higher than those in Germany and lower than those from the US and UK (Sjodin et al 2004).

The incidental consumption and inhalation of household dust, particularly by small children, may be an important pathway for human exposure to PBDEs. Stapleton et al (2005) suggested that exposure to PBDEs in infants and young children via dust, placental transfer and breast feeding in the US, could exceed adult exposure via food.

1.1.3 Surface wipes

BFRs, like many other SOCs (semi-volatile organic compounds), accumulate on surfaces. Surface wipes from glass or equipment have been used to evaluate the presence and/or usage of these chemicals (Schecter et al 2005, Butt et al 2004a) or to evaluate release from a major fire such as those related to the destruction of the World Trade Center in New York City (Butt et al 2004b). To date, no data are available on the concentrations of BFRs on surfaces in indoor environments in Australia.

1.2 Objectives

The overall objective of this project was to increase knowledge about BFRs in indoor environments in Australia and use this information to assess and determine possible pathways of exposure to the Australian population.

Specific aims of this study were to:

- determine the background concentrations and congener compositions of BFRs in indoor and outdoor air; household and office dust; and surface wipes from sites in Australia
- relate BFR concentrations in air, dust and surface wipes to potential sources and 'home specific factors'
- compare the concentration and composition of BFRs in air with dust and surface wipes *and*
- compare the concentration and composition of BFRs in air, dust and surface wipes from Australia with international data.

1.3 Project scope

The BFRs in indoor environments project was implemented in four stages.

Stage 1 - Sampling

Air

Indoor and outdoor air samples were collected using low volume sampling systems. Indoor samples were taken from a variety of environments including offices and homes with different characteristics. Two outdoor air samples from locations adjacent to the indoor air sampling sites were collected for comparison and quality control purposes.

Dust

In addition to air sampling, dust samples were collected from the same indoor environments, using a dedicated vacuum cleaner.

Surface wipes

In two homes, surface wipes were obtained from common household appliances including refrigerators, televisions, stereos and DVD players.

Stage 2: Analysis

Analysis of the samples of air, dust and surface wipes was undertaken at the National Measurement Institute (NMI) to determine the concentrations of PBDE congeners. QC/QA were integrated into all phases of the sampling and analysis processes. Inter-laboratory comparisons were undertaken with 10% of the air, dust and surface wipe samples sent to eurofins/ERGO Research, Germany for analysis.

Stage 3: Collation and processing of data

Data on BFR concentrations in air, dust and surface wipes obtained from Stage 2 were collated and processed.

Stage 4: Reporting of results and conclusions

The results of the study of BFRs in indoor environments are reported in this final report including:

- all raw data
- BFR congener profiles
- a description of the offices and homes including age of building, floor covering and presence or absence of air-conditioning
- suggestions of possible sources of BFRs in indoor environments in Australia and possible contamination pathways *and*
- a comparison of results with international and any Australian studies.

2. Project design

2.1 Sampling programme

This project was designed to determine background concentrations of BFRs in air, dust and surface wipes from buildings with different characteristics which may influence PBDE concentrations. These characteristics were carpet/no carpet, air conditioning/no air conditioning and age of home (less than two years old or greater than five years old). As it was difficult to locate offices less than two years old, the offices were differentiated as being refurbished in the last two years, that is, the carpet, paint and fittings were less than two years old.

Due to time and budgetary constraints it was decided to obtain samples from South East Queensland (SEQ) only as opposed to sampling in various states of Australia. Figure 2.1 shows the sampling locations. There were six samples obtained from Brisbane, one from Logan Shire and one from Maroochy Shire. Homes and offices were sought out to fulfill the criteria listed in Table 2.1.

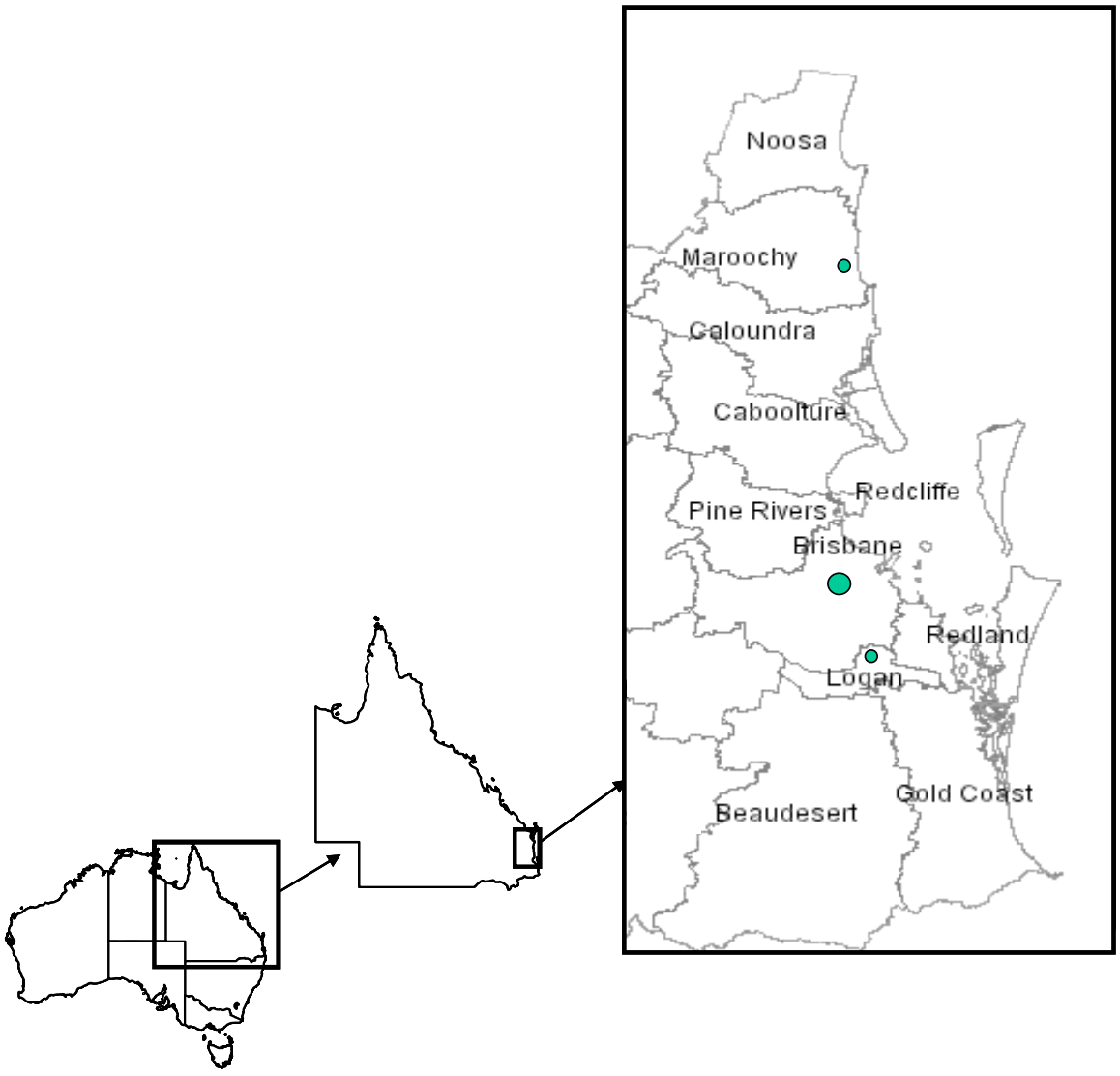

Figure 2.1 Map of sampling locations.

The criteria listed in Table 2.1 were used because it was thought that carpet or carpet underlay, possibly laden with PBDEs, might be a source of PBDEs to the indoor air and dust. Air conditioning was included as a variable since studies from overseas have shown that indoor air is more contaminated than outdoor air and air conditioning may affect both internal circulation as well as retention of air within a building. The authors considered that this may affect the levels of brominated flame retardants in indoor air. Age of the home/office was another criterion, as the use of certain building products containing PBDEs may have been decreased over time, for example penta and octa-BDE commercial products while use of the deca-BDE commercial product may have increased over time.

Table 2.1 Programme for sample collection.

	Air circulation	Age (years)	Floor	Outdoor Air	Indoor Air	Dust	Wipes
Office 1	a/c	> 5 Yr	Carpet	1	1	2	0
Office 2	a/c	< 2 Yr	Carpet	0	1	1	0
Office 3	a/c	< 2 Yr	Carpet	0	1	1	0
Home 1	nil	> 5	No Carpet	0	2	1	5
Home 2	a/c*	> 5	Carpet	1	1	1	0
Home 3	a/c*	> 5	No Carpet	0	1	1	5
Home 4	a/c	< 2	No Carpet	0	1	1	0
Home 5	a/c	< 2	Carpet	0	1	1	0
Total samples				**2**	**9**	**9**	**10**

*not in use at time of sampling
Table includes the criteria used to select offices and homes - air circulation, age and floor covering. Also provided is the number of samples collected at each site

2.1.1 Access to sampling sites

Five homes and three offices were sampled for indoor air with an outdoor sample taken outside at one home and one office. The study team was granted access by the residents to the homes and offices to set up, monitor and dissemble the air samplers, collect dust by vacuum cleaning and obtain surface wipes from various appliances and surfaces.

2.2 Sample collection

Appropriate standard operating procedures (SOPs) were used for all sample collections. For the dust and surface wipes these SOPs were developed specifically for this study. One important point was the possibility that vacuum cleaning could be a potential secondary source for BFRs indoors since the use of the vacuum cleaner may result in the mobilisation of BFRs from flooring. Hence, dust collection occurred before or after the air sampling.

2.2.1 Active air samples

Air samples were collected using a filter-adsorbent active sampling system consisting of a glass fibre filter paper (Whatmann 90mm (GF/A Cat No 1920090)) to collect particle-associated PBDEs and a XAD-2 filled cartridge to collect vapour phase PBDEs. This cartridge was attached to a low volume pump and a gas meter to determine the volume of air sampled.

Prior to sampling the filter papers were rinsed with acetone and placed in the furnace at 450^{o}C for 18 hours. Once removed from the furnace they were placed in foil envelopes which were rinsed with acetone. All glassware was pre-cleaned, rinsed with acetone and wrapped in foil for transport to the sampling site. The glass cartridges were sent to NMI where they were washed in detergent, rinsed with tap water, acetone and hexane and allowed to air dry. They

were then furnaced at 450^{o}C for 16 hours and loaded with XAD-2. The cartridges were capped top and bottom and returned to EnTox on ice.

Cartridges were stored in the freezer prior to sampling and once sampling was complete they were re-capped, wrapped in foil and returned to the EnTox freezer. Filter papers were folded and placed into the cartridge after sampling for combined analysis with the XAD-2. Filter papers and XAD-2 from Office 2 and 3 were not combined but these samples were analysed separately to assess how PBDE congeners are distributed between the particle and gaseous phases. Details of these results are available in Appendix E, however expansion on these results is beyond the scope of this study.

For outdoor air, low volume samplers were deployed with a sampling rate of between 4.5 and 6.5 m^3 per hour with the aim of collecting an air sample of about 3000 m^3 to allow detection of BFRs in the low pg/m^3 range. This also allowed long sampling periods for the outdoor air without the risk of breakthrough from the XAD-2 even at high volume sample collection. The mean air volume collected at the outdoor sites was 3260 m^3.

For indoor air, low volume samplers were deployed with the aim of collecting at least 500 m^3 of air. The mean air volume collected at the indoor sites was 341 m^3. In houses, air samplers were mostly run during the day to avoid disturbing residents and neighbours while the office samplers were run during the evenings/nights to avoid disturbing staff during the day. The sampling rate was selected to ensure that the total indoor air volume was not rapidly depleted during a given sampling event. This coincided with the day/night schedule for houses and offices. When the sampling pump was switched off, a piece of foil rinsed with acetone was placed on top of the glass ring holding the filter paper. The foil was used to protect the filter paper and accumulated particulates from any disturbance while the sampler was not operating. The sampler was mounted with an extension to the exhaust that led outside the home/office so the 'cleaned air' or sampled air was not re-sampled. Where this was not possible in homes/offices due to security issues of leaving doors open or distance from the sampling area to outside, a longer hose was used and the sampled air was exhausted into a stairwell or another room, distant to the air sampler. Figure 2.2 shows a photo of an indoor sampler (left) and an outdoor sampler (right).

Figure 2.2 Photos of indoor (left) and outdoor (right) active air sampling equipment.

2.2.2 Dust samples

Dust samples were collected using a dedicated vacuum cleaner that had multistage filtering in the exhaust system to avoid smaller particles passing through the cleaner which may cause the (re)contamination of the air and surfaces at a site. The vacuum cleaner used was a Nilfisk King 520. A new vacuum bag was used for each sample. The study team cleaned the vacuum cleaning equipment between sample collections to avoid cross contamination between sites. The parts of the vacuum cleaner which came into contact with the dust were the vacuum cleaner head, connector, wand and hose. It was decided that the hose posed the most concern for contamination as it was a crinkled hose and it would be difficult to successfully remove all dust caught in these crinkles. It was also decided that because the vacuum cleaner parts are made mainly of plastic it would not be appropriate to clean them with a solvent as they could be destroyed or eroded possibly leading to further sources of contamination. Therefore a solid plastic hose was inserted into the crinkled hose (see Figure 2.3). This hose was cleaned by pulling a piece of cloth through it three times in between sample collection to remove dust from the previous collection. The vacuum cleaner was purchased specifically for this study and was only used for the collection of the study specific samples. Therefore any contamination caused by the plastic hose or the cleaning technique would be a constant for all samples.

After collection, the vacuum bag was removed from the cleaner and wrapped in foil for transport to EnTox. Once received at EnTox, the bag was removed from the foil and cut open with acetone-rinsed scissors. The contents of the bag were passed through a 2mm metal sieve and the material that passed through the sieve was analysed. The sieve was cleaned first with water and then with acetone and Kimwipes to remove dust between samples. The material which passed through the sieve was placed in amber jars which had been pre-cleaned and rinsed with acetone, toluene and hexane.

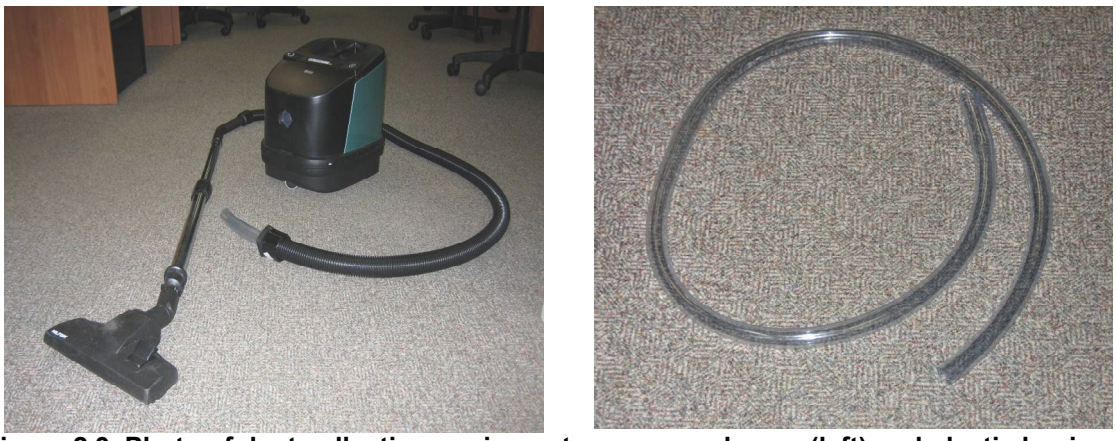

Figure 2.3 Photo of dust collection equipment – vacuum cleaner (left) and plastic hosing (right).

2.2.3 Surface wipes

Whatmann 90mm (GF/A Cat No 1920090) glass microfibre filter papers were rinsed with acetone and allowed to air dry. The filter papers were then placed in acetone rinsed foil envelopes. A metal clip and tweezers were rinsed with acetone prior to sample collection. The sample was collected by folding the filter paper in half and placing it in the metal clip using tweezers. A template was used to ensure a uniform surface area of 10 x 10 cm (100 cm^2) was sampled (Figure 2.4).

It was decided to choose the two homes with the lowest and highest air concentrations of ΣPBDEs (based on the concentrations of ΣPBDEs in pg per cubic metre of air) and obtain

surface wipes from these two homes. The same types of surfaces were sampled and included: televisions, refrigerators, stereos and other electrical appliances such as DVD players. It was agreed between the research team and DEH that this would give an indication of the concentrations of PBDEs in various products and what congeners were possibly released into the indoor environment. Using two sites meant it was possible to assess variation between sites while still investigating an array of different products.

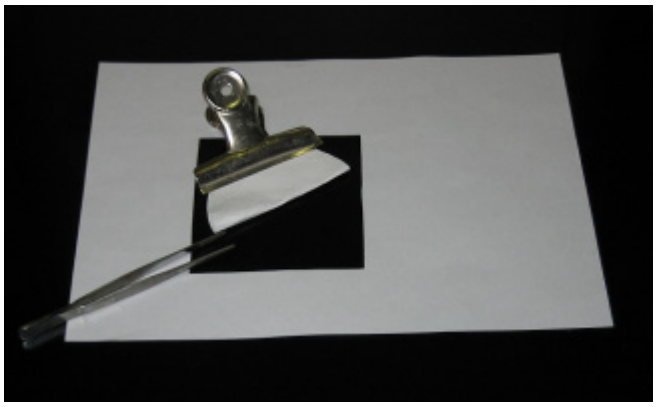

Figure 2.4. Photo of surface wipe equipment

2.3 Ethics

The project was submitted to The University of Queensland Medical Research Ethics Committee and approval was obtained on 22 April 2005. The project was allocated Clearance Number 2005000290. Ethical approval was required as the residents of the homes and offices were asked to complete a questionnaire. A copy of the Ethics approval is given in Appendix A.

2.4 Sample storage and shipping

Air and surface wipe samples were stored in the EnTox freezer and shipped on ice to NMI. The dust samples were stored and then shipped at ambient temperature to NMI.

3. Sample analysis

3.1 Analytical methodology

Samples were analysed at the National Measurement Institute (NMI), Sydney Australia. For the purpose of inter-laboratory comparison, the extracts were split by NMI and half of the split was analysed at eurofins/ERGO in Hamburg, Germany. To the authors' knowledge the NMI is the only laboratory which is NATA accredited for PBDE analysis in Australia.

Briefly, NMI used isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) to determine the concentrations of PBDEs in the air, dust and surface wipe samples. This method provided data on 26 PBDE congeners listed in Table 3.1. The analytical methodology for the determination of PBDEs was based on the Draft USEPA Method 1614.

Table 3.1 BDE congeners analysed by NMI.

BDE Congener	Abbreviation
2,2',4-Tribrominated diphenyl ether	BDE 17
2,4,4'-Tribrominated diphenyl ether	BDE 28
2',3,4-Tribrominated diphenyl ether	BDE 33
2,2',4,4'-Tetrabrominated diphenyl ether	BDE 47
2,2',4,5'-Tetrabrominated diphenyl ether	BDE 49
2,3',4,4'-Tetrabrominated diphenyl ether	BDE 66
2,3',4',6-Tetrabrominated diphenyl ether	BDE 71
3,3',4,4'-Tetrabrominated diphenyl ether	BDE 77
2,2',3,4,4'-Pentabrominated diphenyl ether	BDE 85
2,2',4,4',5-Pentabrominated diphenyl ether	BDE 99
2,2',4,4',6-Pentabrominated diphenyl ether	BDE 100
2,3',4,4',6-Pentabrominated diphenyl ether	BDE 119
3,3',4,4',5-Pentabrominated diphenyl ether	BDE 126
2,2',3,4,4',5'-Hexabrominated diphenyl ether	BDE 138
2,2',4,4',5,5'-Hexabrominated diphenyl ether	BDE 153
2,2',4,4',5,6'-Hexabrominated diphenyl ether	BDE 154
2,3,3',4,4',5-Hexabrominated diphenyl ether	BDE 156
2,3,4,4',5,6-Hexabrominated diphenyl ether	BDE 166
2,2',3,4,4',5',6-Heptabrominated diphenyl ether	BDE 183
2,2',3,4,4',6,6-Heptabrominated diphenyl ether	BDE 184
2,3,3',4,4',5',6-Heptabrominated diphenyl ether	BDE 191
2,2,3,3',4,4',5,6'-Octabrominated diphenyl ether	BDE 196
2,2,3,3',4,4',6,6'- Octabrominated diphenyl ether	BDE 197
2,2,3,3',4,4',5,5',6-Nonabrominated diphenyl ether	BDE 206
2,2,3,3',4,4',5,6,6-Nonabrominated diphenyl ether	BDE 207
Decabromodiphenyl ether	BDE 209

For the air samples, the BDE congeners were reported as a quantity in picograms. This value was divided by the number of cubic metres sampled to determine the pg of PBDEs/m^3 of air.

For the dust samples, the BDE congeners were reported as a concentration in nanograms per gram of dust analysed. For the surface wipe samples, the BDE congeners were reported as a quantity in picograms. This value was then divided by the number of square centimetres of surface to determine the pg of PBDEs/cm^2 of surface. The sum PBDE concentration is the sum of these congeners excluding the limit of detection (LOD) unless indicated otherwise.

Further details of the analytical methodologies for NMI and eurofins/ERGO are included in Appendix B.

3.2 Quality Control/Quality Assurance

QC/QA were undertaken including sampling replication and inter-laboratory calibration. The normalised difference (see Box 1) was used to compare the analytical results for sampling reproducibility and for inter-laboratory comparison. Full details of all results are provided in Appendix C and full details of QC/QA are provided in Appendix D.

Box 1. Normalised differences

In this report, comparisons between replicate samples or replicated analysis have been made using the normalised difference. The normalised difference between two samples is mathematically defined as:

$$\text{normalised difference (\%)} = \frac{\left|\text{value a} - \text{value b}\right|}{\frac{(\text{value a} + \text{value b})}{2}} \times 100$$

The table below provides a demonstration of the normalised difference (ND) values that would result from a range of differences in sample values.

Sample A (pg/g)	Sample B (pg/g)	ND%
1.0	1.2	18
1.0	1.5	40
1.0	2.0	67
1.0	3.0	100
1.0	10.0	160
1.0	100.0	200

The mean normalised difference expresses the average normalised difference for all detected congeners.

3.2.1 Inter-laboratory comparison

Inter-laboratory comparison was undertaken by analysing a selection of samples that had already been analysed by NMI at the eurofins/ERGO laboratories in Hamburg, Germany. Extracts from one sample of each of the air, dust and surface wipes were sent to eurofins/ERGO. The samples were: Home 1 'A' indoor air; Office 1 'A' dust; and Home 2 television 'A' surface wipe.

The results of the inter-laboratory comparison are compared using the mean normalised difference (Box 1). It should be noted that typically for inter-laboratory comparisons the differences can be relatively high particularly for congeners that are found in low concentrations, close to the LOD.

There were 20 congeners analysed by both laboratories. These are: BDE- 17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -156, -183, -197, -207 and -209. The details of the inter-laboratory comparison are in Appendix D.

3.2.1.1 Air

The air sample Home 1 'A' was analysed by both laboratories. Besides an issue with observed contamination in the XAD-2 blank the results of the inter-laboratory comparison for air samples can be best assessed by not considering the blank (ie for this study the extract was divided and analysed by both laboratories so the blank problems were equal).
In total, 11 PBDE congeners were detected by both laboratories with a mean normalised difference of 25%. This indicates very good agreement of the analytical quantification between the two laboratories.

3.2.1.2 Dust

The Office 1 'A' dust sample was analysed by both laboratories. The normalised differences ranged from 1 to 62% and the mean normalised difference was 22%. This indicates good agreement between the two laboratories.

3.2.1.3 Surface wipes

The surface wipe sample Home 2 – television 'A' was analysed by both laboratories. The normalised differences ranged from 1 to 87% and the mean normalised difference was 21%. This indicates good agreement between the two laboratories.

3.2.2 Sampling reproducibility

Sample reproducibility was undertaken to assess the reproducibility of the sampling strategy, that is, whether or not using the prescribed sampling SOPs at the same site by the same personnel resulted in equivalent results. For the air samples a replicate was obtained from Home 1; for the dust samples a replicate was obtained from Office 1; and for the surface wipe samples a replicate was obtained from Home 1 - television.

3.2.2.1 Air

At Home 1, two air samples were collected simultaneously. The sampling procedures for both 'A' and 'B' samples were identical and the results are discussed in Section 4.1. The samples were not analysed in the same batch at NMI.

3.2.2.2 Dust

At Office 1, two dust samples were collected. The first sample was collected and then approximately one month later, the second sample was collected using the same procedures and obtaining dust from the same area as the first sample. The samples were referred to as Office 1 - dust 'A' and 'B' and the results are discussed in Section 4.2. These samples were not analysed in the same batch at NMI.

3.2.2.3 Surface wipes

At Home 1, two television surface wipes were collected. The template was placed on the left-hand side of the top of the television to obtain the wipe from Home 1 - television 'A'. Immediately after this, the template was moved 10 cm to the right and the Home 1 -television 'B' sample was collected. The results of the replicates from Home 1 – television 'A' and 'B' are discussed in Section 4.3. These samples were analysed in the same batch at NMI.

3.2.3 Field blanks

A key component for QC/QA is the evaluation of matrix blanks where this is required. This is particularly important for air sampling where the sampling matrix includes filters for the collection of particle associated chemicals and a sorbent such as XAD-2 for the collection of the vapour phase associated chemicals. Particularly the latter has often caused blank problems. Since the sorbent phase is usually sealed except during sampling, field blanks are unlikely to be different from analysis of matrix blanks. Hence in this study EnTox only used filter papers as field blanks where the field blank was exposed during the preparation of the samplers.

For all air samples, two filter papers were taken to the sampling sites. One filter was used for sampling where the other filter was used as a field blank for both the air and the surface wipe parts of the study. NMI analysed two filter field blanks in total. Results of the field blanks were low. The data are detailed in Appendix D.

Two XAD-2 matrix blanks were also used for the study, and compared to the blank filter showed relatively high levels of PBDEs. Specifically one of the two blanks was so high that a substantial part of the indoor air results may have been potentially affected by the matrix blank.

Problems with the pre-cleaning of XAD-2 is also known for many other air sampling and since this was the first evaluation of PBDEs in air in Australia using XAD-2 this problem may have been anticipated. In hindsight, the problem should have been avoided by a multistage approach with preliminary evaluation of the suitability of the sampling matrix which would have also allowed the increase of the sampling volume to reduce the impact of blank effects. However the short schedule of the study meant that blanks and samples were analysed simultaneously. Hence as a result of the blank contamination with the XAD-2 only a limited number of PBDE congeners in air could be detected based on the blank criteria (data were only accepted if greater than three times the blank values in matrix blank).

3.3. Statistical analysis

Based on the small sample sizes in this study, statistical analysis was not undertaken.

4. Polybrominated diphenyl ether concentrations in indoor environments

The results for the concentration of BFRs in indoor environments are presented here based on sampling and analysis of air, dust and surface wipes.

4.1 Air

The air results are expressed as pg of PBDEs per cubic metre of air (pg/m^3). The number of cubic metres sampled was determined using a gas meter where the volume was measured under negative pressure and using Boyle's law. Overall, 21 out of 26 BDE congeners were detected and those not detected were BDE-77, -126, -138, -166 and -156.

4.1.1 Indoor air

Indoor air was sampled at five homes and three offices. Characteristics of these sites are presented in Table 2.1. The concentrations of ΣPBDEs are presented in Table 4.1. For the homes the summary results in Table 4.1 and 4.2 were calculated including Home 1 'A' and Home 1 'B' as two separate results.

Table 4.1 Summary results for concentration of ΣPBDEs (pg/m^3) in indoor air from homes and offices.

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

The highest concentration of ΣPBDEs was taken at Office 2, an office with carpet, air-conditioning and which had been refurbished in the last two years. The lowest concentration was taken at Home 1, a house with no carpet, no air-conditioning which was greater than five years old. The air concentrations of selected PBDE congeners in homes and offices are given in Table 4.2.

Table 4.2 Mean ± standard deviation concentrations of selected congeners (pg/m^3) to ΣPBDE (%) in indoor air from homes and offices.

	Homes		Offices	
PBDE congener	**Excluding LOD**	**Including LOD**	**Excluding LOD**	**Including LOD**
28 + 33	n.d.	14 ± 15	15 ± 12	19 ± 24
47	12 ± 30	45 ± 32	120*	140 ± 189
99	n.d.	20 ± 4	7 ± 0.4	27 ± 29
100	n.d.	5 ± 4	2 ± 12	9 ± 10
153	2 ± 3	3 ± 3	1*	2 ± 1
154	n.d.	1 ± 1	n.d.	1 ± 1
183	7 ± 12	7 ± 12	2*	2 ± 2
209	23 ± 46	26 ± 45	8 ± 1	9 ± 4
ΣPBDEs	**50** ± 70	**129** ± 82	**173** ± 272	**230** ± 276

n.d. – not detectable. ΣPBDEs includes sum of 26 congeners. * congener only detected in one Office sample

For air in homes, the congener profile (excluding the LODs) was dominated by BDE-209, followed by -47, -183 and -153. When the LOD values were included the profile was dominated by BDE-47 followed by -209, -99, -28, -33 and -183. For offices, the congener profile (excluding LODs) was dominated by BDE-209 followed by BDE-183. The exception was Office 2 where the profile was dominated by BDE-47 followed by BDE-28 + -33 with less than 1% contribution by BDE-209. As discussed in Section 3.2.2 there was some contamination of the XAD-2 blanks. For this reason, a result is only considered to be above the detection limit if it was greater than three times the greatest XAD-2 blank result (see Section 3.2.3 and Appendix D).

Figure 4.1 depicts the concentration of ΣPBDEs in air by age of building for homes and offices. The concentrations were lower in houses less than two years old than in houses greater than five years old, with the exception of one house greater than five years. For offices, the concentrations of ΣPBDEs in air was higher in one office (less than two years old) and similar for the other two offices (less than two years and greater than five years). At this stage, it is not possible to conclude whether or not PBDE concentrations are affected by the age of a building due to the small sample size used.

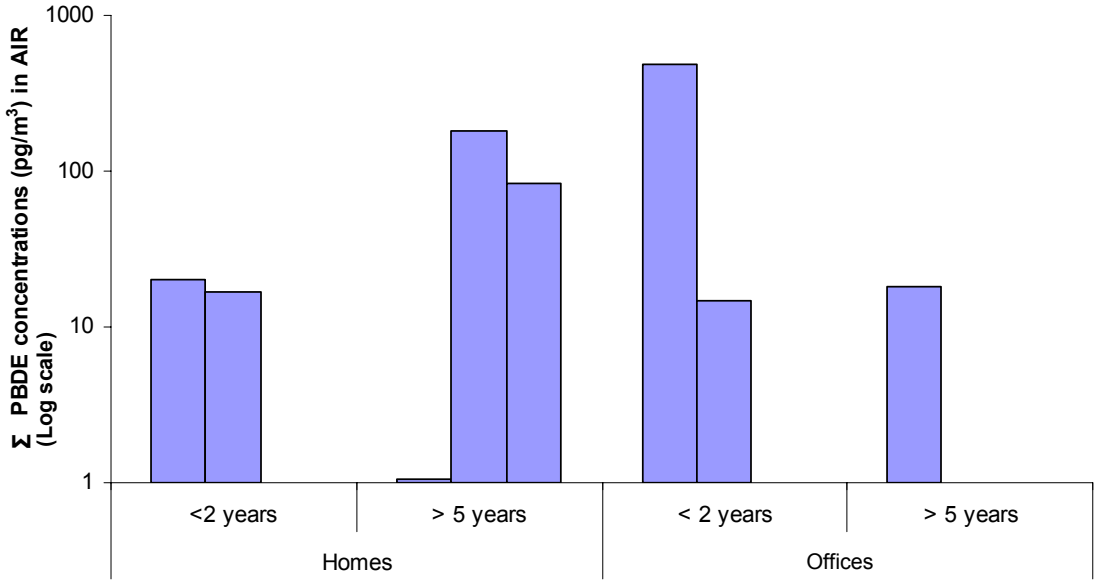

Figure 4.1 Concentrations of ΣPBDEs in air (pg/m^3) by age of building for homes and offices *(Homes, < 2 years n=2; Homes, > 5 years n = 3; Offices, < 2 years n=2; Offices, > 5 years n=1)*

At one site, two air samples were collected at the same time. These samples were Home 1 – air 'A' and air 'B'. The samples 'A' and 'B' were compared using the normalised difference (see Box 1). The normalised difference between samples was only calculated for one congener – BDE-17 and was 79%. This was the only congener detected and therefore it was not possible to determine an overall mean normalised difference.

4.1.2 Outdoor air

Outdoor air was sampled in the grounds of the indoor air sites – Home 2 and Office 1. The concentration of ΣPBDEs in outdoor air was less than in the indoor air as seen in Table 4.3 which is consistent with findings by others (eg Wilford et al 2004; Harrad et al 2004). For the

home, the indoor air concentration was 89 times that of the outdoor air, while at the office site it was just over twice that of the indoor 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.

Table 4.3 Concentration of ΣPBDEs (pg/m^3) in indoor and outdoor air from Home 2 and Office 1.

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

The congener profile was similar for both sites with dominance of BDE-209 followed by BDE-207, -206, -197 and -196. For Home 2, this was followed by BDE-183 and -17 and for Office 1, this was followed by BDE-49, -183, -66, -71 and -184. The concentration of BDE-209 in the Home and Office samples were 1.3 and 5.8 pg/m^3, respectively.

4.2 Dust

PBDEs were detected in all nine dust samples. A total of 24 out of 26 congeners were detected and those not detected in any samples were BDE-126 and -156. The concentrations of PBDEs in dust are reported as ng/g dust. The PBDE concentrations in dust ranged from 87 to 3070 ng/g dust. The mean (± standard deviation) and median excluding the LOD and including the LOD were 897 ± 944 and 591 ng/g dust; and 923 ± 1007 and 653 ng/g dust, respectively. The mean PBDE concentration in dust is included with the median and range for completeness only and should be treated with caution due to the large range of PBDE results and the influence of outliers on averaging the results of these dust samples (see Figure 4.2). The site with the highest ΣPBDE concentration (3070 ng/g dust) was Office 2, an office with carpet, air-conditioning and refurbished in the last two years. The site with the lowest ΣPBDE concentration (87 ng/g dust) in dust was Home 1, a home with no carpet or air-conditioning and greater than five years old. Overall the office sites were higher than the homes except for Home 5 which was similar to Office 1 (Figure 4.2).

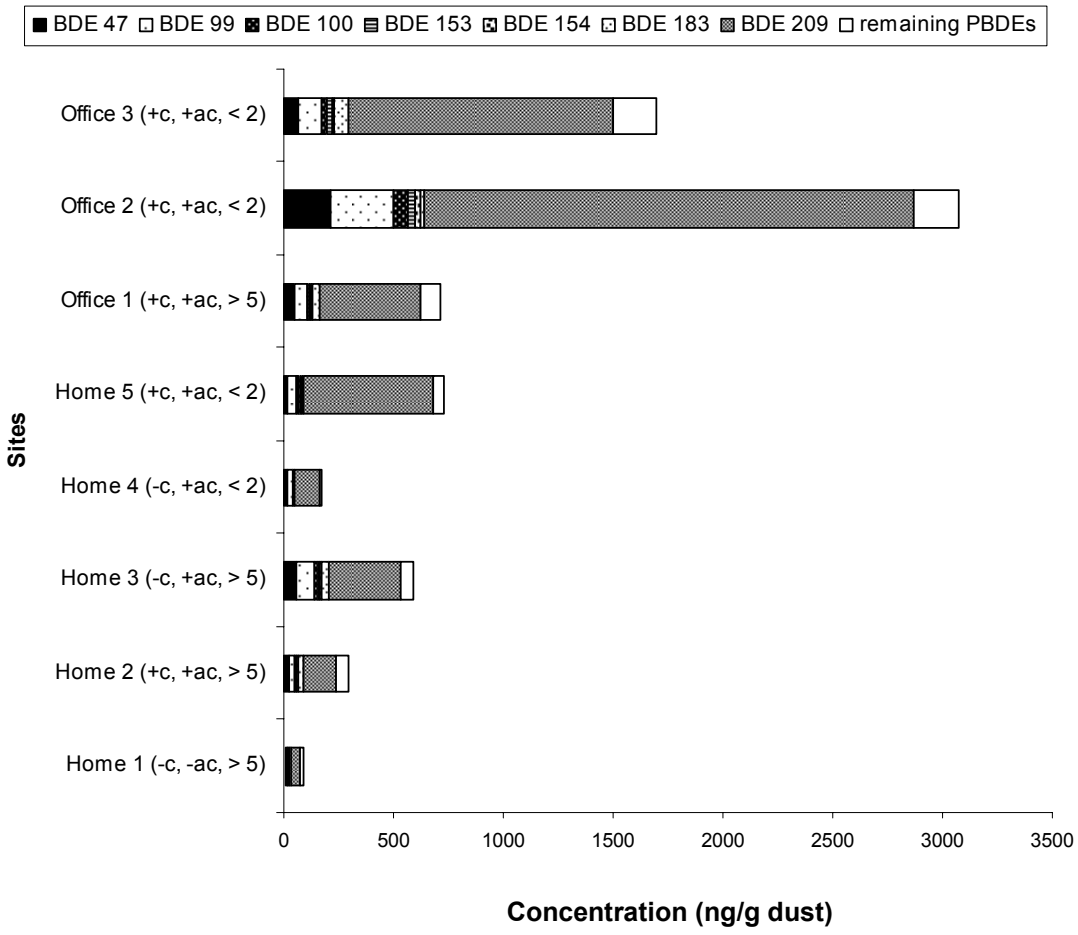

Figure 4.2 Results of dust samples (ng/g dust) by site.
(+ = with, - = without, c=carpet, ac=air-conditioning, <2= <2 years old, >5=>5 years old)

The sites with the lowest and highest dust concentrations also had the lowest and highest air concentrations for ΣPBDEs. However, for the other sites no correlation was apparent between air and dust PBDE concentrations. Due to the small sample sizes these results would need to be replicated before any conclusions can be made.

The congener profile of all samples was dominated by BDE-209, followed to a much lesser degree by BDE-99, -47, -183, -206 and -207. This suggests the concentrations of PBDEs in dust from all sites could be influenced by exposure to the deca-BDE commercial product which contains 97-98% BDE-209 (Darnerud et al 2001). The presence of BDE-99 and -47 could be due to exposure from penta-BDE commercial product which contains 50-62% penta-BDEs including BDE-47 and -99 (Darnerud et al 2001). The profile in homes has a slightly higher contribution from BDE-183, -47 and -99 than the offices while the BDE-209 contribution is less than in offices. Table 4.4 shows the mean contribution of the dominant congeners to the ΣPBDE concentration in dust samples.

Table 4.4 Mean contributions (%) of dominant congeners to the ΣPBDE concentration.

BDE congener	Mean (± standard deviation) contribution to ΣPBDE concentration (%)	
	Homes	*Offices*
BDE-207	3 ± 2	3 ± 1
BDE-206	3 ± 1	4 ± 1
BDE-183	6 ± 4	3 ± 2
BDE-47	8 ± 3	6 ± 2
BDE-99	10 ± 3	8 ± 2
BDE-209	59 ± 14	70 ± 4

Results are reported to two significant figures.

At one site, two dust samples were collected for the same areas with collection times approximately one month apart. These samples were Office 1 – dust 'A' and dust 'B'. The results of these replicates were averaged and the average was used in all summary results of the dust samples.

The samples 'A' and 'B' were compared using the normalised difference (see Box 1). The normalised difference between samples ranged from 3 to 129% with a mean normalised difference of 61%. This indicates that overall there was a three fold difference between the results of sample 'A' and 'B'. The details are available in Appendix D.

4.3 Surface wipes

The aim of the surface wipe samples was to give an indication of the concentrations of PBDEs on the surface of various products in general use in households. PBDEs in these wipes could originate either from the surface itself (ie via direct transfer/bleeding from the surface material into the dust or the wipe), or from the deposition of either gaseous or dust associated PBDEs. At this stage, it is unknown whether these wipes reflect primarily PBDEs that have originated from the surface, or rather from dust which settled on this surface. In addition, the time since the surface was cleaned/wiped or otherwise touched was not determined. Surface wipes were collected from televisions, stereos, refrigerators and DVD players at Homes 1 and 2.

In the surface wipe samples, 19 out of 26 congeners were detected and those not detected were BDE-17, -49, -77, -99, -100, -119 and -126. PBDEs were detected in 9 out of 10 surface wipe samples. The surface where PBDEs were not detected was the stereo from Home 2. Interestingly, this surface was made of metal and was housed in a cabinet behind a closed glass door. The fact that the stereo was housed in a cabinet could have slowed the accumulation of dust from the household environment on this surface as refrigerators are also metal and this study found detectable concentrations of PBDEs on the surfaces of two

refrigerators (not housed in a closed cabinet). A total of 19 out of 26 congeners were detected in the surface wipe samples and those not detected were BDE-17, -49, -77, -99, -100, -119 and -126. The results of the surface wipe analysis are expressed as pg/cm^2 of surface sampled.

The surface with the highest concentration of ΣPBDEs was the television from Home 2 with 23 500 pg ΣPBDEs/cm^2. The surface with the lowest detectable concentration of ΣPBDEs in dust was the DVD player at Home 1 with 12 pg ΣPBDEs/cm^2. The mean ΣPBDE concentrations (pg/cm^2) for the televisions, stereos, refrigerators and DVD players are shown in Table 4.5.

Table 4.5 Concentration of mean ΣPBDEs by surfaces (pg/cm^2)

Surface	Television	Stereo	Refrigerator	DVD player
Mean (excl. LOD)	5950	nd-53*	71	43
Mean (incl. LOD)	5985	58	87	116

*only detected on one stereo surface

A replicate sample was taken from the television wipe at Home 1. These samples were obtained from next to each other on the top of the television using identical sampling procedures and are referred to as Home 1 – television 'A' and 'B'. BDEs -206, -207 and -209 were detected in both samples. BDE-66 was detected only in the 'A' sample, however, at a low concentration. The results of these samples were in good agreement and the mean normalised difference (see Box 1) for the three congeners detected in both samples was 12% (see Appendix D).

For Home 2, a second sample was obtained after the television 'A' wipe was analysed and the result reported. The television 'A' had the highest surface wipe result and a second wipe - television 'B' was taken. However, the repeat sample showed a concentration over a hundred times smaller than the 'A' sample. Due to the good analytical and sampling reproducibility obtained from the Home 1 television 'A' and 'B' samples, it is not believed these factors were the cause of the difference between Home 2 television 'A' and 'B' samples. Further investigation of theses samples revealed that the television represented by the 'A' sample had been moved from an open air situation to being housed inside a cabinet for the 'B' sample. Although this new position of the television was not totally closed off by a glass door like in the case of the stereo, it is believed that accumulation of dust was slowed and could explain the lower concentrations of PBDEs in television 'B'. This brings about an interesting point which, as mentioned above, was unclear at the beginning of the study. That is, perhaps the surface wipe is representing the PBDEs in the household environment which have settled on the surface and not the PBDEs used to flame retard the particular appliance from which the wipe was taken. This warrants further investigation.

This was examined further by looking at the congener profile of the surface wipe samples. The surface wipes obtained from Home 1 were dominated by the higher brominated diphenyl ether congeners with the contribution from BDE-209 ranging from 92-94%. BDE-66 was the only lower brominated congener in the samples from Home 1. It was detected in the television 'A' sample where it contributed 0.2% to the ΣPBDE concentration. The surface wipes from Home 2 showed a different profile. The higher brominated congeners BDE -206, -207 and -209 were present but, there was also some contribution from lower brominated congeners and consistently BDE-183 was present in all samples. BDE-183 contributed between 16 and 62% to the ΣPBDE concentration of the Home 2 surface wipes while BDE-209 contributed 0 and 64%.

4.4 Comparison of PBDEs in indoor environments

For comparative purposes a mean was taken of the surface wipes from each home. The mean was higher at Home 2 (including and excluding the outlying result of Home 2- television 'A') than at Home 1 (300 pg/cm^2 and 5 pg/cm^2, respectively). This was consistent with the air and dust samples which were higher in Home 2 than in Home 1, see Figure 4.3. This relationship should be treated with caution due to the small sample size. More sampling is required to determine if an association exists. As there were two results for air at Home 1 but only one dust result, the two air results were averaged.

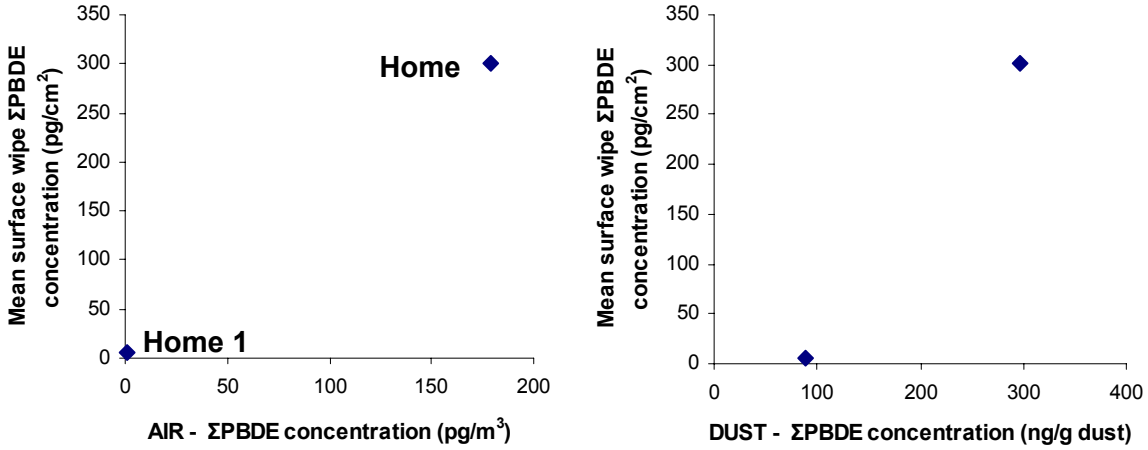

Figure 4.3 Comparison of mean surface wipe concentrations and air (left) and mean surface wipe concentration and dust (right) for Home 1 and Home 2.

For dust, the sites with the lowest and highest concentrations also had the lowest and highest air concentrations for ΣPBDEs. However, for the other samples there did not seem to be any correlation between dust and air concentrations, see Figure 4.4.

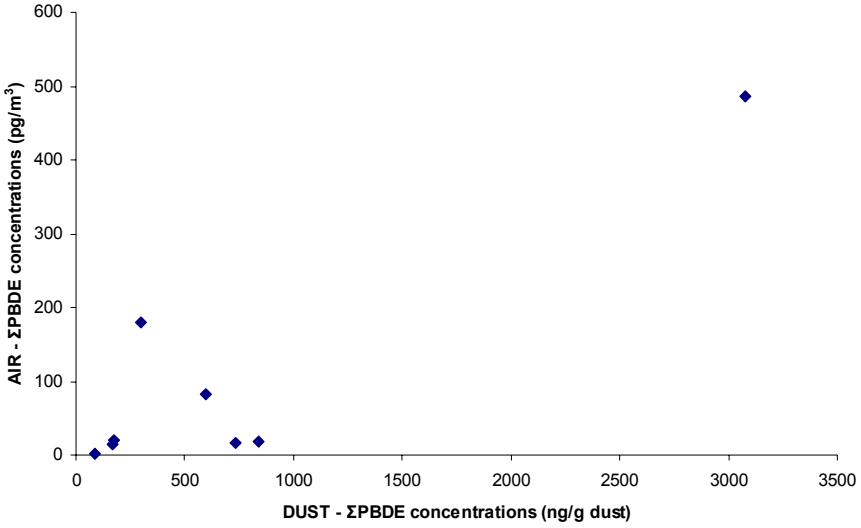

Figure 4.4 Comparison of ΣPBDE concentrations in air and dust for all homes and offices.

5. Comparison of Australian polybrominated diphenyl ether concentrations with other countries

The results of the current study are compared with results from international studies of air, dust and surface wipes. Full details of these international studies are available in Appendix F.

5.1 Air

There is currently some data available on the concentrations of PBDEs in indoor and outdoor air from international studies. Within these studies, some indoor air samples include household samples and some include workplace samples. The studies of air use either active or passive samplers. Due to the limited number of studies on PBDEs in air, both active and passive sampler results are described here, even though the current study used active samplers only.

The results of selected international studies are compared with the results of the current study in Figure 5.1.

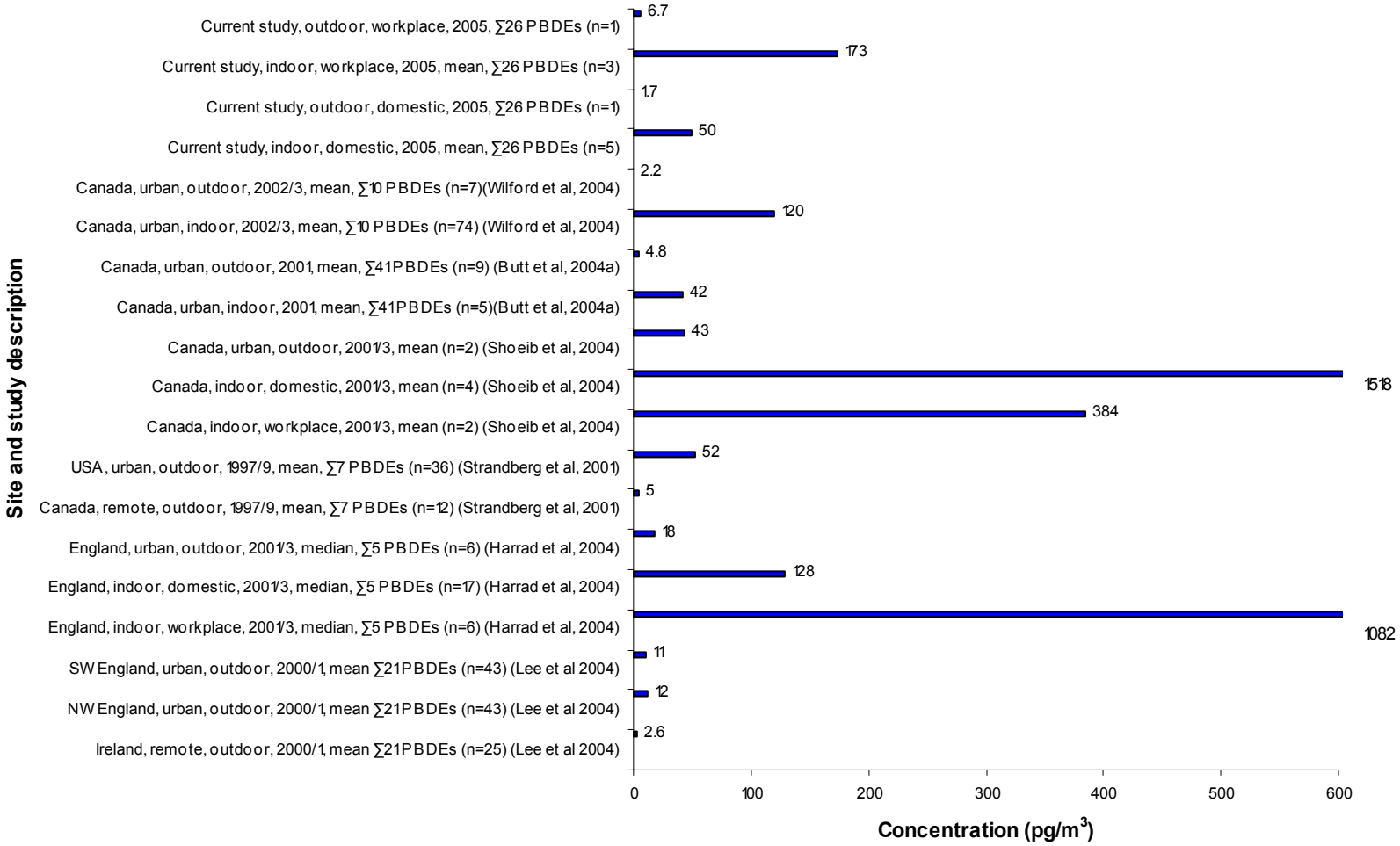

Figure 5.1

Figure 5.1 Comparison of ΣPBDE concentrations (pg/m^3) in air from the current study and international results.

5.2 Dust

The concentrations of PBDEs have been measured and detected in household and occupational dust as an indication of possible human exposure to these chemicals. Occupational samples have demonstrated varying results dependant on the type of workplace where the samples were collected, that is, office or factory. In this comparison the results of the dust from homes in the current study are compared with other household data and the results of the offices are compared with office data (not factories). Figure 5.2 shows the concentrations of BDE-47 and -209 in the current study and in data from Europe and North America as it was difficult to compare ΣPBDEs as different congeners were measured in all studies. For the household dust concentrations, Australia has lower concentrations than Canada, the US and one German study. For another study by Sjodin et al (2004) the results for Germany are lower than the current Australian data. The current Australian study is also lower than a previous Australian study in 2004 (Sjodin et al), however different sampling techniques may account for the variation in results.

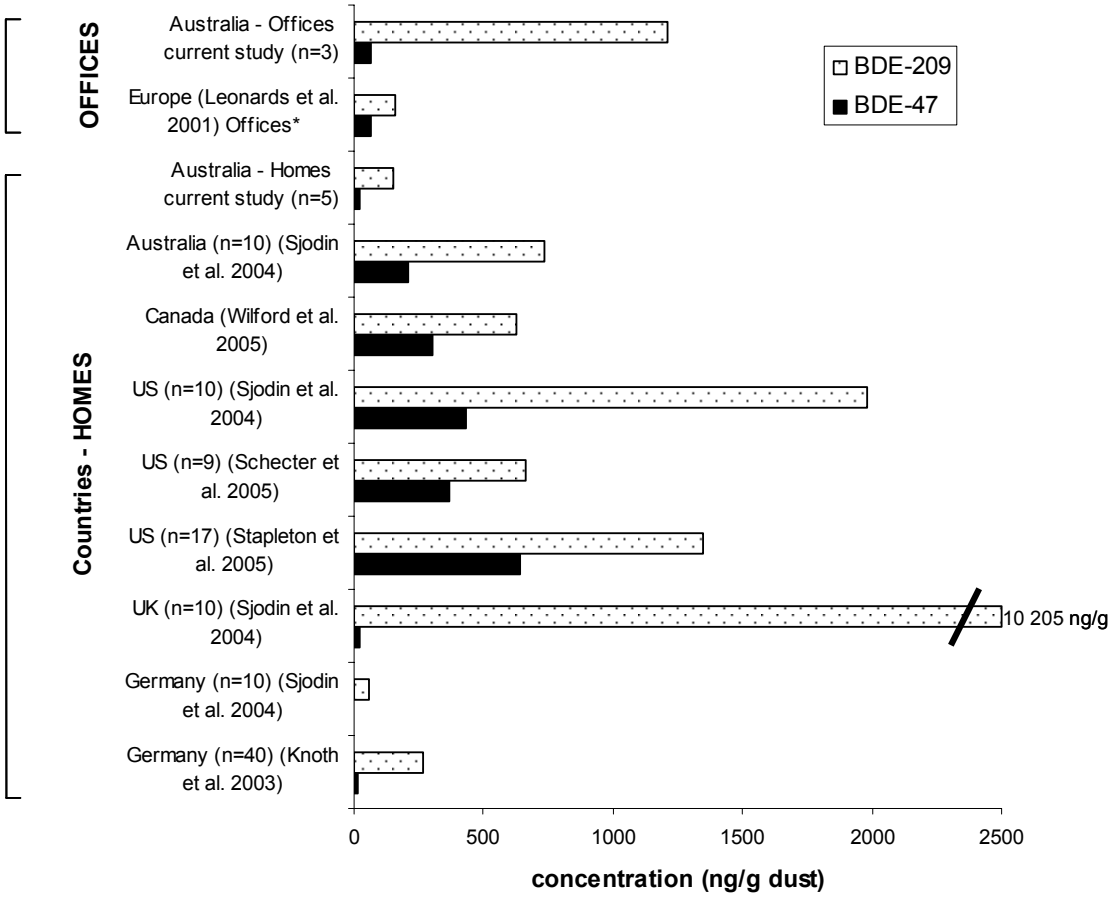

Figure 5.2 Comparison of BDE -47 and -209 (ng/g dust) in household and office dust from Australia and overseas.

5.3 Surface wipes

Schecter et al (2005) analysed surface wipes from computers (n=2) and monitors (n=2). The total ΣPBDE concentration (sum of 17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183 and 209) ranged from 0.77 to 15.4 ng/cm^2. The lowest value was from a monitor at 0.77 ng/cm^2 and the highest was from a computer at 15.4 ng/cm^2. The results from the current study found ΣPBDEs on surfaces to range from non-detect to 23.5 ng/cm^2. The current study did not sample monitors or computers and therefore direct comparison was not possible. The mean ± standard deviation for televisions in the current study was 5.9± 11.7 ng/cm^2 (including the outlier Home 2 – television 'A' 23.5 ng/cm^2) and 0.1 ± 0.06 ng/cm^2 (excluding the outlier). Overall, the concentrations of ΣPBDEs in the surface wipes from Australia were lower than those reported by Schecter et al (2005) in the US

The only other reported study of surface wipes for PBDE concentrations was by Butt et al (2004a). This involved the collection of organic films from indoor and outdoor window surfaces. These results were used to calculate the concentration of PBDEs in air as opposed to on surfaces as was done in the current study and by Schecter et al (2005).

6. Summary of findings

This study involved the investigation of BFRs in indoor environments in Australia. In total, nine indoor air samples, two outdoor air samples, nine dust samples and ten surface wipe samples were collected, processed and analysed. Indoor air samples were obtained from five homes and three offices. Outdoor air samples were obtained from one home site and one office site. Dust samples were obtained from each of the homes and offices. Surface wipe samples were obtained at two homes from four surfaces.

PBDEs were detected in all samples of air and dust and 90% of surface wipe samples demonstrating that PBDEs are ubiquitous in the indoor environment in Australia. The results provide some preliminary indications that building characteristics may affect exposure to these chemicals in indoor environments. However, it should be noted that due to the small sample size used in this study, the results cannot be assumed to be representative of all indoor environments in Australia with further work required to validate these results. The study provides very important results for the evaluation of BFRs in indoor environments in Australia; however it remains difficult to identify the specific pathways that cause exposure and the particular contribution of the indoor environment to the overall exposure of Australians.

7. References

Bromine Science and Environmental Forum (BSEF) http://www.bsef.com/bromine/faq/ [accessed 31 October 2005]

Butt, C. M., M. L. Diamond, et al (2004a). "Spatial distribution of polybrominated diphenyl ethers in Southern Ontario as measured in indoor and outdoor window organic films." Environmental Science and Technology 38: 724-731.

Butt, C., M. Diamond, et al (2004b). "Semivolatile organic compounds in window films from Lower Manhattan after the September 11th World Trade Center attacks." Environmental Science and Technology 38: 3514-3524.

Darnerud, P., G. Eriksen, T. Johannesson, P. Larsen and M. Viluksela (2001). "Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology." Environmental Health Perspectives 109(Suppl. 1): 49-68.

Department of Health and Human Services (US), Public Health Service, Agency for Toxic substances and disease registry. September 2004. "Toxicological Profile for polybrominated biphenyls and polybrominated diphenyl ethers."

de Wit, C. (2002). "An overview of brominated flame retardants in the environment." Chemosphere 46: 583-624.

Harden F, Müller J and Toms L. 2005. "Organochlorine Pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) in the Australian population: levels in human milk." Environment Protection and Heritage Council of Australia and New Zealand.

Harrad, S., Wijesekera, R., Hunter, S., Halliwell, C. and Baker, R. (2004). "Preliminary assessment of UK human dietary and inhalation exposure to polybrominated diphenyl ethers." Environmental Science and Technology, 38**,** 2345-2350.

Kemmlein, S., Hahn, O. and Jann, O. (2003)."Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials." Atmospheric Environment, 37**,** 5485-5493.

Knoth, W., Mann, W., Meyer, R. and Nebhuth, J. (2003). "Brominated diphenyl ether in indoor dust." Organohalogen Compounds, 61**,** 207-210.

Lee, R. G. M., Thomas, G. O. and Jones, K. C. (2004). "PBDEs in the atmosphere of three locations in Western Europe." Environmental Science and Technology, 38**,** 699-706.

Leonards, P., Santillo, D., Brigden, K., van der Veen, I., v. Hesselingen, J., de Boer, J. and Johnston, P. (2001). "Brominated flame retardants in office dust samples" In: Proceedings of the Second International Workshop on Brominated Flame Retardants, 14-16 May, 2001, The Swedish Chemical Society, Stockholm, Sweden (2001)**,** 299-302.

Meironyte, D. and K. Noren (1999). "Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997." Journal of Toxicology and Environmental Health Part A, 58: 329-341.

McLachlan M. (1996). "Bioaccumulation of hydrophobic chemicals in agricultural food chains." Environmental Science and Technology, 30, 252-259.

NICNAS, 2005. "Summary of information on polybrominated flame retardants." Chemical Gazette, No C 5, 3 May 2005".

Rudel, R., Camann, D. E., Sprengler, J. D., Korn, L. R. and Brody, J. G. (2003). "Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust." Environmental Science and Technology, 37**,** 4543-4553.

Schecter, A., Paepke, O., Joseph, J. E. and Tung, K. (2005). "Polybrominated diphenyl ethers (PBDEs) in US computers and domestic carpet vacuuming: possible sources of human exposure." Journal of Toxicology and Environmental Health, 68**,** 501-513.

Shoeib, M., Harner, T., Ikonomou, K. and Kannan, K. (2004). "Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers." Environmental Science and Technology, 38**,** 1313-1320.

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

Stapleton, H. M., Dodder, N. G., Offenberg, J. H., Schantz, M. M. and Wise, S. A. (2005). "Polybrominated diphenyl ethers in house dust and clothes dryer lint." Environmental Science and Technology, 39**,** 925-931.

Strandberg, B., N. G. Dodder, I. Basu and R. A. Hites (2001). "Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air." Environmental Science and Technology 35(6): 1078-1083.

Wilford, B. H., Harner, T., Zhu, J., Shoeib, M. and Jones, K. C. (2004). "Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: implications for sources and exposure." Environmental Science and Technology, 38**,** 5312-5318.

Wilford, B., Shoeib, M., Harner, T., Zhu, J. and Jones, K. C. (2005). "Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: implications for sources and exposure." Environmental Science Technology, 39**,** 7027-7035.

Appendix A Ethics approval

THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

Office of Research and Postgraduate Studies

DIRECTOR
Jan Massey

Tel: (07) 3365 3924
Fax: (07) 3365 4455
Email: humanethics@research.uq.edu.au

The University of Queensland
Cumbrae-Stewart Building
Research Road
Brisbane Qld 4072 Australia
Telephone +61 7 3365 3560
Telephone +61 7 3365 4584
Facsimile +61 7 3365 4455

22 April 2005

Associate Professor Jochen Mueller
National Research Centre for Environmental Toxicology

Dear Associate Professor Mueller

Concerning:Ethical clearance for project:- ***Research of brominated flame retardants in indoor environments in Australia***

Clearance No: 2005000290

The Behavioural and Social Science Ethical Review Committee has approved your project. The Institutional Clearance Form is attached and you will need to refer to this form for any additional notes and/or special conditions.

Please note that:-

(i) The Clearance number should be quoted on the protocol coversheet when applying to a granting agency and in any correspondence relating to ethical clearance;

(ii) Clearance will normally be for the duration of the project unless otherwise stated in the institutional clearance:

(iii) Adverse reaction to treatment by subjects, injury or any other incident affecting the welfare and/or health of subjects attributable to the research should be promptly reported to the Head of School and the Ethics Committee.

(iv) Amendments to any part of the approved protocol (including change of Investigator/s), documents or questionnaires attached to this clearance must be submitted to the Ethics Committee for approval.

2005000290

(v) Advisers on 'Integrity in Research'
As part of the University's commitment to the institutional statement, *Code of conduct for the Ethical Practice of Research (1990)*, and the NH&MRC's *National Statement on Ethical Conduct in Research Involving Humans (1999)*, designated positions have been appointed as advisers on integrity in research. The Chairperson of each ethics committee acts in an advisory capacity to provide confidential advice on such matters as misconduct in research, the rights and duties of postgraduate supervisors, and procedures for dealing with allegations on research misconduct within the University. The contact number for the Chairperson of each ethics committee can be obtained from the Ethics Officer.

(vi) The Committee reserves the right to visit the research site and view materials at any time, and to conduct a full audit of the project.

(vii) It is the Committee's expectation, whenever possible, this work should result in publication and the Committee would require details to be submitted for our records.

Staff and students are also encouraged to contact either the Ethics Officer (3365 3924), or Chairperson on other issues concerning the conduct of experimentation/research (e.g. involvement of children, informed consent) prior to commencement of the project and throughout the course of the study.

Yours sincerely

Per.

Michael Tse
Ethics Officer

Encs.
cc: None

THE UNIVERSITY OF QUEENSLAND

Institutional Approval Form For Experiments On Humans Including Behavioural Research

Chief Investigator:	Associate Professor Jochen Mueller
Project Title:	Research of brominated flame retardants in indoor environments in Australia
Supervisor:	None
Co-Investigator(s)	Michael Bartkow, Leisa Toms, Robert Symons
Department(s):	National Research Centre for Environmental Toxicology
Project Number:	2005000290
Granting Agency/Degree:	
Duration:	21st April 2006

Comments:

Expedited Review on basis that the subjects of the project are residences and office buildings

Name of responsible Committee:-
Behavioural & Social Sciences Ethical Review Committee
This project complies with the provisions contained in the *National Statement on Ethical Conduct in Research Involving Humans* and complies with the regulations governing experimentation on humans.

Name of Ethics Committee representative:-
Dr J Broerse
Chairperson
Behavioural & Social Sciences Ethical Review Committee

Date 21/04/05 Signature

Appendix B Analytical methodology

National Measurement Institute

The same analytical methodology was used for the air, dust and surface wipe samples.

High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) was used to determination the levels of PBDEs in environmental matrices. This method provided data on 26 PBDE congeners determined by the isotope dilution HRMS quantification technique. The detection limits and quantification levels in this method were usually dependent on the level of interferences rather than instrumental limitations. The method is 'performance based'. The analytical methodology for the determination of PBDEs was based on USEPA Draft Method 1614.

Clean up was effected by partitioning with sulfuric acid then distilled water. Further purification was performed using column chromatography on acid, base and neutral modified silica gels and basic alumina. After cleanup, the extract was concentrated to near dryness. Immediately prior to injection, internal standards were added to each extract, and an aliquot of the extract was injected into the gas chromatograph. The analytes were separated by the GC and then detected by a high-resolution (≥10,000) mass spectrometer. The quality of the analysis was assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

PBDE analyses

The following standards were all purchased from Wellington Laboratories (Ontario, Canada) and were used for calibration, quantification and determination of recovery of PBDEs:

- MBDE-MXE labelled surrogate spiking solution
- MBDE-138 internal standard solution *and*
- BDE-CVS-E calibration and verification solutions (CS1-CS5).

Acetone, dichloromethane, hexanes, and toluene were all OmniSolv® grade sourced from Merck KgaA (Darmstadt, Germany). Anhydrous sodium sulfate (granular) was both AR grade sourced from Mallinckrodt (Kentucky, USA). AnalaR® sulfuric acid S.G. was sourced from Merck (Victoria, Australia). All chromatographic columns were purchased from Fluid Management Systems Inc. (Watertown, MA, USA) and were used without any further treatment. They comprised multi-layer (acidic/basic/neutral) silica and basic alumina which are packed in individual Teflon® columns and vacuum sealed in Mylar® packages.

Sample preparation

A Dionex ASE100 accelerated solvent extractor (Dionex Corporation, Sunnyvale, CA, USA) was used to extract all samples operated under the conditions listed in Table B.1. Samples were weighed into an appropriately sized ASE cell and spiked with a known amount of the respective isotopically labelled $^{13}C_{12}$ PBDE surrogate solutions. Moisture determination on a separate portion was then calculated gravimetrically after drying overnight in an oven set at 105^{o}C.

Table B.1 ASE Operating Conditions

Solvent	Toluene
Temperature	150°C
Equilibration time	5 minutes
Static	5 minutes
Flush Volume	60%
Purge Time (Nitrogen)	180 seconds
Static Cycles	2
Pressure	1750 psi

Toluene extracts were concentrated under vacuum using a BÜCHI Syncore® Analyst (BÜCHI Labortechnik AG, Flawil, Switzerland) and solvent exchanged into hexanes. The hexanes solutions were subjected to multiple extractions with concentrated sulfuric acid until the acid layer remained colourless and then washed several times with water and dried through cleaned anhydrous sodium sulfate. The extracts were then concentrated prior to clean-up on a Fluid Management Systems, Inc. (FMS, Watertown, MA, USA) Power-Prep System™. The Power-Prep System™ consists of a number of chromatography panels comprising a valve module, a valve drive module and pump modules which are all computer controlled. The chromatographic columns used are disposable silica (acid, base, and neutral mix) and basic alumina columns also manufactured by FMS. These columns are made of Teflon® and individually sealed in Mylar® packaging.

Elution through the different columns is computer controlled and requires applying the hexane extract first onto the multi-layer silica and using hexane at a flow rate of 10 mL/min directly onto the alumina column. Dichloromethane:hexane (2:98) at 10 mL/min is used initially and then the solvent strength is modified to dichloromethane:hexane (50:50) in the forward direction at 10 mL/min. The fraction containing the PBDEs is collected from the alumina column directly into 200 mL BÜCHI Syncore® Analyst tubes. This fraction is concentrated to near dryness and the recovery standard (MBDE-138) is added and then further concentrated using clean dry nitrogen to a final volume of 40 µL prior to HRGC/HRMS analysis.

High-Resolution Gas Chromatography High-Resolution Mass Spectrometric (HRGC-HRMS) Analysis

All experiments were conducted on a MAT95XL HRMS (ThermoFinnigan MAT GmbH, Bremen, Germany) coupled to an Agilent 6890 GC (Palo Alto, CA, USA) equipped with a CTC A200S auto sampler. A DB-5 (J and W Scientific, Folsom, CA, USA) capillary column (15m x 0.25mm i.d., film thickness 0.25µm) was used as the primary analytical column with ultra-high purity Helium as the carrier gas. A flow rate of 1.0 mL/min was maintained throughout the chromatographic run. The temperature programme for the PBDE analysis was: 100°C (isothermal for 2 min.) then ramp 1 to 230°C at 15°C/min, ramp 2 to 270°C at 5°C/min and then ramp 3 to 320°C at 10°C/min (isothermal 5 min). A 1µL splitless injection with an injector temperature of 280°C for PBDE analysis was employed for standards and sample extracts. The mass spectrometer operating conditions were: ion source and transfer line temperatures, 240°C and 280°C, respectively; ionisation energy 45eV, filament current 0.7mA and electron multiplier voltage set to produce a gain of 10^6. Resolution was maintained at 10,000 (10% valley definition) throughout the sample sequence. Multiple ion detection (MID) experiments were performed in the electron impact mode with monitoring of

the exact masses of appropriate ions for native and labelled compounds. Individual congeners are identified using the GC retention time and ion abundance ratios with reference to internal standards.

Table B.2 gives a list of the PBDE congeners included in this method. Table B.3 shows the theoretical abundance ratios and QC limits and Table B.4 lists the MID windows for the PBDEs.

Table B.2. List of PBDE Congeners Analysed

BDE Congener	Abbreviation
2,2',4-Tribrominated diphenyl ether	BDE 17
2,4,4'-Tribrominated diphenyl ether	BDE 28
2',3,4-Tribrominated diphenyl ether	BDE 33
2,2',4,4'-Tetrabrominated diphenyl ether	BDE 47
2,2',4,5'-Tetrabrominated diphenyl ether	BDE 49
2,3',4,4'-Tetrabrominated diphenyl ether	BDE 66
2,3',4',6-Tetrabrominated diphenyl ether	BDE 71
3,3',4,4'-Tetrabrominated diphenyl ether	BDE 77
2,2',3,4,4'-Pentabrominated diphenyl ether	BDE 85
2,2',4,4',5-Pentabrominated diphenyl ether	BDE 99
2,2',4,4',6-Pentabrominated diphenyl ether	BDE 100
2,3',4,4',6-Pentabrominated diphenyl ether	BDE 119
3,3',4,4',5-Pentabrominated diphenyl ether	BDE 126
2,2',3,4,4',5'-Hexabrominated diphenyl ether	BDE 138
2,2',4,4',5,5'-Hexabrominated diphenyl ether	BDE 153
2,2',4,4',5,6'-Hexabrominated diphenyl ether	BDE 154
2,3,3',4,4',5-Hexabrominated diphenyl ether	BDE 156
2,3,4,4',5,6-Hexabrominated diphenyl ether	BDE 166
2,2',3,4,4',5',6-Heptabrominated diphenyl ether	BDE 183
2,2',3,4,4',6,6-Heptabrominated diphenyl ether	BDE 184
2,3,3',4,4',5',6-Heptabrominated diphenyl ether	BDE 191
2,2,3,3',4,4',5,6'-Octabrominated diphenyl ether	BDE 196
2,2,3,3’,4,4’,6,6’- Octabrominated diphenyl ether	BDE 197
2,2,3,3',4,4',5,5',6-Nonabrominated diphenyl ether	BDE 206
2,2,3,3',4,4',5,6,6-Nonabrominated diphenyl ether	BDE 207
Decabromodiphenyl ether	BDE 209

Table B.1. Theoretical Ion Abundance Ratios and QC Limits

No of Bromine Atoms	*m/z's forming the ratio (R/Q)	Theoretical Ratio	QC limits	
			Lower	Upper
1	M/(M+2)	1.03	0.88	1.18
2	(M+2)/(M+4)	0.51	0.43	0.59
2	M/(M+2)	0.43	0.47	0.59
3	M-Br_2/(M+2)-Br_2	1.06	0.82	1.22
3	(M+2)/(M+4)	1.03	0.88	1.18
4	M-Br_2/(M+2)-Br_2	0.53	0.41	0.61
4	(M+2)/(M+4)	0.70	0.60	0.81
4	(M+4)/(M+6)	1.54	1.31	1.77
5	(M+2)-Br_2/(M+4)-Br_2	1.06	0.82	1.22
5	(M+4)/(M+6)	1.03	0.88	1.18
6	(M+2)-Br_2/(M+4)-Br_2	0.71	0.54	0.82
6	(M+4)/(M+6)	0.77	0.65	0.89
6	(M+6)/(M+8)	1.37	1.16	1.58
7	(M+4)-Br_2/(M+6)-Br_2	1.06	0.82	1.22
7	(M+6)/(M+8)	1.03	0.88	1.18
8	(M+6)/(M+8)	0.82	0.70	0.94
9	(M+8)/(M+10)	1.03	0.88	1.18
10	(M+8)/(M+10)	0.73	0.86	0.99

Table B.2. The MID Windows for PBDEs

MID Window	Accurate Mass	Ion Id	Analyte (I= internal standard)
1	245.9675	M-Br_2	TriBDE
	247.9655	(M+2)-Br_2	TriBDE
	258.0077	M-Br_2	TriBDE(I)
	260.0057	(M+2)-Br_2	TriBDE(I)
2	323.8780	M-Br_2	TeBDE
	325.8760	(M+2)-Br_2	TeBDE
	335.9182	M-Br_2	TeBDE(I)
	337.9162	(M+2)-Br_2	TeBDE(I)
	483.7106	M+2	TeBDE
	485.7085	M+4	TeBDE
3	561.6231	M+2	PeBDE
	563.6211	M+4	PeBDE
	565.6190	M+6	PeBDE
	573.6634	M+2	PeBDE(I)
	575.6613	M+4	PeBDE(I)
	577.6593	M+4	PeBDE(I)
4	481.6976	(M+2)-Br_2	HxBDE
	483.6956	(M+4)-Br_2	HxBDE
	485.6937	(M+6)-Br_2	HxBDE
	493.7372	(M+2)-Br_2	HxBDE(I),(IS)
	495.7352	(M+4)-Br_2	HxBDE(I),(IS)
	497.7331	(M+6)-Br_2	HxBDE(I),(IS)
5	559.6082	(M+2)-Br_2	HpBDE
	561.6062	(M+4)-Br_2	HpBDE
	563.6042	(M+6)-Br_2	HpBDE
	571.6477	(M+2)-Br_2	HpBDE(I)
	573.6457	(M+4)-Br_2	HpBDE(I)
	575.6436	(M+6)-Br_2	HpBDE(I)
6	639.5160	(M+2)-Br_2	OcBDE
	641.5140	(M+4)-Br_2	OcBDE
	643.5120	(M+6)-Br_2	OcBDE
	651.5562	(M+2)-Br_2	OcBDE (I)
	653.5542	(M+4)-Br_2	OcBDE (I)
	665.5521	(M+6)-Br_2	OcBDE (I)
7	717.7265	(M+2)-Br_2	NoBDE
	719.4245	(M+4)-Br_2	NoBDE
	721.4225	(M+6)-Br_2	NoBDE
	729.4667	(M+2)-Br_2	NoBDE (I)
	731.4647	(M+4)-Br_2	NoBDE (I)
	733.4626	(M+6)-Br_2	NoBDE (I)
7	797.3350	(M+2)-Br_2	DeBDE
	799.3329	(M+4)-Br_2	DeBDE
	801.3308	(M+6)-Br_2	DeBDE
	809.3752	(M+2)-Br_2	DeBDE (I)
	811.3732	(M+4)-Br_2	DeBDE (I)
	813.3711	(M+6)-Br_2	DeBDE (I)

TriBDE- Tribrominated diphenyl ether
TeBDE- Tetrabrominated diphenyl ether
PeBDE- Pentabrominated diphenyl ether
HxBDE-Hexabrominated diphenyl ether
HpBDE-Heptabrominated diphenyl ether
OcBDE-Octabrominated diphenyl ether
NoBDE-Nonabrominated diphenyl ether
DeBDE-Decabrominated diphenyl ether

Analyte identification and quantification criteria

For positive identification and quantification, the following criteria must be met: the retention time of the analyte must be within 1 second of the retention time of the corresponding $^{13}C_{12}$ surrogate standard; the ion ratio obtained for the analyte must be ± 20% of the theoretical ion ratio; the signal to noise ratio must be greater than 3:1; levels of PBDE congeners in a sample must be greater than 3 times any level found in the corresponding laboratory blank analysed; and surrogate standard recoveries must be in the range 25-150%.

Quantification using the Isotope Dilution Technique

The naturally occurring (native) compound was determined by reference to the same compound in which one or more atoms were isotopically enriched. In this method, all carbon atoms for selected PBDE molecules were substituted with carbon-13 to produce $^{13}C_{12}$-labelled analogs of the brominated diphenyl ethers. The $^{13}C_{12}$-labelled PBDEs were spiked into each sample and allowed identification and correction of the concentration of the native compounds in the analytical process. The proprietary chromatographic integration package supplied with the Thermo Finnigan instrument, (Xcalibur®), was used to target all monitored compounds and create a text file that was further manipulated in Excel to produce the final certificate of analysis.

Quality Assurance

In order to manage quality assurance, batch sizes were typically 6-8 samples. A laboratory blank was analysed with each batch of samples. The HRMS resolution, performance and sensitivity were established for each sequence and the recoveries of all isotopically labelled surrogate standards were calculated and reported.

Data reporting

The basis of reporting for primary and quality control samples is as follows: pg/g on a dry weight basis; PBDEs data were corrected for recovery of $^{13}C_{12}$ surrogate standards; for all samples, data for quantified analytes were reported to 2 or 3 significant figures; and limit of detection data for non-quantified analytes were reported to 1 significant figure.

Eurofins/ERGO

PBDE analysis

In this case the extraction of the samples was not performed at ERGO. The three delivered extracts were already spiked with 20µL of the 13C-PBDE surrogate prior to extraction. The specific contents of the 13C-PBDE surrogate were as follows:

Table B5

Internal Standards (^{13}C-UL) PBDE	Congener Number	Concentration pg/µL
4-BromoDE	BDE 3L	200
4,4'-DibromoDE	BDE 15L	200
2,4,4'-TribromoDE	BDE 28L	200
2,2',4,4'-TetrabromoDE	BDE 47L	200
2,2',4,4',5-PentabromoDE	BDE 99L	200
2,2',4,4',5,5'-HexabromoDE	BDE 153L	400
2,2',4,4',5,6'-HexabromoDE	BDE 154L	400
2,2',3,4,4',5',6-HeptabromoDE	BDE 183L	400
2,2',3,3',4,4',6,6'-OctabromoDE	BDE 197L	400
2,2',3,3',4,4',5,6,6'-NonabromoDE	BDE 207L	1000
DecabromoDE	BDE 209L	1000

Sample Preparation

The clean-up of the sample extracts was performed in brown glass. 2,2',3,4,4',6-Hexabromdiphenylether (Hexa-BDE 139 ^{13}C-UL labelled) was used as syringe standard. The single column clean-up was performed by means of silica-gel and alumina columns (B). The multi column clean-up was performed by means of silica-gel, alumina and K/SiO_2-columns (C). The sample delivered 13C-PBDE surrogate was used with in house available native PBDE-Standards.

Table B6

IUPAC-code	Internal Standards (^{13}C-UL) PBDE		Calculation basis
3	4-	Mono-BDE	1, 2, **3**
15	4,4'-	Di-BDE	7, 10, 13, **15**
28	2,4,4'-	Tri-BDE	17, 25, **28**, 35
47	2,2',4,4'-	Tetra-BDE	**47**, 49, 66, 71, 75, 77
99	2,2',4,4',5-	Penta-BDE	85, **99**, 100, 116, 119, 126
153	2,2',4,4',5,5'-	Hexa-BDE	138, 140, **153**, 156
154	2,2',4,4',5,6'-	Hexa-BDE	**154**, 155
183	2,2',3,4,4',5',6-	Hepta-BDE	181, **183**
197	2,2',3,3',4,4',6,6'-	Octa-BDE	**197**, 203
207	2,2',3,3',4,4',5,6,6'-	Nona-BDE	**207**
209	2,2',3,3',4,4',5,5',6,6'-	Deca-BDE	**209**

High-Resolution Gas Chromatography High-Resolution Mass Spectrometric (HRGC-HRMS) Analysis

The measurement is done by means of HRGC/HRMS (high resolution gas chromatography/ high resolution mass spectrometry, VG Autospec resp. Finnigan MAT 95 XL) using a DB 5 column for gaschromatographic separation. The quantification is performed by means of internal / external standards (isotope dilution).

The analytical method is not part of the accreditation.

Appendix C results

Appendix C includes the results for the air samples (Table C.1), the dust samples (Table C.2) and the surface wipe samples (Table C.3).

Table C. 1 Air results in pg/m3

PBDE Congener	Home 1 'A'	Home 1 'B'	Home 2	Home 3	Home 4	Home 5	Office 1	Office 2	Office 3	Outdoor 1	Outdoor 2
m^3 sampled	**168**	**192**	**452**	**494**	**330**	**259**	**475**	**328**	**372**	**4009**	**2511**
BDE 17	1.2	0.52	2.54	2.00	2.30	0.36	1.50	20.9	<0.3	<0.2	0.06
BDE 28 + BDE 33	<43.9	<5.21	<8.89	<17	<8.61	<2.3	<5	46.3	<5.3	<0.4	<1
BDE 47	<92.3	<16.67	<26.11	73.00	<45	<14	<40	358.1	<23.2	<3.2	<2
BDE 49	<1.4	<0.42	1.42	2.20	1.36	<0.4	2.00	17.7	<2	0.20	<0.08
BDE 66	<1	<0.22	0.80	1.40	<0.6	<0.3	1.10	7.9	0.09#	0.10	<0.05
BDE 71	0.1	<0.03	0.10	0.14	<0.09	0.08	0.21	1.5	0.13*	0.01	<0.02
BDE 77	<0.1	<0.03	<0.02	<0.02	<0.2	<0.2	<0.06	<0.08	<0.04	<0.01	<0.02
BDE 85	<1.3	<0.31	<0.64	<1.1	<0.3	<0.4	<0.3	0.76#	<0.4	<0.05	<0.06
BDE 99	<41.6	<10.42	<18	<34	<8	<8	<10	20.03#	<10.3	<1.4	<1
BDE 100	<9.3	<2.08	<3.9	<9	<3	<2	<3	4.6#	<2.7	<0.4	<0.03
BDE 119	<0.1	<0.1	0.04	<0.02	<0.3	<0.2	<0.06	<0.43	<0.13	<0.01	<0.04
BDE 126	<0.1	<0.05	<0.02	<0.02	<0.3	<0.2	<0.06	<0.08	<0.05	<0.002	<0.02
BDE 138 + BDE 166	<0.2	<0.1	<0.4	<0.12	<0.3	<0.8	<0.1	<0.18	<0.08	<0.01	<0.08
BDE 153	<2.4	<0.52	7.85	1.90	<0.7	<1.3	<1	1.65#	0.75#	<0.1	<0.1
BDE 154	<1.7	<0.42	<2.2	<1.8	<0.4	<0.8	<0.6	1.25#	<0.54	<0.1	<0.1
BDE 156	<0.1	<0.05	<0.04	<0.02	<0.2	<0.2	<0.1	<0.04	<0.05	<0.02	<0.03
BDE 183	0.3	<0.16	31.40	0.40	4.55	2.43	3.70	0.88#	1.48#	0.12	0.1
BDE 184	<0.1	<0.05	0.16	<0.06	<0.3	<0.4	<0.2	<0.12	<0.16	0.01	<0.08
BDE 191	<0.2	<0.03	0.14	<0.06	<0.6	<0.4	<0.2	<0.05	<0.05	<0.01	<0.04
BDE 196	<0.2	<0.1	2.30	0.07	0.45	0.37	0.27	<0.12	<0.16	0.05	0.03
BDE 197	<0.2	<0.1	3.90	0.09	1.12	0.50	0.65	<0.21	<0.3	0.05	0.03
BDE 206	<0.3	<0.36	5.90	0.50	<0.3	0.58	0.55	<0.43	0.7#	0.27	0.06
BDE 207	<0.3	<0.47	6.10	<0.4	0.97	1.35	0.97	<0.42	<0.94	0.24	0.13
BDE 209	<4.2	<3.65	117.00	<8.1	9.55	11.24	6.95	5.21#	11.8#	5.80	1.28
Sum of PBDE congeners											
Excluding LOD values	**1.6**	**0.5**	**179**	**83**	**20**	**17**	**18**	**486**	**15**	**7**	**1.7**
Incl. ½ LOD values	**195**	**21**	**184**	**145**	**76**	**39**	**66**	**488**	**38**	**10**	**4**
Incl. LOD values	**202**	**42**	**240**	**154**	**90**	**48**	**78**	**549**	**64**	**13**	**7**

not detected on XAD-2, value detected on filter included here

Table C. 2 Dust results in ng/g dust

PBDE Congener	DUST – Home 1 (-c, -ac, >5)	DUST – Home 2 (+c, +ac, >5)	DUST – Home 3 (-c, +ac, >5)	DUST – Home 4 (-c, +ac, <2)	DUST - Home 5 (+c, +ac, <2)	DUST – Office 1 (+c, +ac, >5) 'A'	DUST – Office 1 (+c, +ac, >5) 'B'	DUST – Office 2 (+c, +ac, <2)	DUST – Office 3 (+c, +ac, <2)
BDE 17	0.047	0.26	0.66	0.11	0.12	0.4	0.26	1.11	0.36
BDE 28 + BDE 33	<0.5	<2	1.73	<0.6	<0.5	1.34	<2	4.21	<2
BDE 47	7.81	21.4	53.6	17.7	18.2	46.6	47.9	210	64.2
BDE 49	0.41	0.84	1.89	0.55	0.56	2.02	1.46	7.52	2.3
BDE 66	0.29	0.7	1.52	0.4	0.49	1.7	1.25	6.2	2.36
BDE 71	<0.03	0.045	0.12	0.031	0.043	0.2	0.11	0.48	0.15
BDE 77	<0.005	<0.02	<0.01	<0.008	<0.008	0.035	<0.05	<0.06	0.063
BDE 85	0.62	1.19	4.56	1.13	2.6	2.47	2.23	13	5.73
BDE 99	10.8	25.1	81.8	19.4	41.3	63	49.4	294	110
BDE 100	0.69	5.05	16.9	4.31	7.77	11.1	9.22	61.2	18.8
BDE 119	<0.1	<0.05	<0.9	<0.08	<0.06	<0.3	0.083	0.69	<0.2
BDE 126	<0.02	<0.03	<0.04	<0.01	<0.04	<0.05	<0.04	<0.1	<0.01
BDE 138 + BDE 166	0.29	0.78	1.44	0.32	0.91	1.49	0.61	3.05	2.73
BDE 153	3.21	7.31	14	2.91	7.41	19.3	6.01	33.8	26.2
BDE 154	1.31	2.95	8.73	1.81	4.59	6.93	3.92	25	9.85
BDE 156	<0.03	<0.04	<0.03	<0.02	<0.03	<0.09	<0.01	<0.09	<0.01
BDE 183	9.49	26.7	28	2.89	10.1	55.8	12.1	17.3	63.8
BDE 184	<0.1	0.4	<2	<0.1	0.17	<1	0.11	0.42	0.33
BDE 191	0.063	0.36	0.15	<0.03	0.097	0.45	0.14	0.16	0.19
BDE 196	2.78	13.6	6.41	1.07	2.77	14.7	4.22	6.66	14.4
BDE 197	4.55	11.7	10.2	1.42	3.79	23.6	5.48	8.58	27.1
BDE 206	2.84	10.1	16.7	5.07	27.9	36	20.9	94.3	78.4
BDE 207	4.68	14.2	13.8	4.02	16.9	36.8	15.9	62	63.4
BDE 209	37	151	329	112	587	512	401	2230	1210
Sum of PBDE congeners									
Excl. LOD values	**86.8**	**294**	**591**	**175**	**733**	**836**	**583**	**3070**	**1700**
Incl. ½ LOD values	**87.3**	**295**	**593**	**176**	**733**	**837**	**583**	**3080**	**1700**
Incl. LOD values	**87.7**	**296**	**594**	**176**	**733**	**837**	**584**	**3080**	**1703**

Table C. 3 Surface wipe results in pg/cm2 of surface

PBDE Congener	Home 1 - television A	Home 1 - television B	Home 1 - stereo	Home 1 - DVD player	Home 1 - refrigerator	Home 2 - television A	Home 2 - television B	Home 2 - stereo	Home 2 - DVD player	Home 2 - refrigerator
BDE 17	<0.07	<0.06	<0.07	<0.04	<0.1	<0.3	<0.03	<0.05	<0.04	<0.2
BDE 28 + BDE 33	<5	<6	<9	<7	19.3	<5	13.8	<4	<6	<6
BDE 47	<10	<9	<10	<10	28	<10	28.7	<9	<10	<10
BDE 49	<0.10	<0.1	<0.1	<0.08	<0.1	<0.4	<0.1	<0.05	<0.1	<0.2
BDE 66	0.085	<0.05	<0.03	<0.04	0.11	<0.4	0.096	<0.04	0.1	<0.7
BDE 71	<0.01	<0.04	<0.08	<0.01	<0.01	<0.4	<0.02	<0.005	0.018	<0.8
BDE 77	<0.06	<0.04	<0.06	<0.09	<0.05	<0.4	<0.08	<0.04	<0.04	<0.2
BDE 85	<0.10	<1	<0.3	<0.2	0.39	<1	<0.2	<0.5	<0.3	<1
BDE 99	<6	<6	<7	<6	<10	<20	<10	<5	<7	<8
BDE 100	<2	<1	<2	<1	<3	<2	<2	<1	<2	<2
BDE 119	<0.5	<0.04	<0.3	<0.06	<0.2	<1	<0.02	<0.4	<0.6	<1
BDE 126	<0.2	<0.5	<0.2	<0.1	<0.2	<1	<0.2	<0.4	<0.2	<1
BDE 138 + BDE 166	<0.08	<0.07	<0.05	<0.09	0.1	55.8	<0.08	<0.1	<0.08	<0.6
BDE 153	<0.6	<0.5	<0.5	<0.4	<1	1250	2.5	<0.4	<1	<1
BDE 154	<0.3	<0.3	<0.4	<0.3	0.66	270	0.76	<0.3	<0.5	<0.5
BDE 156	<0.06	<0.03	<0.02	<0.03	<0.04	<0.6	<0.05	<0.04	<0.04	<0.5
BDE 183	<0.4	<1	<0.3	<0.8	<0.1	14600	50.3	<0.4	26.5	3.4
BDE 184	<0.8	<1	<0.1	<0.2	<0.9	51.5	<0.1	<0.5	<0.8	<2
BDE 191	<0.8	<1	<3	<0.7	<0.5	27.5	<0.7	<0.5	<0.6	<2
BDE 196	<0.2	<0.2	<0.2	<0.7	<0.7	1470	5.8	<0.2	3.6	<0.5
BDE 197	<0.3	<0.2	0.17	<0.6	<0.5	3240	16.5	<0.7	10.3	1
BDE 206	2.3	2.7	2	0.51	0.59	170	2.5	<0.2	5.5	1
BDE 207	2.1	2	1.5	0.33	0.49	1530	12.3	<0.1	11.8	2.5
BDE 209	54.2	62.8	49.3	11.5	15	864	40.1	<4	104	13.3
Sum of PBDE congeners										
Excluding LOD values	**59**	**68**	**53**	**12**	**65**	**23500**	**173**	**0**	**162**	**21**
Incl. 1/2 LOD values	**72**	**82**	**70**	**27**	**73**	**23550**	**180**	**14**	**176**	**40**
Incl. LOD values	**86**	**96**	**87**	**41**	**82**	**23571**	**187**	**28**	**191**	**59**

Appendix D Quality control/Quality assurance

D.1 Inter-laboratory comparison

Table D.1 Results of inter-laboratory comparison of air from Home 1 'A'. Concentrations are in pg/m^3 and normalised differences are expressed as a percentage.

PBDE congeners	NMI		eurofins/ERGO		Norm. Diff.	Norm. Diff.
	without correction for blank	with correction for blank	without correction for blank	with correction for blank	without correction for blank	with correction for blank
BDE 17	1.2	1.2	0.5	0.5	**79%**	**79%**
BDE 28 + BDE 33	43.9	<43.9	42.0	<42	**4%**	**n.c.**
BDE 47	92.3	<92.3	106.4	<106.4	**14.2%**	**n.c.**
BDE 49	1.4	<1.4	1.4	<1.4	**0.2%**	**n.c.**
BDE 66	1.0	<1	0.9	<0.9	**7.6%**	**n.c.**
BDE 71	0.1	0.1	<0.42	<0.42	**n.c.**	**n.c.**
BDE 77	<0.1	<0.1	<0.21	<0.21	**n.c.**	**n.c.**
BDE 85	1.3	<1.3	2.1	<2.1	**52.8%**	**n.c.**
BDE 99	41.6	<41.6	44.0	<44	**5.5%**	**n.c.**
BDE 100	9.3	<9.3	8.0	<8	**15.7%**	**n.c.**
BDE 119	<0.1	<0.1	<0.13	<0.13	**n.c.**	**n.c.**
BDE 126	<0.1	<0.1	<0.53	<0.53	**n.c.**	**n.c.**
BDE 138 + BDE 166	0.2	<0.2	<0.37	<0.37	**n.c.**	**n.c.**
BDE 153	2.4	<2.4	1.5	<1.5	**47.1%**	**n.c.**
BDE 154	1.7	<1.7	1.6	<1.6	**2.6%**	**n.c.**
BDE 156	<0.1	<0.1	<0.44	<0.44	**n.c.**	**n.c.**
BDE 183	0.3	0.3	0.5	0.5	**48.9%**	**44%**
BDE 197	<0.2	<0.2	<0.99	<0.99	**n.c.**	**n.c.**
BDE 207	<0.3	<0.3	<6.86	<6.86	**n.c.**	**n.c.**
BDE 209	<4.2	<4.2	5.9	5.9	**n.c.**	**n.c.**
Sum of PBDE congeners Excluding LOD values	**197**	**1.6**	**215**	**6.9**		
Mean normalised difference					**25%**	**62%**

n.c. not possible to calculate < = not detected

Table D.2 Results of inter-laboratory comparison of dust from Office 1 'A'. Concentrations are in ng/g dust and normalised differences are expressed as a percentage.

PBDE Congener	NMI	eurofins/ERGO	Norm. Diff.
BDE 17	0.4	0.3	**15%**
BDE 28 + BDE 33	1.3	0.9	**34%**
BDE 47	47	49	**4%**
BDE 49	2.0	3.1	**44%**
BDE 66	1.7	1.9	**9%**
BDE 71	0.2	<0.511	**n.c.**
BDE 77	0.04	<0.087	**n.c.**
BDE 85	2.5	4	**54%**
BDE 99	63	64	**1%**
BDE 100	11	9	**18%**
BDE 119	<0.3	<0.611	**n.c.**
BDE 126	<0.05	<0.123	**n.c.**
BDE 138 + BDE 166	1.5	2.0	**30%**
BDE 153	19	15	**22%**
BDE 154	6.9	7.3	**6%**
BDE 156	<0.09	<0.042	**n.c.**
BDE 183	56	55	**1%**
BDE 197	24	26	**11%**
BDE 207	37	70	**62%**
BDE 209	512	626	**20%**
Sum of PBDE congeners Excluding LOD values	**785**	**935**	
Mean normalised difference			**22%**

n.c. not possible to calculate < = not detected

Table D.3 Results of inter-laboratory comparison of surface wipe Home 2 – television 'A'.
Concentrations are in pg/cm^2 and normalised differences are expressed as a percentage.

PBDE Congener	NMI	eurofins/ ERGO	Norm. Diff.
BDE 17	<0.3	<0.2	**n.c.**
BDE 28 + BDE 33	<5	1.3	**n.c.**
BDE 47	<10	6.1	**n.c.**
BDE 49	<0.4	0.6	**n.c.**
BDE 66	<0.4	<0.6	**n.c.**
BDE 71	<0.4	<0.7	**n.c.**
BDE 77	<0.4	<0.3	**n.c.**
BDE 85	<1	<0.5	**n.c.**
BDE 99	<20	15	**n.c.**
BDE 100	<2	2	**n.c.**
BDE 119	<1	<6	**n.c.**
BDE 126	<1	<0.9	**n.c.**
BDE 138 + BDE 166	55.8	59	**5%**
BDE 153	1250	1066	**16%**
BDE 154	270	270	**1%**
BDE 156	<0.6	<1.5	**n.c.**
BDE 183	14600	14071	**4%**
BDE 197	3240	3446	**6%**
BDE 207	1530	3893	**87%**
BDE 209	864	1139	**27%**
Sum of PBDE congeners Excluding LOD values	**21810**	**23969**	
Mean normalised difference			**21%**

n.c. not possible to calculate
< = not detected

D.2 Sampling reproducibility

Sampling reproducibility was assessed for the air, dust and surface wipe samples.

Table D.4 Normalised difference (%) for air samples collected at Home 1. PBDE concentrations in air are expressed as pg/m^3

PBDE Congener	Home 1 'A'	Home 1 'B'	Normalised difference
m^3 sampled	**168**	**192**	
BDE 17	1.2	0.52	**79%**
BDE 28 + BDE 33	<43.9	<5.21	**n.c.**
BDE 47	<92.3	<16.67	**n.c.**
BDE 49	<1.4	<0.42	**n.c.**
BDE 66	<1	<0.22	**n.c.**
BDE 71	0.1	<0.03	**n.c.**
BDE 77	<0.1	<0.03	**n.c.**
BDE 85	<1.3	<0.31	**n.c.**
BDE 99	<41.6	<10.42	**n.c.**
BDE 100	<9.3	<2.08	**n.c.**
BDE 119	<0.1	<0.1	**n.c.**
BDE 126	<0.1	<0.05	**n.c.**
BDE 138 + BDE 166	<0.2	<0.1	**n.c.**
BDE 153	<2.4	<0.52	**n.c.**
BDE 154	<1.7	<0.42	**n.c.**
BDE 156	<0.1	<0.05	**n.c.**
BDE 183	0.3	<0.16	**n.c.**
BDE 184	<0.1	<0.05	**n.c.**
BDE 191	<0.2	<0.03	**n.c.**
BDE 196	<0.2	<0.1	**n.c.**
BDE 197	<0.2	<0.1	**n.c.**
BDE 206	<0.3	<0.36	**n.c.**
BDE 207	<0.3	<0.47	**n.c.**
BDE 209	<4.2	<3.65	**n.c.**
Sum (excl. LOD values)	**1.6**	**0.5**	
Mean normalised difference			**n.c.**

n.c. - not possible to calculate due to non-detect value for one or both samples

Table D.5 Normalised difference (%) for dust samples obtained from Office 1. PBDE concentrations from dust are expressed as pg/ g dust.

	Office 1 - dust 'A'	Office 1 - dust 'B'	Normalised difference
PBDE congeners			
BDE 17	0.4	0.26	**42%**
BDE 28 + BDE 33	1.34	<2	**n.c.**
BDE 47	46.6	47.9	**3%**
BDE 49	2.02	1.46	**32%**
BDE 66	1.7	1.25	**31%**
BDE 71	0.2	0.11	**58%**
BDE 77	0.035	<0.05	**n.c.**
BDE 85	2.47	2.23	**10%**
BDE 99	63	49.4	**24%**
BDE 100	11.1	9.22	**19%**
BDE 119	<0.3	83	**n.c.**
BDE 126	<0.05	<40	**n.c.**
BDE 138 + BDE 166	1.49	0.61	**84%**
BDE 153	19.3	6.01	**105%**
BDE 154	6.93	3.92	**55%**
BDE 156	<0.09	<0.01	**n.c.**
BDE 183	55.8	12.1	**129%**
BDE 184	<1	0.11	**n.c.**
BDE 191	0.45	0.14	**105%**
BDE 196	14.7	4.22	**111%**
BDE 197	23.6	5.48	**125%**
BDE 206	36	20.9	**53%**
BDE 207	36.8	15.9	**79%**
BDE 209	512	401	**24%**
Sum (excl. LOD values)	**836**	**583**	
Mean normalised difference			**61%**

n.c. - not possible to calculate due to non-detect value for one or both samples

< = not detected

Table D.6 Normalised difference (%) for surface wipe samples obtained from Office 1. PBDE concentrations from surface wipes are expressed as pg/ cm^2.

	Home 2 - television 'A'	Home 2 - television 'B'	Normalised difference
PBDE Congener			
BDE 17	<7	<6	**n.c.**
BDE 28 + BDE 33	<500	<600	**n.c.**
BDE 47	<1000	<900	**n.c.**
BDE 49	<10	<10	**n.c.**
BDE 66	8.5	<5	**n.c.**
BDE 71	<1	<4	**n.c.**
BDE 77	<6	<4	**n.c.**
BDE 85	<10	<100	**n.c.**
BDE 99	<600	<600	**n.c.**
BDE 100	<200	<100	**n.c.**
BDE 119	<50	<4	**n.c.**
BDE 126	<20	<50	**n.c.**
BDE 138 + BDE 166	<8	<7	**n.c.**
BDE 153	<60	<50	**n.c.**
BDE 154	<30	<30	**n.c.**
BDE 156	<6	<3	**n.c.**
BDE 183	<40	<100	**n.c.**
BDE 184	<80	<100	**n.c.**
BDE 191	<80	<100	**n.c.**
BDE 196	<20	<20	**n.c.**
BDE 197	<30	<20	**n.c.**
BDE 206	230	270	**16%**
BDE 207	210	200	**5%**
BDE 209	5420	6280	**15%**
Mean normalised difference			**12%**

n.c. - not possible to calculate due to non-detect value for one or both samples
< = not detected

D.3 Field blanks

The results of the analysis of field blanks for filters and laboratory blanks for XAD-2 are presented here in picograms.

Table D.7 Results of analysis of blank filter papers and XAD-2 resin (pg)

	Home 3 Blank Filter Paper	Home 4 Blank Filter Paper	Resin Blank 1 XAD-2 Resin	Resin Blank 2 XAD-2 Resin
PBDE congener				
BDE 17	<30	<20	<30	26
BDE 28 + BDE 33	<500	<500	2320	3000
BDE 47	<1000	<1000	5000	9570
BDE 49	<40	<20	15	110
BDE 66	<80	<50	<10	110
BDE 71	<40	<20	<10	<10
BDE 77	<40	<20	<10	<10
BDE 85	<20	<20	<50	290
BDE 99	<700	<600	<3000	8630
BDE 100	<200	<200	<600	1760
BDE 119	<70	<60	<10	<10
BDE 126	<70	<60	<10	<10
BDE 138 + BDE 166	<60	<100	<10	66
BDE 153	<60	<50	<100	740
BDE 154	<50	<50	<100	590
BDE 156	<50	<50	<20	<20
BDE 183	<200	<80	<30	<30
BDE 184	<70	<80	<30	<30
BDE 191	<70	<80	<30	<30
BDE 196	<20	<40	<30	<30
BDE 197	<30	<40	<30	<30
BDE 206	<40	<40	<100	<50
BDE 207	65	59	<100	<50
BDE 209	<200	630	<2000	<700
Sum of PBDE congeners Excluding LOD values	**65**	**690**	**7340**	**24900**

< = not detected

Appendix E filter and XAD-2 concentrations

Presented here are the results of the separate analysis of the filter and XAD-2 for Office 2 and 3. These results are presented as picograms and expansion of the interpretation of these results is beyond the scope of this study.

Table E. 1 Results of filter and XAD-2 PBDE concentrations (pg) for Office 2 and 3.

	Office 2 Filter	Office 2 XAD-2 Resin	Office 3 Filter	Office 3 XAD-2 Resin
PBDE Congener				
BDE 17	34	6810	<10	<100
BDE 28 + BDE 33	<300	15200	<200	<1760
BDE 47	7450	110000	<1000	<7630
BDE 49	210	5590	<40	<300
BDE 66	190	2400	33	<160
BDE 71	17	460	<9	47
BDE 77	<5	<20	<5	<10
BDE 85	250	<230	<40	<100
BDE 99	6570	<13000	<1000	<2830
BDE 100	1510	<5080	<300	<720
BDE 119	<40	<100	<20	<30
BDE 126	<20	<7	<10	<7
BDE 138 + BDE 166	<40	<20	<20	<10
BDE 153	540	<200	280	<200
BDE 154	410	<250	<100	<100
BDE 156	<7	<6	<10	<9
BDE 183	290	<20	550	<20
BDE 184	<30	<10	<40	<20
BDE 191	<10	<5	<10	<8
BDE 196	<20	<20	<30	<30
BDE 197	<50	<20	<80	<30
BDE 206	<100	<40	230	<50
BDE 207	<100	<40	<300	<50
BDE 209	1710	<700	4390	<600
Sum of PBDE congeners Excluding LOD values	19200	140460	5480	47

< = not detected

Appendix F international data

F.1 Air

United Kingdom

In England, Harrad et al (2004) determined the concentration of ΣPBDEs (-47, -99, -100, -153 and -154) in air from a range of offices (n=6) and indoor home microenvironments (n=17). The median ΣPBDE concentrations in outdoor and indoor air were 18 and 762 pg/m^3, respectively. The median daily human exposure to ΣPBDEs via inhalation was 6.9 ng/person and 90.5 ng/person via diet but the relative significance of these pathways may vary considerably between individuals. The median concentrations in indoor air were higher in workplace (1082 pg/m^3) than in domestic environments (128 pg/m^3) and substantial differences in air from different rooms in the same office building were found. There was a significant positive correlation ($p<0.001$) between PBDE concentrations and both the number of electrical appliances and polyurethane foam-containing chairs (excluding the only mechanically ventilated room) in the room.

Lee et al (2004) sampled two rural/semi-rural sites in England and one remote site on the west coast of Ireland in 2001 and 2000, respectively. Concentrations of ΣPBDEs (BDEs- 17, -28, -32, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -119, -138, -153, -154, -166, -181 and -190) at Mace Head in Ireland ranged from 0.22 – 5.0 pg/m^3 with a mean of 2.6 pg/m^3. The concentration of ΣPBDEs at Hazelrigg in England ranged from 2.8-37 pg/m^3 with a mean of 12 pg/m^3 and at Chilton, southwest England ranged from 3.4-33 pg/m^3 with a mean of 11 pg/m^3. The average mixture of PBDEs in air was similar to that of commercial penta-BDE products. The authors state that movement of air over local/regional sources influenced concentrations of PBDEs at all sites. In summer, concentrations of PBDEs were strongly influenced by temperature, indicating that air-surface exchange processes play an important role and as temperatures decreased, PBDE concentrations increased. Factors identified as influencing atmospheric concentrations of PBDEs were: advection from local/regional sources; long range atmospheric transport; temperature dependent air-surface exchange; and diffuse combustion sources. Other factors suggested include: supply from urban areas, deposition and degradation processes.

North America

Butt et al (2004a) collected organic films from indoor and outdoor window surfaces in Toronto, Ontario, Canada. The samples were collected in 2001 at 9 outdoor sites and 5 indoor sites. Films were sampled by scrubbing window surfaces with Kimwipes. For outdoor surfaces, the urban ΣPBDE concentrations were ~10 times greater than the rural concentrations. For indoor surfaces, urban ΣPBDE concentrations were 3 times greater than rural concentrations. ΣPBDEs included BDE- 1, -2, -3, -10, -7, -8/11, -10, -12, -13, -15, -17, -25, -28/33, -30, -32, -35, -37, -47, -49, -66, -71, -77, -75, -85, -99, -100, -105, -116, -119, -126, -138/166, -140, -153, -154, -155, -181, -183, -190, -206, -207, -208 and -209. Indoor films were 1.5 -20 times greater than outdoor films. The congener profile was dominated by BDE-209 (51.1%) followed by -99, -47 and -183. The gas-phase air concentrations were back-calculated from film concentrations using the film-air partition coefficient (K_{FA}). The mean calculated ΣPBDE air concentrations were 4.8 pg/m^3 for outdoor urban sites and 42.1 pg/m^3 for indoor urban sites. The authors state that organic films have been shown to form on impervious building surfaces in both urban and rural areas. The authors state the composition

of the organic film is representative of ambient air quality since the film is hypothesised to form through the condensation of primary gas-phase species and secondary organic aerosols. The authors conclude that organic carbon reservoir in window films can be used as a time-integrated passive sampler for gas-phase air concentrations.

Strandberg et al (2001) sampled and analysed air from one urban, two rural and one remote outdoor sites near the Great Lakes in 1997-1999. This study used high volume air samplers. ΣPBDEs (including BDEs-47, -99, -100, -153, -154, -190 and -209) ranged from 4.4 to 21 pg/m^3 (mean 5 pg/m^3) at the rural and remote sites and from 33-77 pg/m^3 (mean 52 pg/m^3) at the urban site for the years 1997-1999.

In Canada, Shoeib et al (2004) used high volume samplers to collect indoor and outdoor air. The ratios of ΣPBDE concentration between indoor and outdoor air was 15. Ten indoor and three outdoor samples were collected. The indoor air ΣPBDE concentrations (sum of 17, 28/33, 47, 85, 99, 100, 153, 154, 183.) ranged from 76-2 088 pg/m^3 for four house samples and 358-410 pg/m^3 for two laboratories. BDE-47 was the most abundant congener representing approximately 46% of the total PBDE concentration. The authors state that the composition of indoor air resembled that of the penta-BDE commercial product Bromkal 70-5E.

Wilford et al (2004) sampled 74 randomly selected homes in Ottawa, Canada along with seven outdoor sites during 2002-03. This study used passive air samplers. The indoor air concentrations of ΣPBDEs (BDEs – 17, -28, -47, -66, -71, -85, -99, -100, -153 and -154) (log normally distributed) had a geometric mean of 120 pg/m^3 and a median 100 pg/m^3. The ΣPBDE concentration (BDEs – 17, -28, 47, -99 and -100) in outdoor samples ranged from <0.1 to 4.4 pg/m^3. The maximum daily human exposure via the inhalation pathway based on median PBDE levels found in this survey was estimated to be 1.9 ng/day (female) and 2.0 ng/day (male) representing 4.1% and 4.4% of overall daily intakes. Indoor PBDE concentrations ranged from 2 to 3600 pg/m^3 with PBDEs detected in all samples. Several outdoor samples were below the limit of detection and detectable values ranged between 1.5 to 4.4 pg/m^3, about 50 times lower than the average indoor concentrations. The authors state there was a marked indoor-outdoor gradient however no correlation was found between indoor air concentrations of PBDEs and house age or percentage of the home carpeted.

F.2 Dust

Household environments

The concentrations of PBDEs have been measured in household and occupational dust as an indication of possible human exposure to these chemicals. PBDEs were detected in all household dust samples from the US, Germany, the UK and Australia (Stapleton et al 2005; Rudel et al 2003; Knoth et al 2003; Sjodin et al 2004). Occupational samples have demonstrated varying results dependant on the workplace and industry where the samples were collected.

In the US, the median concentrations of BDE-47, -99, -100 and -209 from 17 homes collected in 2004 were 644, 676, 119 and 1 350 ng/g dust, respectively (Stapleton et al 2005). In this study, PBDEs were detected in every house dust sample collected and the ΣPBDE concentration (Σ22 congeners – BDEs – 17, -28, -47, -66, -85, -71, -99, -100, -138, -153,

-154, -156, -183, 184, -190, -191, -196, -197, -206, -207, -208 and -209) ranged from 780-30 100 ng/g dry mass. The authors state the concentrations in dust were almost an order of magnitude higher in US homes relative to homes in the European Union, similar to the trend in breast milk, blood and fish. The congener profile of the dust was dominated by BDE-209 with contribution from BDE-47, -99, -183, -196 and -197. A significant inverse relationship between the area of each home and the contribution of BDE 209 to the total PBDE concentration was found.

In Germany, the concentration of PBDEs from 40 homes in 2001-2003 was lower than in the US. The authors report some large variation in results caused by a small number of values with a mean many times greater than the median. In this study the median for BDE-47, -99, -100 and -209 was 17.1, 23.9, 4.2 and 265 ng/g dust, respectively (Knoth et al 2003).

Sjodin et al (2004) analysed the levels of PBDEs in household dust from 10 homes each from the US, UK, Germany and Australia. For the US the median results for BDE-47, -99, -100 and -209 were 230, 880, 150 and 2 000 ng/g dust, respectively. These results were in agreement with those by Stapleton et al (2005). For Germany, the median results for BDE-47, -99, -100 and -209 were <14, 10, <6 and 60 ng/g dust, respectively which are lower than the concentrations found by Knoth et al (2003). For the UK the median results for BDE-47, -99, -100 and -209 were 22, 28, 4 and 10 205 ng/g dust, respectively. For Australia, the median results for BDE-47, -99, -100 and -209 were 60, 106, 18 and 732 ng/g dust, respectively. The British and Australian results were lower than those found for the US but higher than those found for Germany except for the concentration of BDE-209 in the UK

Occupational environments

Occupational exposure has been assessed by determining the concentrations of PBDEs in dust from workplace settings. The results of these studies consistently find PBDE concentrations in occupational dust to be higher than concentrations in indoor household dust, with congener profiles varying with regard to the type of workplace, that is, office or factory where the dust was collected.

Leonards et al (2001) analysed office dust from 8 countries (Austria, Denmark, Finland, Germany, Italy, Netherlands, Sweden, UK) in 2000. PBDEs were found in all samples with BDE-209 dominant followed by BDE – 47 and – 99 or vice versa depending on the sample. The highest concentrations of PBDEs were from parliament buildings in Italy followed by Finland, The Netherlands and Sweden while the lowest concentrations found in dust were from buildings of internet providers in The Netherlands. The concentrations of BDE- 47, -99, -100, - 153 and -209 ranged from 10-180, 10-170, 2.5-36, 6.1-59 and 260-6 900 ng/g dust, respectively.

A thorough review of the literature failed to find any other studies of office dust and PBDEs.

F.3 Surface wipes

Schecter et al (2005) analysed surface wipes from computers (n=2) and monitors (n=2). The ΣPBDE concentration (sum of 17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183 and 209) ranged from 0.77 to 15.4 ng/cm^2. The lowest value was from a monitor at 0.77 ng/cm^2 and the highest was from a computer at 15.4 ng/cm^2.

The only other reported study of surface wipes for PBDE concentrations was by Butt et al (2004a). This involved the collection of organic films from indoor and outdoor window surfaces. These results were used to calculate the concentration of PBDEs in air as opposed to on surfaces as was done in the current study and by Schecter et al (2005).