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POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN INDOOR AND OUTDOOR ENVIRONMENTS

by

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) have become ubiquitous contaminants found in humans (i.e. breast milk, adipose tissue, placenta and serum), animals (i.e. fish consuming birds and marine mammals), and various outdoor (i.e. air, soil, sediment and precipitation) and indoor environments especially homes, cars and workplaces all over the world. These chemicals are global pollutants of concern as they are persistent, can bioaccumulate and biomagnify and have the potential for long-range atmospheric transport. PBDEs are also toxicants of particular significance to human health since they affect thyroid hormones, endocrine systems and neurobehavioural development as well as possibly causing cancer. The overall hypothesis tested in this study is that the use of PBDEs in consumer goods and materials is leading to contamination of indoor environments at levels that may be detrimental to human health. The main aims of this thesis were to investigate concentrations of PBDEs in a broad range of home and workplace outdoor/indoor environments in Thailand and the U.K. as well as to characterize the spatial and temporal variations in PBDE concentrations in indoor dust sampled from Birmingham, U.K.

A GC-MS using electron ionization (EI) was employed for the separation and quantification of tri- to hexa-BDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154; Σ_{10}PBDEs) in various samples including outdoor and indoor air as well as house, workplace and car dust, while a GC-ECNI/MS was used for the separation and determination of hepta- to deca-BDEs (BDEs 181, 183, 184, 191, 196, 197, 203, 206, 207, 208 and 209), DBDPE and BB-209 in workplace dust. PBDEs were detected in all air and dust samples. The PBDE congener profile in both outdoor and indoor air samples from Thai e-waste storage facilities and homes was dominated by BDE-47 and 99, whilst the predominant BFRs in all dust samples from Thai e-waste storage facilities were BDE-209, BDE-208, BDE-207, BDE-206, BDE-197, BDE-183, BDE-99, BDE-47 and DBDPE. Furthermore, BDEs 99 and 47 were the most abundant congeners in all dust samples from Thai houses and cars and UK homes. Examinations of linear correlations among concentrations in dust from Thai e-waste storage plants of Σ_{10}PBDEs (equates to Penta-BDE), BDE-183, BDE-209, DBDPE and BB-209 suggested a significant and positive correlation between levels of BDE-209 and DBDPE ($r^2 = 0.554$, $p < 0.001$), but no other correlations. A t-test analysis indicated that Σ_{10}PBDE concentrations in dust samples from Thai residences were significantly greater than those from Thai cars ($p = 0.001$).

Additionally, dust levels of all PBDE congeners studied, except for BDE-28, were significantly higher in Thai homes than in Thai automobiles (p = 0.000-0.004). Principal Component Analysis (PCA) demonstrated no differences in PBDE congener patterns between Thai house and vehicle dust, but revealed some subtle differences in the congener pattern between house dust samples in Thailand and the UK.

Occupational and non-occupational exposure to BDE-99 and BDE-209 via dust ingestion and air inhalation was calculated using dust and air concentrations obtained from this study. Under realistic high-end scenarios of occupational exposure to BDE-99 via dust ingestion (0.56-1.69 ng/kg bw/day), workers in Thai e-waste storage facilities were exposed above a recently-published Health Based Limit Value for this congener (0.23–0.30 ng/kg bw/day). In contrast, all estimated exposures of Thai workers to BDE-209 via dust ingestion (0.06-47 ng/kg bw/day) were below the U.S. EPA’s reference dose (RfD) of daily oral exposure to this congener (7 μg/kg bw/day). For non-occupational exposure, exposure estimates of Thai adults for BDE-99 via air inhalation (0.001-0.005 ng/kg bw/day) and dust ingestion (0.0001-0.01 ng/kg bw/day) were well within a health-based limit value proposed by Netherlands researchers (0.23–0.30 ng/kg bw/day). For both male and female Thai children aged 2 years, low-end (0.0017-0.0019 ng/kg bw/day) and “typical” BDE-99 exposure estimates (0.015-0.017 ng/kg bw/day) involving dust ingestion did not exceed the proposed HBLV. Conversely, under a high-end exposure scenario, the exposure to BDE-99 of such Thai children via dust ingestion (0.22-0.25 ng/kg bw/day) is either very close to or in exceedance of the HBLV.

The within-room spatial variation observed in this study suggested that PBDE concentrations in most of the areas monitored within the same rooms were not statistically significantly different (p > 0.05). Interestingly, highly elevated levels of PBDEs were detected in areas located close to the potential PBDE sources. The results of the within-house spatial variability study indicated that concentrations of PBDEs in the majority of rooms within the same houses were not statistically significantly different between rooms (p > 0.05). Nevertheless, a room containing an old carpeted floor displayed higher PBDE concentrations than a room in the same house containing a new bare wooden floor. Within-room temporal variations monitored in this study result mainly from room-specific factors (particularly changes in room contents over time) rather than building-specific factors, seasonal variation and environmental conditions of the room investigated like temperature, humidity, air flow and ventilation rates. In general, PBDE concentrations in summer (June to August) and autumn (September to November) exceed those observed in winter (December to February) and spring (March to May), although the seasonal differences for Σ_{10}PBDEs, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 in almost all of the studied areas were not statistically significant ($p>0.05$).

Possible dilution of PBDE levels in dust with increasing dust loadings has been identified in a small number of rooms in which temporal variation in PBDE concentrations in dust were studied. This is manifested by a significant negative linear correlation between log PBDE concentration and log dust loading (g dust per m^2 floor surface).

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2. Muenhor, D., Harrad, S., Ali, N. and Covaci, A. 2010. Brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand. *Environment International*, 36: 690-8.

ABBREVIATIONS

ABS	Acrylonitrile butadiene-styrene
ANOVA	Analysis of variance
ASE	Accelerated solvent extraction
ATSDR	Agency for Toxic Substances and Disease Registry
BB-209	Decabromobiphenyl
BDE-209	Decabromodiphenyl ether
BFRs	Brominated flame retardants
BMI	Body mass index
Bp	Boiling point
Br	Bromine
BSEF	Bromine Science and Environmental Forum
Bw	Body weight
CEPA	Canadian Environmental Protection Act
CH_2Cl_2	Dichloromethane also known as methylene chloride
CS_2	Carbon disulfide
DBDPE	Decabromodiphenylethane
DED	Daily exposure dose
DL	Detection limit
Dw	Dry weight
E-waste	Electronic waste
EC	European Commission
ECD	Electron capture detection
ECNI	Electron capture negative ionization
EDCs	Endocrine-disrupting compounds
EI	Electron ionization
EI^+	Electron impact ionisation
EU	European Union
FSH	Follicle stimulating hormone
Fw	Fresh weight
GC	Gas chromatography
GC-CIMS	Gas chromatography-chemical ionization mass spectrometry
GC-ECD	Gas chromatography-electron capture detection
GC-MS	Gas chromatography-mass spectrometry
GFF	Glass fibre filter
GMF	Glass microfiber filter
GPC	Gel permeation chromatography
HBLV	Health-based limit value
Heptacosa	Perfluorotributylamine ($C_{12}F_{27}N$; PFTBA)

HPLC	High pressure liquid chromatography
HRGC	High resolution gas chromatography
HRMS	High-resolution mass spectrometry
IPCS	International Programme on Chemical Safety
IRIS	Integrated Risk Information System
IS	Internal standard
K_{OA}	Octanol–air partition coefficients
K_{OW}	Octanol–water partition coefficients
KS	Kolmogorov-Smirnov
LH	Luteinizing hormone
LOEL	Lowest Observed Effect Level
LRAT	Long range atmospheric transport
LRATP	Long Range Atmospheric Transport Protocol
LRMS	Low-resolution mass spectrometry
Lw	Lipid weight
M/Z	Mass to charge ratio
MAE	Microwave-assisted extraction
MRL	Method reporting limit
MS	Mass spectrometry
MSW	Municipal solid waste
MW	Molecular Weight
NIST	National Institute of Standards and Technology
NOAEL	No-observed-adverse-effects-level
OC	Organic carbon
LD-50	Lethal Dose, 50%
PASs	Passive air samplers
PBDD	Polybrominated dibenzodioxins
PBDD/Fs	Polybrominated dibenzo-*p*-dioxins/dibenzofurans
PBDEs	Polybrominated diphenyl ethers
PBDFs	Polybrominated dibenzofurans
PC	Personal computer
PCA	Principal component analysis
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxin/furans
$PM_{2.5}$	Particles with diameter smaller than 2.5 µm
POPs	Persistent organic pollutants
PUF	Polyurethane foam
QA/QC	Quality assurance/ quality control
RDS	Recovery determination standard

RfD	Reference dose
RRF	Relative response factor
RRT	Relative retention time
RSD	Relative standard deviation
S/N	Signal to noise ratio
SD	Standard deviation
SES	Sampling efficiency standard
SFE	Supercritical fluid extraction
SHBG	Sex hormone binding globulin
SIM	Selected ion monitoring
SRM	Standard reference material
T4	Thyroxine
TBBP-A	Tetrabromobisphenol A
TSP	Total suspended particles
TV	Television
UK	United Kingdom
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
US	United States
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VWM	Volume weighted mean
WHO	World Health Organization
Ww	Wet weight

CHAPTER 1

Introduction

1.1 Background

At present, because of rapidly increasing industrialization and globalization, numerous countries are encountering serious environmental pollution problems such as air, water and soil pollution. Some of the critical environmental problems are caused by persistent organic pollutants (POPs), which have been defined as "chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment (United Nations Environment Programme (UNEP), 2006; European Commission, 2006)". Examples of POPs, as defined under the terms of the UNEP Stockholm Convention and the United Nations Economic Commission for Europe (UNECE) Long Range Atmospheric Transport Protocol (LRATP), include: polybrominated diphenyl ethers (PBDEs), aldrin, dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) (Stockholm Convention on POPs, 2009a; Harrad, 2001). PBDEs have been labelled the "next generation of POPs" (Blake, 2005) or "emerging" chemicals (Schecter *et al.*, 2005a; Tanabe, 2004; Palm *et al.*, 2002), and are suspected to cause various detrimental effects on ecosystems and human health.

PBDEs are one of the most widely used brominated flame retardants (BFRs) which have attracted tremendous interest during the recent decade (Covaci *et al.*, 2003). They are added to several polymers used in electronic circuitry, plastics, textiles, and other products to prevent the spread of fires (WHO/IPCS, 1994, 1997). PBDEs have been used extensively as three formulations: decabromodiphenylether [deca-BDE]; octabromodiphenylether [octa-BDE]; and pentabromodiphenylether [penta-BDE] (La Guardia *et al.*, 2006).

As a result of their physicochemical properties, PBDEs are global contaminants of concern because they are persistent, and can bioaccumulate and biomagnify; thus compounding their toxicity (Wu *et al.*, 2008; Voorspoels *et al.*, 2007a; Burreau *et al.*, 2006; Shen *et al.*, 2006; Hites, 2004; Law *et al.*, 2003; Darnerud, 2003; de Wit, 2002; Darnerud *et al.*, 2001).

Additionally, PBDEs have the potential for long-range atmospheric transport (LRAT), deposition and revolatilization (a process known as the “grasshopper effect”) that effects their transport from their emission sources to remote areas like the polar regions (Hale *et al*., 2008, 2003; Wang *et al*., 2007; Cheng *et al.* 2007, de Wit *et al*., 2006; Wurl *et al*., 2006; Gouin *et al*., 2004). These properties can result in their accumulation and magnification in humans, wildlife, and ecosystems. Hence, there is an enormous number of studies world-wide providing strong evidence of increasing PBDE contamination of people, biotic and abiotic environments (Garcia-Jares *et al*., 2009; Toms *et al*., 2009a; Sepulveda *et al*., 2010; Law *et al*., 2008, 2006; Hale *et al*., 2006; 2003; Hites, 2004; Watanabe and Sakai, 2003).

PBDEs are also toxicants of particular significance to human health because they affect endocrine systems, thyroid hormones and neurobehavioural development as well as possibly causing cancer (ATSDR, 2004; Darnerud, 2003; Branchi *et al*., 2003; McDonald, 2002). Netherlands researchers have derived a preliminary health-based limit value (HBLV) of 0.23-0.30 ng/kg bw/day for BDE-99 (Bakker *et al*., 2008), and the U.S. EPA’s Integrated Risk Information System (IRIS) Toxicological Evaluation recommends a reference dose (RfD) of daily oral exposure to BDE-209 of 7 µg/kg bw/day that is considered to be without appreciable risk of detrimental effects (U.S. EPA, 2008). Recently, PBDE pollution has become the subject of much concern and public outcry. Furthermore, an expanding number of health concerns relating to PBDEs and PBDE contamination provides evidence that the PBDE pollution problem requires urgent attention (Harrad, 2010; Allsopp *et al*., 2001).

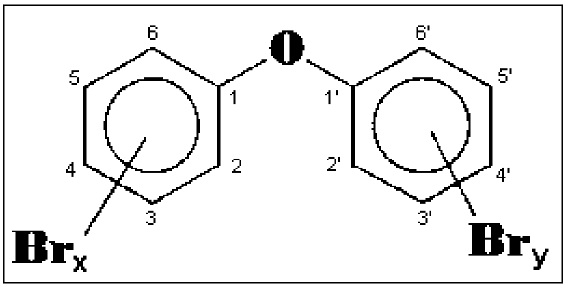
1.2 Polybrominated diphenyl ethers (PBDEs)

1.2.1 Production and applications of PBDEs

PBDEs are a group of brominated compounds consisting of 209 congeners (Hui-Ying *et al.*, 2007; Gouin and Harner, 2003; Wania and Dugani, 2003). These congeners are different in both number and position of bromine atoms on the molecule (Figure 1.1). The PBDE congeners are also classified into 10 homologue groups according to the degree of bromination, ranging from monobromodiphenyl ether (1 Br substituent) to decabromodiphenyl ether (10 Br substituents). Congeners containing the same number of bromine atoms are called as homologues (ATSDR, 2004; de Wit, 2002). The substitution pattern of the PBDE congeners involved in this study is present in Table 1.1.

PBDEs do not occur naturally in the environment, but they are commercially produced by bromination of diphenyl ether in the presence of a Friedel-Craft catalyst such as $AlCl_3$ in a solvent such as dibromomethane (Alaee *et al*., 2003; WHO/IPCS. 1994).

Figure 1.1 Chemical structure of PBDEs



Note: 2, 2', 3, 3', 4, 4', 5, 5', 6 & 6' = Ten open positions of bromine atoms on two phenyl (benzene) rings

Source: Miller, 2009

Table 1.1 Substitution pattern of PBDE congeners involved in this study

BDE #	Bromine substitution	BDE #	Bromine substitution
17	2,2',4-tri BDE	183	2,2',3,4,4',5',6-hepta BDE
28	2,4,4'-tri BDE	184	2,2',3,4,4',6,6'-hepta BDE
47	2,2',4,4'-tetra BDE	191	2,3,3',4,4',5',6-hepta BDE
49	2,2',4,5'-tetra BDE	196	2,2',3,3',4,4',5,6'-octa BDE
66	2,3',4,4'-tetra BDE	197	2,2',3,3',4,4',6,6'-octa BDE
85	2,2',3,4,4'-penta BDE	203	2,2',3,4,4',5,5',6-octa BDE
99	2,2',4,4',5-penta BDE	206	2,2',3,3',4,4',5,5',6-nona BDE
100	2,2',4,4',6-penta BDE	207	2,2',3,3',4,4',5,6,6'-nona BDE
153	2,2',4,4',5,5'-hexa BDE	208	2,2',3,3',4,5,5',6,6'-nona BDE
154	2,2',4,4',5,6'-hexa BDE	209	2,2',3,3',4,4',5,5',6,6'-deca BDE
181	2,2',3,4,4',5,6-hepta BDE		

PBDEs are one of the most widely used brominated flame or fire retardants (BFRs) added to diverse polymers used in a large variety of consumer and industrial products such as electronic and electrical devices, textiles, furniture and plastics to prevent the spread of fires or delay the time of flashover (WHO/IPCS, 1994, 1997). When heated, they release bromine atoms (Br) which displace the oxygen needed for a fire to burn, generating a very thin protective layer of bromine gas on the surface of the treated product which restricts access of the fire to fuel sources (U.S. EPA, 2005). The three most extensively produced and commercially used PBDE formulations are decabromodiphenylether [deca-BDE]; octabromodiphenylether [octa-BDE]; and pentabromodiphenylether [penta-BDE] (La Guardia *et al*., 2006; de Boer and Cofino, 2002). The Bromine Science Environmental Forum (BSEF) estimated that the deca-BDE is the most widely used, accounting for approximately 83% of the total PBDE production worldwide (Table 1.2).

Table 1.2 Global use of PBDE products in 2001 (tonnes)

Product	**Americas**	**Europe**	**Asia**	**Rest of the World**	**Total**
Deca-BDE	24,500	7,600	23,000	1,050	56,150
Octa- BDE	1,500	610	1,500	180	3,790
Penta- BDE	7,100	150	150	100	7,500
Total	33,100	8,360	24,650	1,330	67,440

Source: BSEF, 2009.

Deca-BDE formulation is a white powder, which contains 83% bromine by weight, primarily comprises BDE-209 (97-98%), with a minor quantity of nona-BDEs (0.3-3%) (Alaee *et al*., 2003). It is mixed principally with polymers such as polystyrene, polyester resins, polycarbonates, polyvinyl chloride, polyolefins, polyamindes, acrylonitrile butadiene-styrene (ABS) and rubber, which are used in upholstery textiles and denser plastics like high impact polystyrene intended for electrical and electronic appliances especially TV sets (Gevao *et al.*, 2006a; Inoue *et al*., 2006; Alaee *et al*., 2003).

Penta-BDE is a viscous liquid, with 70% bromine content by weight. It contains 44-45% penta-BDEs (mostly BDE-99 and to a lesser extent BDE-100), 41-42% tetra-BDEs (chiefly BDE-47) and 6-7% hexa-BDEs (BDE-153 and -154) (Alaee *et al*., 2003). The penta-product is applied predominantly to polyurethane foam (PUF) in seat foam, other upholstered furniture, rigid insulation, carpet underlay and bedding (Gevao *et al.*, 2006a; Gearhart and Posselt, 2006; Morland *et al*., 2005). It is also used in epoxy and phenol resins, polyesters, and textiles (WHO/IPCS, 1994).

Octa-BDE is a white powder constituting 79% bromine. The product composition varies among batches because the degree of bromination is dependent on stoichiometry or reaction kinetics (Alaee *et al*., 2003). It consists mainly of BDE-183, contributing > 40% and four octa-BDEs, constituting > 30% of the product (La Guardia *et al*., 2006). The octa-formulation is the least extensively used of the three PBDE formulations and primarily used in high-impact plastics and ABS resins used in plastic housing for electronic items like fax machines and computers, telephones and kitchen devices (Gevao *et al.*, 2006a; Gearhart and Posselt, 2006; Inoue *et al*., 2006; Alaee *et al*., 2003).

Table 1.3 provides examples of applications of the three principal commercial PBDE formulations. The applications of these compounds relating to electrical and electronic equipments are the use of octa-BDE in ABS plastic parts, and the use of deca-BDE in most other types of plastics mainly added to the outer housings/casings of consumer electronics in particular TVs and computers (Directorate-General Environment, 2005; Choi *et al*., 2009; MBH and MDEP, 2005). Nowadays, due to the growing number of both human health and environmental concerns associated with PBDEs, the penta- and octa-BDE formulations have been banned in the European Union (EU) and in some US states from 2004; while deca-BDE was severely restricted within the EU in July 2008. (Directorate-General Environment, 2005; U.S. EPA, 2006; Vonderheide *et al*., 2008; Kemmlein *et al*., 2009; Kierkegaard *et al*., 2009). Moreover, the penta- and octa-BDE products were listed under the Stockholm Convention on POPs in May 2009 (Stockholm Convention on POPs, 2009b). A brief outline of the history of PBDEs is given in Table 1.4.

Table 1.3 Applications of the three commercial PBDE mixtures

PBDEs	Products[a]	%[b]
Deca	Hard plastics (casings of TV/computer) & backings to textiles (curtains & carpets)	83
Penta	Polyurethane foam (chairs, cushions of couches & car seats)	11
Octa	Plastics (small electrical devices & circuit boards) & coverings of wiring & cable	6

Source: [a]McDonald, 2005; [b]BSEF, 2009.

Table 1.4 The history of PBDEs

Year	**PBDE relevant events**
1871	Hoffmeister synthesizes BDE-15 by bromination of diphenyl ether using bromine in carbon disulfide (CS_2) (Teclechiel, 2008).
1910	Tetrabromo congener is synthesized by Cook (Vonderheide *et al*., 2008).
1965	The commercial production of PBDEs as flame retardants starts (NIWR, 2005).
1975	Toxicity study on Sprague-Dawley rats demonstrates that deca-BDE is non-toxic (MDEQ, 2007).
1979	Deca-BDE (BDE-209) is found for the first time in abiotic samples (i.e., soil and sludge) and biota collected from areas surrounding a PBDE manufacturing factory in New Jersey, the USA (Alaee, 2003; Teclechiel, 2008).
1981	Br_3-Br_6 PBDE congeners are first detected in pike taken along Viskan River in Sweden (Anderson and Blommkist, 1981).
1987	PBDEs are first identified as global pollutants via their detection in fish consuming birds and marine mammals in the Baltic Sea, North Sea and Arctic Ocean (Jansson *et al*., 1987).
1989	Germany and the Netherlands voluntarily phase out the sale of products containing PBDEs (PPRC, 2005; Thorpe, 2005).
1990	PBDEs are detected in human adipose tissue (Remmers *et al*., 1990).
1995	Deca-BDE is considered possibly carcinogenic to humans by U.S. EPA (U.S. EPA., 1995).
1998	PBDEs are observed in sperm whales, suggesting that they have reached deep Ocean sea waters (de Boer *et al*., 1998).
2000	Study in Sweden suggests that PBDE concentrations in breast milk samples increase remarkably over the years (Noren and Meironyte, 2000).
2001	The estimated global demand for PBDEs is around 67,440 tonnes (BSEF, 2009).
2004	Production of penta- and octa-BDE is banned in the EU and Norway and is voluntarily ceased in North America (La Guardia *et al*., 2006; Thorpe, 2005; PPRC, 2005).
2006	PBDEs (tetra- through deca-BDE) are added to the "List of Toxic Substances" under the Canadian Environmental Protection Act (CEPA) (MacDonald *et al*., 2009). China stops the use of penta-and octa-BDEs in new electrical and electronic goods (MacDonald *et al*., 2009). The use of deca-BDE in textiles, furniture and some electronics is restricted in Sweden (MacDonald *et al*., 2009).

Table 1.4 The history of PBDEs (continued)

Year	PBDE relevant events
2008	Canada prohibits the production of all PBDEs. The use of deca-BDE is forbidden in new Norwegian consumer products, in electrical and electronic equipments within the EU, and in mattresses and furniture in the states of Maine and Washington (USA) (MacDonald *et al*., 2009).
2009	Penta- and octa-BDE listed under the Stockholm Convention on POPs (Stockholm Convention on POPs, 2009b).

1.2.2 Emission sources of PBDEs

PBDEs are added to polymers during polymer manufacture, but are not chemically bonded to the polymers, and so can readily migrate from these materials to the surface (a process known as blooming) (Australian Government, 2007) and then into the surrounding environments throughout the lifecycle of the products (Vonderheide *et al*., 2008; Santillo *et al*., 2001).

PBDEs are released into the environment through a variety of routes such as volatilization or dust formation during the use of treated products in homes, car interiors and workplaces (Harrad and Diamond, 2006), emissions during manufacture of PBDEs or PBDE containing goods, ensuing waste disposal, including processing of waste treatment at incineration plants (ter Schure *et al*., 2004a; Agrell *et al*., 2004), landfills (St-Amand *et al*., 2008; Kim *et al*., 2006; Osako *et al*., 2004) and sewage treatment plants (Hale *et al*., 2008; Song *et al*., 2006; de Boer *et al*., 2003) and spraying of treated wastewater for irrigation (Goel *et al*., 2006) as well as during recycling of products containing PBDEs (Sepulveda *et al*., 2009; Destaillats *et al*., 2008; U.S. EPA, 2006; Streets *et al*., 2006; Morf *et al*., 2005;Hale *et al*., 2002; Sjodin *et al*., 2001). Lately, it has been suggested that debromination of constituents of the deca-BDE formulation may also be a potential source for less brominated PBDEs in the environments (La Guardia *et al*., 2006).

1.2.3 Physicochemical properties, environmental fate, behaviour and distribution of PBDEs

PBDEs are highly hydrophobic compounds with low vapour pressures and high octanol-water partition coefficient (log K_{OW}) values. Vapour pressure and water solubility both decrease with increasing bromine content; in contrast, the log K_{OW} increases (Kierkegaard, 2007;

Teclechiel, 2008). Therefore, with increasing bromine content there is increased propensity for PBDEs to be adsorbed to soil, sediment and air particles, rather than dissolve in water or partition to the vapour phase (Kierkegaard, 2007). Physicochemical properties vary considerably among the various PBDE congeners (Table 1.5), which results in concomitant differences in their environmental fate, behaviour, distribution, exposure pathways, and toxicological effects (Hui-Ying *et al.*, 2007; Kierkegaard, 2007). These properties also determine how PBDEs emitted from their sources will be transported, distributed, degraded and eventually accumulated in several environmental compartments including humans (U.S. EPA, 2005).

Table 1.5 Physicochemical properties of selected PBDE congeners

Congener	**Molar mass^{a}**	**Vapour pressure (Pa)^{a}**	**Melting point (^{o}C)^{a}**	**Water solubility (mol/m^{3})^{a}**	**Henry's law constant (Pa-m^{3}/mole)^{a}**	**Log K_{OW}^{a}**	**Log K_{OA} (25 ^{o}C)^{b}**
BDE-28	407.1	2.19 x 10^{-3}	64–64.5	1.72 x 10^{-4}	5.1	5.98	9.5
BDE-47	485.82	1.87 x 10^{-4}	83.5–84.5	3.09 x 10^{-5}	1.5	6.55	10.53
BDE-66	485.82	1.22 x 10^{-4}	104–108	3.71 x 10^{-5}	0.5	6.73	10.82
BDE-85	564.75	9.87 x 10^{-6}	119–121	1.06 x 10^{-5}	0.11	7.03	11.66
BDE-99	564.75	1.76 x 10^{-5}	90.5–94.5	1.66 x 10^{-5}	0.23	7.13	11.31
BDE-100	564.75	2.87 x 10^{-5}	100–101	7.08 x 10^{-5}	0.069	6.86	11.13
BDE-153	643.62	2.09 x 10^{-6}	160–163	1.35 x 10^{-6}	0.067	7.62	11.82
BDE-154	643.62	3.80 x 10^{-6}	131–132.5	1.35 x 10^{-6}	0.24	7.39	11.92

Source: [a]Tittlemier *et al.*, 2002; [b]Harner and Shoeib, 2002.

PBDEs are of environmental and human health concern as a consequence of their high resistance to degradation processes, high log K_{ow} indicating high hydrophobicity, coupled with their potential for toxicity in both animals and humans. They readily bioaccumulate and have been demonstrated to undergo long range atmospheric transport (LRAT) (Palm *et al.*, 2002; Rahman *et al.*, 2001; Birnbaum and Staskal, 2004). With their high persistence, low vapour pressures, low water solubility and high log K_{ow} values, it is expected that PBDEs entering the environments will tend to bind strongly to the organic fraction of particulate matter, particularly in soils and sediments, with only small amounts partitioning into water and air (Environment Canada, 2004; Hale *et al.*, 2006). Hence, soils and sediments will serve as long-term reservoirs for PBDE emissions (La Guardia *et al.*, 2006).

Generally, lower brominated PBDEs are more bioaccumulative and persistent in the environment than the higher brominated varieties, e.g. penta- and octa-congeners are highly bioaccumulative, while deca-BDE is considered “non-bioavailable” (de Wit, 2002; NIWR, 2005). The lighter PBDE molecules like tetra-, penta- and octa-congeners are of most concern because they are both present in human breast milk and serum and other biota and tend to remain available in the environment, while heavier molecules such as BDE-209 tend to strongly bind to particles that ultimately end up in environmental sinks such as aquatic sediments or terrestrial soils (de Boer *et al*., 2003; de Wit, 2002; Palm *et al*., 2002; Hale *et al*., 2006; La Guardia *et al*., 2006). Volatilization from water surfaces and wet soils is believed to represent a crucial environmental pathway for tetra- to penta-BDEs, whereas this is regarded to be an inconsequential fate process for the higher PBDE molecules, evidenced by their low Henry’s Law constants (NIWR, 2005).

In the atmosphere, the lower brominated congeners such as tetra- to penta- BDEs generally occur in both the gaseous and particulate phases in contrast to higher brominated congeners like BDE-209 which undergo atmospheric transport only in the particulate phase (NIWR, 2005; MBH and MDEP, 2005). The potential for LRAT is high for less brominated PBDEs, whilst for higher brominated congeners the potential is governed by the transport distance of air particles (Gouin *et al*., 2006; Wania and Dugani, 2003).

Biodegradation is not a significant pathway for PBDE transformation, but photodegradation may play a critical role (Rahman *et al*., 2001), reflected by the formation of PBDFs and photolytic debromination of deca-BDE (BDE 209) to penta- through nona-BDEs (Olsman *et al*., 2002) and to hepta- through nona-BDEs (Hagberg *et al*., 2006) when it is dissolved in toluene (solvent) and subjected to artificial ultraviolet (UV) irradiation for four hours. Deca-BDE also photolytically debrominates into lower brominated PBDEs when dissolved in certain solvents or is present in artificial and natural soil, sediment and sand (Soderstrom *et al*., 2004; Eriksson *et al*., 2004). In addition, transformation of PBDEs occurs under thermal stress conditions as they are present in production or recycling processes leading to the formation of PBDD (polybrominated dibenzodioxins) and PBDF (polybrominated dibenzofurans) (Weber and Kuch, 2003; Ebert and Bahadir, 2003).

The estimated degradation half-lives of some PBDE congeners in various environmental matrices are provided in Table 1.6. In diverse environmental media, all PBDE congeners have the longest degradation half-lives in sediment, implying their persistence, low vapour pressures, low water solubility and high log K_{ow} values.

Table 1.6 Estimated degradation half-lives (hrs.) of some PBDE congeners in various environmental matrices

Matrix	**BDE congener #**						
	28	**47**	**99**	**100**	**153**	**183**	**209**
Air	128	256	467	357	1,110	1,540	7,620
Water	1,440	3,600	3,600	3,600	3,600	3,600	3,600
Soil	1,440	3,600	3,600	3,600	3,600	3,600	3,600
Sediment	5,760	14,400	14,400	14,400	14,400	14,400	14,400

Source: Wania and Dugani, 2003.

In spite of the fact that the penta- and octa-BDE formulations have already been banned or have had their use restricted severely by several jurisdictions including the European Union, a wealth of published research has reported relatively high concentrations of PBDEs in indoor environments (indoor air, domestic dust and indoor window surfaces) as PBDEs slowly undergo release from the existing in-use reservoir and enter indoor air and dust (Harrad and Diamond, 2006; U.S. EPA, 2006; ODHS, 2009). The persistence and global distribution of these pollutants has resulted in their accumulation and magnification in ecological food chains and human populations. Thus, there are a large number of studies worldwide providing strong evidence of increasing PBDE concentrations and contamination of wildlife, ecosystems and human beings (Toms *et al*., 2009a; Law *et al*., 2008, 2006, 2003; Wu *et al*., 2008; Voorspoels *et al*., 2007a; Hale *et al*., 2006; Burreau *et al*., 2006; Watanabe and Sakai, 2003).

1.3 Strategies for investigating PBDEs in air and dust

1.3.1 Sampling methods for investigating PBDEs in air and dust

Outdoor and indoor air

The most widely used air samplers for PBDE investigation are high-volume active air samplers, low-volume active air samplers and passive air samplers (i.e., polyurethane foam (PUF) disk and XAD-based passive air samplers (PASs)) (Harrad *et al*., 2010; Shen *et al.,* 2006; Julander *et al*., 2005). Both high- and low-volume active air samplers are equipped with filters (i.e. glass fibre filter (GFF), quartz fibre filter, Tissuquartz filter, Whatman glass microfiber filter and polytetrafluoroethylene filter) or adsorbents (i.e. polyurethane foam (PUF) and XAD-2) to capture particle- and vapour-phase PBDEs respectively (Harrad *et al.*, 2010; Batterman *et al.*, 2009; Johnson-Restrepo and Kannan, 2009; Wilford *et al.*, 2008; St-Amand *et al.*, 2008; Cahill *et al.*, 2007; Allen *et al.*, 2007; Karlsson *et al.*, 2007; Gouin *et al.*, 2006; Wurl *et al.*, 2006; ter Schure *et al.*, 2004b; Hayakawa *et al.*, 2004; Covaci *et al.*, 2003; Rudel *et al.*, 2003; Strandberg *et al.*, 2001).

Active air samplers require an electrical power supply to operate. Therefore, they cannot be deployed in remote areas where electricity is unavailable (Wang *et al.*, 2007). On the other hand, passive air samplers do not require electricity and thus they can be used in a wide variety of sampling areas including remote regions, vehicles, workplaces and homes (Nothstein *et al.*, 2000). High- and low-volume active air samplers underestimate concentrations if the volume of the environment collected is exceeded during collecting e.g. when deploying the samplers for extended periods in confined areas such as cars (Harrad *et al.*, 2010).

Passive air sampling approaches are based upon the diffusion of vapour-phase target chemicals to a sampling medium (Hazrati and Harrad, 2007). Hence, passive air samplers collect principally the gas phase while ineffectively sampling the particle phase (Batterman *et al.*, 2009; Chaemfa *et al.*, 2009; Hazrati and Harrad, 2007). This limitation may hinder their use in investigation of particle-bound pollutants such as BDE-209 (Harrad *et al.*, 2010). It has been reported that indoor air concentrations of tetra- to hexa-BDEs range between about 14%-80% correlated with the particulate phase (Harrad *et al.*, 2004), which may result in the lower concentrations investigated by the particle-bound PBDE underestimated samplers. The benefits of employing passive air samplers are that they are much smaller than high-volume air samplers, more cost-effective, reusable, and simple to deploy as well as being unobtrusive and silent, as no pump or electricity is needed for sampling (Nothstein *et al.*, 2000). These attributes of passive samplers enable their widespread deployment in atmospheric, domestic and workplace environments without disrupting day-to-day activities.

Indoor dust

There is no standardized method for sampling indoor dust. However, collecting dust for PBDEs has been carried out through two approaches: (a) the participant-collected dust sample approach (Cunha *et al.*, 2010; Gevao *et al.*, 2006a; Wilford *et al.*, 2005) and (b) the researcher-collected dust sample approach (Toms *et al.*, 2009b; Allen *et al.*, 2008a; Wu *et al.*, 2007). A U.S. study reported that PBDE concentrations in researcher-collected dust significantly exceeded those in house vacuum bag dust and were not strongly correlated with each other (Allen *et al.*, 2008a). The advantages and drawbacks of these approaches are summarized in Table 1.7.

Table 1.7 Advantages and drawbacks of different approaches for sampling dust

Approach	Advantages	Drawbacks
Participant-collected dust sample	- Cost effective - Enhances donor compliance - Provides an integrated measure of contamination & potential exposure from all sampled rooms	- Vacuum cleaner may be used in environments not frequented by the donor - Variable vacuum cleaner sampling rates - Multiple uses of the same bag - Potential for cross & post contamination - Not reflect accurately varying levels of contamination between different rooms
Researcher-collected dust sample	- Facilitates comparability between samples - Maximizes sampling consistency & also minimizes analyte loss & sample contamination if pre-extracted sample receptacles (i.e., socks/Soxhlet thimbles) placed within the sampling train are used	- Not cost effective - Possibly impeding donor compliance

Source: Harrad *et al*., 2010.

1.3.2 Analytical methods for investigating PBDEs in air and dust

Table 1.8 summarises analytical methods for investigating PBDEs in air and dust. For PBDE analysis, the air and dust samples are first extracted with an organic solvent like toluene, dichloromethane, acetone, petroleum ether, diethyl ether, hexane, hexane/acetone mixtures, acetone/dichloromethane/hexane mixtures, hexane/dichloromethane mixtures, hexane/diethyl ether mixtures, ether/hexane mixtures or other different combinations thereof using Soxhlet extraction, accelerated solvent extraction (ASE), supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) and ultra-sonication. In the extraction step, the PBDEs are isolated from the air and dust and transferred to the organic solvent (Covaci *et al*., 2003). The crude extracts from air and dust samples normally contain lipids which have to be eliminated using sulfuric acid treatment or gel permeation chromatography (GPC) methods. In some cases, the sample extracts require a further clean-up step using some form of column adsorption chromatography to remove other interfering compounds (e.g., other high molecular weight compounds), which can produce serious interferences during the gas chromatographic separation of PBDEs (Covaci *et al*., 2003; de Wit, 2002). Known quantities of each purified extract are often injected in splitless or on-column mode and then analyzed by gas chromatography-mass spectrometry (GC-MS) using electron ionization (EI) or electron capture negative ionization (ECNI), or gas chromatography-electron capture detection (GC-ECD). The benefits and disadvantages of different injection and detection techniques for PBDEs are listed in Table 1.9 and Table 1.10 respectively. Due to their longer retention times, the higher brominated PBDEs including BDE-209 are frequently analysed using a shorter GC column (Ma *et al.*, 2009; Takigami *et al*., 2009a; Wilford *et al*., 2005, 2008; Tan *et al.*, 2007; Karlsson *et al*., 2007; Agrell *et al*., 2004; ter Schure *et al*. 2004b; Gevao *et al.*, 2006c; Sellstrom *et al*., 1998).

Table 1.8 Summary of analytical methods for investigating PBDEs in air and dust

Analytical methods	Reference
Organic solvent used for extraction	
Toluene	Fromme *et al*., 2009; Takigami *et al*., 2009a; Hayakawa *et al*., 2004; Pettersson-Julander *et al*., 2004.
Dichloromethane	Batterman *et al*., 2009; Allen *et al*., 2007; Cahill *et al*., 2007; Gouin *et al*., 2005; Stapleton *et al*., 2005b; Sjodin *et al*., 2001.
Acetone	Takigami *et al*., 2009a; Toms *et al*., 2009a.
Petroleum ether	Allen *et al*., 2007; Harner *et al*., 2006; Pozo *et al*., 2004; Wilford *et al*., 2004.
Diethyl ether	Kierkegaard *et al*., 2009; Covaci *et al*., 2003.
Hexane	Toms *et al*., 2009a; Sjodin *et al*., 2008a; Harrad *et al*., 2008a, 2006; St-Amand *et al*., 2008.
Hexane/acetone mixtures	Agrell *et al*., 2004; ter Schure *et al*., 2004b; Chen *et al*., 2009; Harrad *et al*., 2008a.
Hexane/dichloromethane mixtures	Cunha *et al*., 2010; Johnson-Restrepo and Kannan, 2009; Ma *et al*., 2009; Tan *et al*., 2007; Gevao *et al*., 2006a; Harrad *et al*., 2004.
Hexane/diethyl ether mixtures	Rudel *et al*., 2003; Meeker *et al*., 2009.
Ether/hexane mixtures	Zota *et al*., 2008.
Acetone/dichloromethane/hexane mixtures	Deng *et al*., 2007.
Other different conbinations thereof	Kierkegaard *et al*., 2009; Covaci *et al*., 2003.
Extraction technique	
Soxhlet extraction	Cunha *et al*., 2010; Fromme *et al*., 2009; Meeker *et al*., 2009; Ma *et al*., 2009; Takigami *et al*., 2009b; Chen *et al*., 2009; Zota *et al*., 2008; Choi *et al*., 2008; St-Amand *et al*., 2008; Harrad *et al*., 2008a; Cahill *et al*., 2007; Karlsson *et al*., 2007; Harner *et al*., 2006; Gevao *et al*., 2006b; Wilford *et al*., 2005; Agrell *et al*., 2004; ter Schure *et al*., 2004b; Gouin *et al*., 2002; Rudel *et al*., 2003.
Accelerated solvent extraction (ASE)	Cunha *et al*., 2010; Toms *et al*., 2009a; Fromme *et al*., 2009; Sjodin *et al*., 2008a; Harrad *et al*., 2008a, 2006; Stapleton *et al*., 2005b.
Supercritical fluid extraction (SFE)	Kierkegaard *et al*., 2009; Covaci *et al*., 2003.
Microwave-assisted extraction (MAE)	Wurl *et al*., 2006; Tan *et al*., 2007.
Ultra-sonication	Sjodin *et al*., 2001.
Defatting technique	
Sulfuric acid treatment	Cunha *et al*., 2010; Ma *et al*., 2009; Sjodin *et al*., 2008a; Harrad *et al*., 2004, 2006, 2008a; Hazrati and Harrad, 2006; Wilford *et al*., 2004, 2005, 2008.
Gel permeation chromatography (GPC) methods	Harner *et al*., 2006; Lee *et al*., 2004; Jaward *et al*., 2004; Tan *et al*., 2007; Deng *et al*., 2007; Chen *et al*., 2009.

Table 1.8 Summary of analytical methods for investigating PBDEs in air and dust (continued)

Analytical methods	Reference
A further clean-up step to remove other interfering compounds	
Column adsorption chromatography	Farrar *et al*., 2006; Gouin *et al.*, 2002, 2005; Harner *et al.*, 2006; Lee *et al.*, 2004; Harrad *et al*., 2004, 2006, Jaward *et al*., 2004; Gevao *et al.*, 2006c; Tan *et al.*, 2007.
PBDE analysis	
GC-MS using EI	Johnson-Restrepo and Kannan, 2009; Fromme *et al*., 2009; Toms *et al*., 2009a; Takigami *et al.*, 2009a, 2009b; Sjodin *et al*., 2008a; Wu *et al.*, 2007; Hayakawa *et al*., 2004; Harrad *et al*., 2004; Strandberg *et al.*, 2001; Wurl *et al.*, 2006; Choi *et al*., 2008; Deng *et al.*, 2007; Hazrati and Harrad, 2006.
GC-MS using ECNI	Cunha *et al.*, 2010; Batterman *et al*., 2009; Shen *et al.*, 2006; Farrar *et al*., 2006; Gouin *et al.*, 2002; Gevao *et al.*, 2006c; Wilford *et al*., 2008; St-Amand *et al*., 2008; Chen *et al*., 2008; Tan *et al.*, 2007; Stapleton *et al.*, 2005b; Cahill *et al.*, 2007; Pettersson-Julander *et al*., 2004; Allen *et al.*, 2008a; Wu *et al.*, 2007; Allen *et al*., 2007; Sjodin *et al*., 2001; Strandberg *et al.*, 2001.
GC-ECD	Agrell *et al*., 2004; ter Schure *et al*. 2004b; Gouin *et al.*, 2006; Wilford *et al*., 2008; Ma *et al.*, 2009; Johnson-Restrepo and Kannan, 2009.

Table 1.9 Benefits and disadvantages of different injection techniques for PBDEs

Injector	Injection volumes	Benefits	Disadvantages
Splitless	1- 3 μL	- Extensively used - Ease of use - Dirty samples can be injected	- Thermal degradation - Syringe-needle discrimination - Large internal surface areas - Discrimination against high boiling point (bp) chemicals
On-column	1- 3 μL	- High reproducibility - No discrimination - No thermal degradation	- Column contamination - Risk of peak splitting

Source: Kierkegaard *et al*., 2009.

Table 1.10 Benefits and disadvantages of different detection techniques for PBDEs

Detection	Benefits	Disadvantages
EI-HRMS	- Very good selectivity - Good sensitivity	- Difficult to use - Purchase & maintenance cost - Higher “down-time”
EI-LRMS	- Good selectivity - Facilitates the use of labelled standards	- Low sensitivity
ECNI-LRMS	- Good selectivity for brominated compounds - Good sensitivity	- Frequent source maintenance needed
ECD	- Easy to use - Purchase & maintenance cost	- Very low selectivity - Instability of linear range - Fair sensitivity for BFRs

Source: Covaci *et al*., 2003.

1.4 Concentrations of PBDEs in air and dust

Multiple studies have reported the concentrations, fate and behaviour of PBDEs in both indoor and outdoor environments. Unsurprisingly, in view of the fact that PBDEs have been widely used in indoor applications particularly indoor and domestic products, elevated concentrations are observed in indoor environments (Wilford *et al*., 2004; Hazrati and Harrad, 2006; Harrad *et al*., 2004). PBDEs have been detected in indoor air and dust due to emissions from in-use products (i.e. plastics in TVs and computers, furniture and carpet foam) (Harrad and Diamond, 2006; U.S. EPA, 2006). In the U.S., levels of PBDEs in the air of many homes are approximately 20 to 50-fold higher than in outdoor air (ODHS, 2009). Both outdoor and indoor concentrations vary seasonally with higher levels in summer and spring (Hazrati and Harrad, 2006; Goel *et al*., 2006). Concentrations of PBDEs in outdoor air, indoor air and dust reported in the existing literature are summarised in Table 1.11, illustrating the following salient points:

- A large quantity of data on higher brominated PBDEs such as BDE-209 in indoor dust is available, but there are fewer data on these PBDEs in outdoor and indoor air, since most studies determining airborne PBDEs have used PUF disk passive air samplers which capture mainly the gaseous fraction. Given the substantial proportion of (especially higher molecular weight) PBDEs that exist in the particulate phase (Harrad *et al.*, 2004); employment of such samplers has likely underestimated concentrations of such higher brominated congeners.
- On the whole, BDE-209 is the predominant congener in outdoor air, indoor air and dust.
- PBDEs can undergo long-range atmospheric transport (LRAT) to remote regions.
- Indoor air concentrations of PBDEs are higher than outdoor air concentrations. Airborne levels of Σtrihexa-BDEs decreased from indoor (i.e. homes) to garages to outdoor microenvironments.
- Atmospheric PBDE levels in urban sites exceed those in rural, remote and oceanic locations, but are lower than those in industrial and e-waste processing areas.
- Generally, concentrations of PBDEs in offices are greater than those in homes, but lower than those in workplaces where PBDEs are used directly (e.g. electronic waste treatment).
- Indoor environments, especially contaminated dust and air, are an important source of human non-occupational exposure to PBDEs.
- Occupational exposure to PBDEs may occur at e-waste and electronic recycling facilities.
- North American dusts contain both deca- and penta-commercial mixtures, whilst U.K. dusts primarily contain the deca-formulation.
- In general, PBDE levels in North American indoor dust exceed those in elsewhere such as UK, Canada, Germany, Australia, Kuwait, Japan and Singapore. The reason for the higher levels is most likely a greater application of PBDEs in this country (BSEF, 2009).
- For workplace and industrial environments, outdoor PBDE concentrations in Chinese e-waste treatment regions are greater than those in an US automotive shredding and metal recycling facility, a Kuwait industrial area and oil lakes, a Swedish municipal solid waste incinerator plant and a Korean steel complex site. Additionally, indoor air of an American e-waste dismantling hall showed higher PBDE levels than that of Swedish e-waste treatment facilities and Chinese workplace offices.

- Differences exist in PBDE concentrations between microenvironment categories in the same country. On the whole, vehicle dust displays higher levels than home, office and garage dust. These differences may be correlated with differences in PBDE emission sources in the microenvironment.
- Most studies place emphasis on houses, offices and then industrial sites or workplaces, particularly e-waste treatment plants. This information could provide estimates of occupational and non-occupational exposure to PBDEs via air inhalation and dust ingestion within different microenvironment categories. Far fewer data are available for cars, but measurable levels of PBDEs were detected in American, UK and Portuguese automobiles with the highly elevated levels being found in some dust samples.
- Significant differences in PBDE concentrations were observed between rooms in the same house: dust PBDE levels in the main living area were 97% higher than the bedroom for deca-BDE and 72% higher for penta-BDE, but there was no significant difference in octa-BDE congeners.

Table 1.11 Summary of PBDE concentrations in outdoor and indoor air (pg m^{-3}) and indoor dust (ng g^{-1})

Outdoor air (mean/average concentrations)										
		Category of outdoor environment								
Number of samples & location	Target PBDEs	Ocean	Remote	Rural	Semi-rural	Suburban	Urban	Domestic	Plant/ Industry	Reference
n=6 and 9 for rural and urban sites along the coastal length of India respectively	ΣBDEs (exc.BDE-209)	-	-	8	-	-	34	-	-	Zhang *et al*., 2008
Eagle Harbor (remote), Sturgeon Point (rural) and Chicago (urban) in USA	ΣBDEs (inc.BDE-209)	-	5.5	7.2	-	-	52	-	-	Strandberg *et al.*, 2001
Mace Head in Ireland (remote) and Hazelrigg in England (semi-rural)	ΣBDEs (exc.BDE-209)	-	2.6	-	12	-	-	-	-	Lee *et al.*, 2004
Bishops Wood (rural), Weoley Castle (suburban) and Centenary Square (urban) in the West Midlands of the UK	Σtrihexa-BDEs	-	-	2.8	-	14	23	-	-	Harrad and Hunter, 2006
n=6 for each semi-rural, residential and steel complex site in Southern Korea	ΣBDEs (exc.BDE-209)	-	-	-	11.7	-	-	12.2	25.2	Choi *et al*., 2008
Gotska Sandon, Baltic Sea	ΣBDEs (inc.BDE-209)	-	8.6	-	-	-	-	-	-	ter Schure *et al*., 2004b
The open Indian Ocean (an oceanic background site	ΣBDEs (inc.BDE-209)	1.5	-	-	-	-	-	-	-	Wurl *et al.*, 2006
Kyoto, Japan (vapour phase)	ΣBDEs (inc.BDE-209)	-	-	-	-	-	58	-	-	Hayakawa *et al*., 2004
n=9 for Guangzhou (an industrial city), China	ΣBDEs (exc.BDE-209)	-	-	-	-	-	-	890	-	Chen *et al*., 2008
n=9 for Guangzhou (an industrial city), China	BDE-209	-	-	-	-	-	-	13,000	-	Chen *et al*., 2008
Twelve homes, Michigan, USA (vapour phase)	Σtrihexa-BDEs	-	-	-	-	-	-	710	-	Batterman *et al.*, 2009
Twelve homes, Michigan, USA (particle phase)	Σtrihexa-BDEs	-	-	-	-	-	-	480	-	Batterman *et al.*, 2009
n=7 for Ottawa, Canada	Σtripenta-BDEs	-	-	-	-	-	-	2.2	-	Wilford *et al*., 2004
n=17 for a municipal solid waste incinerator (MSW) plant in Sweden	ΣBDEs (inc.BDE-209)	-	-	-	-	-	-	-	17	Agrell *et al*., 2004
n=6 for an automotive shredding and metal recycling facility, USA	ΣBDEs (inc.BDE-209)	-	-	-	-	-	-	-	810	Cahill *et al*., 2007
n=6 for an automotive shredding and metal recycling facility, USA	BDE-209	-	-	-	-	-	-	-	560	Cahill *et al*., 2007
n=30 for an e-waste recycling site in Guiyu, China	ΣBDEs (exc.BDE-209)	-	-	-	-	-	-	-	21,000	Deng *et al*., 2007
An e-waste dismantling region in Guiyu, China (diurnal air)	ΣBDEs (inc.BDE-209)	-	-	-	-	-	-	-	8,900	Chen *et al*., 2009
An e-waste dismantling region in Guiyu, China (diurnal air)	BDE-209	-	-	-	-	-	-	-	1,900	Chen *et al*., 2009
n=14 for an industrial area and oil lakes in Kuwait	ΣBDEs (exc.BDE-209)	-	-	-	-	-	-	-	9.3	Gevao *et al*., 2006c

Table 1.11 Summary of PBDE concentrations in outdoor and indoor air (pg m^{-3}) and indoor dust (ng g^{-1}) (continued)

Indoor air (mean/average concentrations)

		Microenvironment category					
Number of samples & location	**Target PBDEs**	**Homes**	**Offices**	**Garages**	**Cars**	**Workplaces**	**Reference**
n=31, 33 and 25 for homes, offices and cars in Birmingham, UK respectively	Σtrihexa-BDEs	52	170	-	710	-	Harrad *et al*., 2006
n=7 and 10 for domestic and workplace sites in Birmingham, UK respectively	Σtetrahexa-BDEs	530	-	-	-	2,800	Harrad *et al*., 2004
n=46 and 24 for homes and offices in Kuwait respectively	ΣBDEs (exc.BDE-209)	15	33	-	-	-	Gevao *et al*., 2006b
Twelve homes and twelve garages in Michigan, USA (vapour phase)	Σtrihexa-BDEs	4,500	-	2,500	-	-	Batterman *et al*., 2009
Twelve homes and twelve garages in Michigan, USA (particle phase)	Σtrihexa-BDEs	1,200	-	720	-	-	Batterman *et al*., 2009
n=12 for homes in New York, USA	ΣBDEs (inc.BDE-209)	3,200	-	-	-	-	Johnson-Restrepo and Kannan, 2009
n=74 for homes in Ottawa, Canada	Σtrihexa-BDEs	260	-	-	-	-	Wilford *et al*., 2004
n=34 for homes in Bavaria, Germany	ΣBDEs (inc.BDE-209)	73	-	-	-	-	Fromme *et al*., 2009
n=12 for an e-waste dismantling hall in Sweden	ΣBDEs (inc.BDE-209)	-	-	-	-	64,000	Sjodin *et al*., 2001
n=12 for an e-waste dismantling hall in Sweden	BDE-209	-	-	-	-	36,000	Sjodin *et al*., 2001
n=12 for an electronics recycling facility in Sweden (inhalable dust fraction)	ΣBDEs (inc.BDE-209)	-	-	-	-	210,000	Julander *et al*., 2005
n=12 for an electronics recycling facility in Sweden (inhalable dust fraction)	BDE-209	-	-	-	-	190,000	Julander *et al*., 2005
n=11 for e-waste dismantlers in Sweden (personal air)	ΣBDEs (inc.BDE-209)	-	-	-	-	77,000	Pettersson-Julander *et al*., 2004
n=11 for e-waste dismantlers in Sweden (personal air)	BDE-209	-	-	-	-	30,000	Pettersson-Julander *et al*., 2004
n=4 for an e-waste dismantling hall in USA	ΣBDEs (inc.BDE-209)	-	-	-	-	650,000	Cahill *et al*., 2007
n=4 for an e-waste dismantling hall in USA	BDE-209	-	-	-	-	600,000	Cahill *et al*., 2007
n=14 and 6 for homes and workplace offices in Guangzhou (an industrial city), China respectively	ΣBDEs (exc.BDE-209)	1,000	-	-	-	2,300	Chen *et al*., 2008
n=14 and 6 for homes and workplace offices in Guangzhou (an industrial city), China respectively	BDE-209	1,974	-	-	-	2,448	Chen *et al*., 2008

House dust (mean concentrations)

		Sample type			
Number of samples & location	**Target PBDEs**	**Main living area**	**Bedroom**	**Home vacuum bag**	**Reference**
n=20 for each sample type investigated in Boston, USA	Octa-BDEs	50	55	35	Allen *et al*., 2008a
n=20 for each sample type investigated in Boston, USA	Penta-BDEs	5,500	2,600	1,200	Allen *et al*., 2008a
n=20 for each sample type investigated in Boston, USA	Deca-BDEs	4,700	1,900	1,900	Allen *et al*., 2008a

Table 1.11 Summary of PBDE concentrations in outdoor and indoor air (pg m^{-3}) and indoor dust (ng g^{-1}) (continued)

House dust (median concentrations)

Number of samples & location	Target PBDEs	Country									Reference
		UK	Germany	USA	Canada	Australia	New Zealand	Japan	Kuwait	Singapore	
n=16, 17 and 7 for UK, USA and Canada respectively	ΣBDEs (inc.BDE-209)	2,900	-	3,500	950	-	-	-	-	-	Harrad *et al*., 2008a
n=28, 20, 10 and 20 for UK, USA, Canada and New Zealand respectively	Σtrihexa-BDEs	59	-	1,600	620	-	96	-	-	-	Harrad *et al*., 2008a
n=10 for each country (UK, Germany, USA and Australia)	ΣBDEs (inc.BDE-209)	10,000	74	4,200	-	1,200	-	-	-	-	Sjodin *et al*., 2008a
n=10 for each country (UK, Germany, USA and Australia)	BDE-209	10,000	63	2,000	-	730	-	-	-	-	Sjodin *et al*., 2008a
n=19, 17 and 31 for Japan, Kuwait and Singapore respectively	ΣBDEs (inc.BDE-209)	-	-	-	-	-	-	700	90	1,200	Suzuki *et al*., 2006; Gevao *et al*., 2006a ; Tan *et al*., 2007

Indoor dust (mean/average concentrations)

Number of samples & location	Target PBDEs	Microenvironment category						Reference
		Homes	Offices	Garages	Cars	TV interiors	Workplaces	
n=30, 18 and 20 for homes, offices and cars in Birmingham, UK respectively	Σtrihexa-BDEs	77	250	-	2,300	-	-	Harrad *et al*., 2008b
n=18, 15 and 9 for homes, offices and cars in Birmingham, UK respectively	BDE-209	260,000	30,000	-	410,000	-	-	Harrad *et al*., 2008b
Twelve homes, twelve garages and twelve cars in Michigan, USA	ΣBDEs (inc.BDE-209)	49,000	-	210,000	15,000,000	-	-	Batterman *et al*., 2009
Twelve homes, twelve garages and twelve cars in Michigan, USA	BDE-209	11,000	-	200,000	15,000,000	-	-	Batterman *et al*., 2009
Two homes, offices (n=14) and TV interiors (n=5) in Japan	BDE-209	620 (Home 1) & 160 (Home 2)	2,400	-	-	240,000	-	Takigami *et al*., 2009a; Suzuki *et al*., 2006; Takigami *et al*., 2008
n=10 and 9 for homes and cars in Portugal respectively (sieved dust fraction)	ΣBDEs (inc.BDE-209)	840	-	-	4,400	-	-	Cunha *et al*., 2010
n=10 and 9 for homes and cars in Portugal respectively (sieved dust fraction)	BDE-209	750	-	-	2,800	-	-	Cunha *et al*., 2010
n=60 for cars in USA	BDE-209	-	-	-	270,000	-	-	Lagalante *et al*., 2009
n =5 for an e-waste facility in Taizhou, China	Σtrihexa-BDEs	-	-	-	-	-	31,000	Ma *et al*., 2009
n =5 for an e-waste facility in Taizhou, China	BDE-209	-	-	-	-	-	30,000	Ma *et al*., 2009

1.5 Variations in PBDE concentrations in air and dust

Few studies have investigated temporal and spatial variations in concentrations of PBDEs in air and dust. These variations may have important implications for source contributions and estimates of human exposure (Harrad *et al*., 2008b, 2010). The extent of seasonal variation in PBDE levels in outdoor air, indoor air and dust has been studied. For air, this variation in outdoor air appeared more significant than for indoor air (Hazrati and Harrad, 2006). The Canadian studies reported seasonally variable atmospheric concentrations, with PBDE concentrations peaking during spring owing to an "early spring pulse", and falling shortly after bud-burst because of the high sorption capacity of freshly emerging vegetation (Gouin *et al*., 2002, 2005). In 4 U.K. homes and offices, indoor air levels of Σtri- through hexa-BDEs in warmer months were generally higher than those in colder months (Hazrati and Harrad, 2006). Conversely, the study of Batterman *et al*. (2009) reported no seasonal variation in indoor concentrations of tri- to hexa-BDEs in 12 U.S. homes over the two season investigating period, possibly due to the fact that indoor temperatures remain essentially constant. Furthermore, in this study, PBDE levels in dust sampled from the houses in two different seasons showed little consistency, while indoor particle determinations across seasons revealed moderate agreement, with somewhat lower temporal variation than gas or dust.

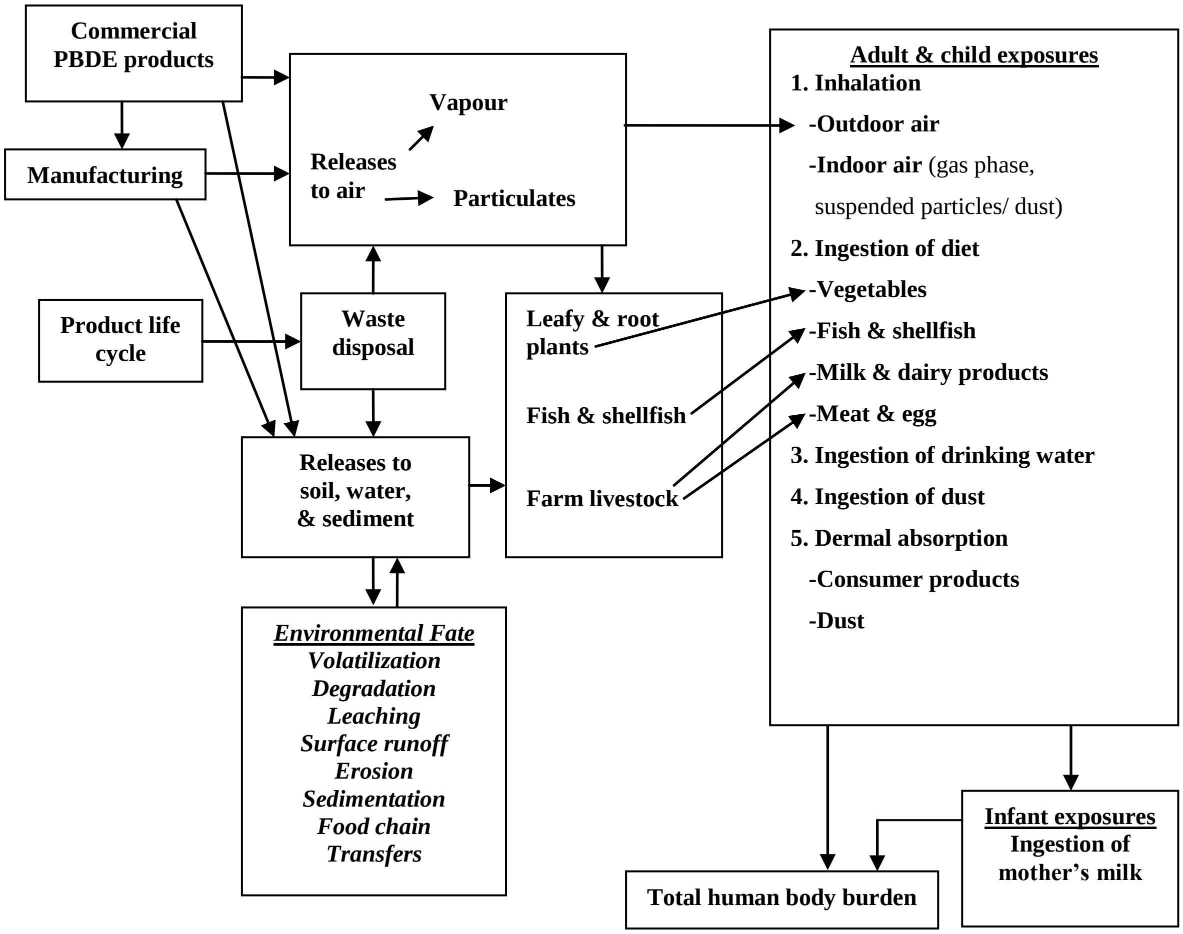
With respect to temporal variability in PBDE concentrations, there have been three studies of this variation. The findings received from one U.K. study suggested that the temporal variation was related to changes in room characteristics especially the replacement, introduction or removal of PBDE-treated products (i.e. TVs, computers and other electronic items) to one room. In this, Hazrati and Harrad (2006) reported the influence of personal computers (PCs), which was illustrated by levels of Σtri- through hexa-BDEs in office air declining markedly (nearly 75%) following the exchange of a computer assembled in 1998 for one dating from 2003. In another U.K. study, considerable temporal variability for PBDEs was also seen in dust collected monthly in 30 houses over a 9-10 month period. The maximum Σtri- to hexa-BDEs levels were higher than the minimum by a factor of ~50, 3.5 and 5.5 in the three residences respectively, whilst for BDE-209, these corresponding figures were 7.5, ~400 and ~35 (Harrad *et al.*, 2008b). Allen *et al.* (2008a) examined temporal variability in domestic dust samples collected from 20 Boston houses. In this U.S. study, there was a statistically significant difference in Octa-BDE levels, but no significant change in Deca- and Penta-BDE levels in dust samples collected from the same rooms eight months apart. This is attributable to little changes in room contents during the monitoring period.

In addition to temporal variations, spatial variations in both air and dust contamination have been the subject of three studies. A study conducted in 30 U.K. homes suggested that the spatial variability in PBDE levels in dust within the same room substantially exceeded that attributable to sampling and analytical variability (Harrad *et al.*, 2008b). In a U.S. study, Deca- and Penta-BDE concentrations in 20 Boston homes were only moderately correlated between the two rooms (main living room and bedroom) monitored in each residence, demonstrating that indoor air levels of PBDEs might vary over different rooms in a house, likely as a consequence of dissimilar PBDE emission sources in each room (Allen *et al.,* 2007). In a later U.S. study, Allen *et al.* (2008a) reported no significant difference in Octa-BDE congeners in household dust, but Deca- and Penta-BDE congeners in the houses were significantly lower in the bedroom than the main living room.

1.6 Human exposure to PBDEs

Humans may be exposed to lower brominated PBDEs by consumption of contaminated foods (i.e., fish, meat and dairy products) and possibly inhalation of polluted ambient or indoor air. Inhalation exposure could occur from outgassing of PBDEs from electronic and electrical equipment and furniture into indoor atmospheres. Dermal exposure to PBDEs could occur by contact with PBDE-containing products like plastics or textiles (ATSDR, 2004; Siddiqi *et al*., 2003). Figure 1.2 gives an overview of the human exposure pathways for PBDEs.

Figure 1.2 Overview of human exposure pathways for PBDEs



Source: Modified from Wenning, 2002 and Frederiksen *et al*., 2009.

It has long been believed that general populations are exposed to PBDEs via the food chain (ODHS, 2009). Although dietary exposure is an important pathway of exposure to PBDEs to the general human population (Frederiksen *et al*., 2009; Fromme *et al*., 2009; Gomara, *et al*., 2006; Domingo *et al*., 2006; Domingo, 2004; Watanabe and Sakai, 2003; Ohta *et al*., 2002; Darnerud *et al*., 2001), there is mounting evidence that inhalation of indoor air and ingestion of indoor dust can be the principal exposure pathway for some individuals and age groups (primarily toddlers and children) (Table 1.12) (Harrad *et al*., 2010 and references therein). Also, occupational exposure via air inhalation and dust ingestion may occur by use, manufacture and disposal of PBDEs and in workplaces where BFR-containing plastic and foam products are recycled, or where electronic and electrical devices are repaired or dismantled (ATSDR, 2004; Chen *et al*., 2008; Julander *et al*., 2005; Pettersson-Julander *et al*., 2004; Sjodin *et al*., 2001).

Table 1.12 Upper-bound estimate of PBDE daily intake for the general Canadian population

Exposure pathway	Estimated intake (µg/kg-bw per day) of PBDEs by various age groups						
	0-6 months (Formula fed)	**0-6 months (Breast fed)**	**0.5-4 years**	**5-11 years**	**12-19 years**	**20-59 years**	**60+ years**
Diet	1.4×10^{-3}	2.4	5.8×10^{-1}	4.8×10^{-1}	2.7×10^{-1}	2.6×10^{-1}	1.7×10^{-1}
Drinking water			5.9×10^{-7}	4.6×10^{-7}	2.6×10^{-7}	2.8×10^{-7}	2.9×10^{-7}
Dust/soil	2.3×10^{-1}	2.3×10^{-1}	3.6×10^{-1}	1.2×10^{-1}	2.8×10^{-2}	2.4×10^{-2}	2.3×10^{-2}
Indoor air	4.4×10^{-4}	4.4×10^{-4}	9.3×10^{-4}	7.3×10^{-4}	4.1×10^{-4}	3.6×10^{-4}	3.1×10^{-4}
Outdoor air	7.7×10^{-5}	7.7×10^{-5}	1.7×10^{-4}	1.3×10^{-4}	7.3×10^{-5}	6.3×10^{-5}	5.5×10^{-5}
Total intake	2.3×10^{-1}	2.6	9.5×10^{-1}	6.0×10^{-1}	3.0×10^{-1}	3.0×10^{-1}	1.9×10^{-1}

Source: Health Canada, 2009.

PBDEs have been found in the U.S. diet, mother's milk and blood at the highest levels in the world (Schecter *et al*., 2005a). The U.S. population were observed to have some of the most elevated concentrations of these contaminants in breast milk (Schecter *et al*., 2003; Noren and Meironyte, 2000), body fat (Johnson-Restrepo *et al*., 2005; She *et al*., 2002) and blood (Sjodin *et al*., 2008b; Schecter *et al*., 2005b). In the U.S., PBDE levels in human samples are generally 10-100 times greater than levels found in Europe, New Zealand and Asia (Table 1.13) (Kimbrough *et al*., 2009; Sudaryanto *et al*., 2008; Choi *et al*., 2003; Kalantzi *et al*., 2004; Sjodin *et al*., 2004b, 2008b; Inoue *et al*., 2006; Harrad and Porter, 2007; Gomara *et al*., 2007). This is most likely owing to the fact that the world's use of Penta-BDE formulation, whose congeners are highly bioconcentrative and biomagnify in organisms, is highest in the Americas (approximately 95%) (BSEF, 2009; McDonald, 2005).

The existing data on human exposure to PBDEs, with special emphasis on external exposure pathways (i.e., diet, dust and air) and internal exposure pathways (i.e., human milk and blood) has been reviewed recently by Frederiksen *et al*. (2009). The authors suggested that the use of diverse consumer products can contribute to exposure in domestic environments. Dust appears an additional source of indoor PBDE exposure, and its ingestion conveys the greatest intake of BDE-209 of all sources, likely also of other congeners. PBDE exposure via dust is important for toddlers as they ingest more dust than adults, while infants are also exposed to PBDEs through human milk.

Table 1.13 PBDE concentrations (range in parentheses) in human samples (ng g^{-1} lipid) from different countries

Country	Type of human sample	No. of samples	Year of sampling	PBDE congeners studied	ΣBDEs (range)	Reference
Japan	Adipose tissue	10	1970	28, 47, 99, 100, 153, 154 & 183	0.0292^{a} (0.0068-0.0784)	Choi *et al*., 2003
Japan	Adipose tissue	10	2000	28, 47, 99, 100, 153, 154 & 183	1.29^{a} (0.47-2.75)	Choi *et al*., 2003
Vallecas District, Madrid, Spain	Placenta	30	2003-2004	17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 184, 191, 196, 197 & 209	1.9^{a} (0.19-9.7)	Gomara *et al*., 2007
Japan	Milk	12	NR^{b}	28, 47, 99, 100, 153 & 154	(0.7-2.8)	Ohta *et al*., 2000
Japan	Milk	12	1999	28, 47, 99, 153 & 154	1.72^{c}	Ohta *et al*., 2002
Japan	Milk	89	2005	15, 28, 47, 99, 100, 153, 154, 183, 196, 197, 206, 207 & 209	1.54^{a} (0.49-4.55)	Inoue *et al*., 2006
South Seoul, Korea	Milk	17	2007	17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 207 & 209	120^{c,d} (7.6-570)	Kang *et al*., 2010
UK	Milk	54	2001-2003	17, 28, 32, 35, 37, 47, 49, 71, 75, 85, 99, 100, 119, 153 & 154	6.3^{a}	Kalantzi *et al*., 2004
Canada	Milk	98	2001-2002	28, 47, 99, 100 & 153	22^{c}	Pereg *et al*., 2003
Finland	Milk	11	1994-1998	28, 47, 99 & 153	2.25^{c} (0.9-5.9)	Strandman *et al*., 2000
Sweden	Milk	40	1997	28, 47, 66, 85, 99, 100, 153 & 154	4^{c}	Noren and Meironyte, 2000
Vallecas District, Madrid, Spain	Milk	22	2003-2004	17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 184, 191, 196, 197 & 209	6.1^{a} (1.5-63)	Gomara *et al*., 2007
Germany	Milk	93	2001-2003	28, 47, 99, 153, 154, 183 & 209	1.78^{a}	Vieth *et al*., 2004
USA	Milk	16	2004	28, 32, 33, 47, 66, 71, 85, 99, 100, 153, 154, 183 & 209	48.5^{a}	She *et al*., 2004
Indonesia	Milk	30	2001-2003	3, 15, 28, 47, 99, 100, 153, 154, 183, 196, 197, 206, 207 & 209	1.4^{a} (<0.03-15)	Sudaryanto *et al*., 2008
Japan	Serum	89	2005	15, 28, 47, 99, 100, 153, 154, 183, 196, 197, 206, 207 & 209	2.99^{a} (0.74-21.19)	Inoue *et al*., 2006
New Zealand	Serum	23	2001	47, 99, 100, 153, 154 & 183	6.83^{c,d}	Harrad and Porter, 2007
USA	Serum	7	2000-2002	17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 203 & 209	61^{a}	Sjodin *et al*., 2004b
Netherlands	Serum	78	2001-2002	47, 99, 100, 153 & 154	9.3^{a}	Weiss *et al*., 2004

Table 1.13 PBDE concentrations (range in parentheses) in human samples (ng g^{-1} lipid) from different countries (continued)

Country	Type of human sample	No. of samples	Year of sampling	PBDE congeners studied	ΣBDEs (range)	Reference
USA	Serum (foam workers)	12	2006	17, 28, 47, 66, 99, 100, 153, 154 & 183	160[a] (67-973)	Stapleton *et al.*, 2008a
USA	Serum (carpet layers)	3	2006	17, 28, 47, 66, 99, 100, 153, 154 & 183	178[a] (125-241)	Stapleton *et al.*, 2008a
Vallecas District, Madrid, Spain	Maternal serum	61	2003-2004	17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 184, 191, 196, 197 & 209	12[a] (5.5-43)	Gomara *et al.*, 2007
South Seoul, Korea	Maternal serum	20	2007	17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 207 & 209	37[c,d] (0.00-270)	Kang *et al.*, 2010
Getafe District, Madrid, Spain	Paternal serum	53	2003-2004	17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 184, 191, 196, 197 & 209	12[a] (4.2-108)	Gomara *et al.*, 2007
Vallecas District, Madrid, Spain	Umbilical cord serum	44	2003-2004	17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 184, 191, 196, 197 & 209	17[a] (6.3-82)	Gomara *et al.*, 2007
South Seoul, Korea	Umbilical cord serum	20	2007	17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 207 & 209	89[c,d] (0.00-480)	Kang *et al.*, 2010

[a] Median concentrations.

[b] NR = not reported.

[c] Mean concentrations.

[d] Lower bound concentrations.

1.6.1 Dietary exposure

Due to the fact that PBDEs are highly persistent and hydrophobic compounds like many other POPs, they accumulate in the lipid-rich tissues of animals. As a result, PBDEs have been found at high levels in fatty foods of animal origin including fish from high trophic positions, lipid-rich oils, meat and dairy products, with the highest concentrations mostly found in fish. The diet is thus an important route of exposure to these chemicals for the general population (Frederiksen *et al*. 2009; Voorspoels *et al*., 2007b; Schecter *et al*., 2006; Bocio *et al*., 2003). Detailed data on PBDE levels in different food types reported in the previous studies is summarised in Table 1.14.

Fish and shellfish

Because of its ability to bioaccumulate contaminants, fish is considered to be the key contributor of PBDEs in the foods (Darnerud *et al*., 2006; Kiviranta *et al*., 2004; Bocio *et al*., 2003) and hence it has been measured to a larger degree than other food items. Furthermore, fish samples have been analysed for PBDEs in several environmental and ecological surveys (Burreau *et al*., 2006; Alaee, 2003; Law *et al*., 2003; de Boer *et al*., 1998; Anderson and Blommkist, 1981).

Based on fish levels presented in Table 1.14, The mean levels of ΣPBDEs in American, Belgian, Spanish, Swedish, Finnish and Chinese fish were respectively 1,120, 480, 334, 634, 850 and 231 (mean of medians) ng/kg ww (Schecter *et al*., 2006; Voorspoels *et al*., 2007b; Bocio *et al*., 2003; Darnerud *et al*. 2006; Kiviranta *et al*., 2004; Meng *et al*., 2007). BDE-209 was included in the U.S. and Chinese study, accounting for nearly 92 and 71 ng/kg ww respectively (Schecter *et al*., 2006; Meng *et al*., 2007). Of all countries reported, fish from the USA had the greatest mean concentrations of PBDEs. A wide variation in PBDE levels between fish species in the same geographic climatic region has been seen. Also, variations in the same fish species from different areas have been found. For example, salmon has been analysed for PBDEs in studies from various countries. Salmon caught in the U.S., Spain, Belgium and Japan contained 3,082, 2,015, 1,580 and 836 ng/kg ww ΣPBDEs, respectively (Schecter *et al*., 2006; Domingo *et al*., 2006; Voorspoels *et al*., 2007b; Ohta *et al*., 2002). BDE-209 was included in the U.S. study only, but it was not detected, that makes the PBDE levels more comparable, although the studied congeners are different. In general, American salmon appear to be heavily contaminated, evidenced by the fish having the highest PBDE levels among the reported salmon.

A Belgian study examined the concentration differences between fresh and smoked salmon. The general observation is that PBDE levels in fresh salmon (1,580 ng/kg ww) exceeded those in smoked salmon (1,030 ng/kg ww) (Voorspoels *et al*., 2007b). Additionally, the differences between fatty and lean fish were investigated by Gomara *et al*. (2006). The results showed that the concentrations of PBDEs are slightly greater in the lipid-rich fish (211 ng/kg ww) compared to lean fish (157 ng/kg ww).

Shellfish including cuttlefish, clam or shrimps frequently contain relatively low PBDE content compared to other items of seafood. Cuttlefish (Spain), short-necked clam (Japan), shrimp (Spain) and shrimp (Belgium) contained respectively 16, 52.4, 20 and 70 ng/kg ww $\Sigma\mathrm{PBDEs}_{\mathrm{ex209}}$, that is generally low compared to levels in fish sampled in the same area (Table 1.14). BDE-47 and 99 as well as 100 are the predominant congeners in fish, shrimps, squid and mussels (Schecter *et al*., 2006; Meng *et al*., 2007; Domingo *et al*., 2006). BDE-209 was not included in all reported studies, but it has also been observed. On the whole, BDE-209 accounted for less than 10% of the total ΣPBDEs in fish, based on fish concentrations shown in Table 1.14 (Schecter *et al*., 2006; Gomara *et al*., 2006). A study by Meng *et al*. (2007) did not find BDE-209 in any of 13 Chinese fish species which were measured.

It has been concluded from many previous studies that the important dietary exposure pathway for PBDEs is the ingestion of fish (Darnerud *et al*., 2006; Kiviranta *et al*., 2004; Bocio *et al*., 2003). The factors such as bioaccumulative potential of PBDEs in different fish species, age of fish, tissues selected for analyses, sampling areas (i.e. heavily contaminated area), sampling times, seasonal variations and trophic levels in food chain and food web are likely to influence the levels of PBDEs in fish.

Meat products and eggs

Concentrations of ΣPBDEs in eggs seem to be comparable for the U.S. (85 ng/kg ww) (Schecter *et al*., 2006) and Europe including Belgium, Spain and Sweden (42-170 ng/kg ww) (Voorspoels *et al*., 2007b; Bocio *et al*., 2003; Darnerud *et al*. 2006). BDE-209 was included in the U.S. study and detected at a fairly high concentration of 10 ng/kg ww (Schecter *et al*., 2006). The ΣPBDE concentrations in North American (41-283 ng/kg ww), European (10-172 ng/kg ww) and Asian meat (6-64 ng/kg ww) are different. BDE-209 was included in the North American study, and it ranged from below the detection limit to 48.5 ng/kg ww (Schecter *et al*., 2006). Chicken breast from the U.S. showed higher levels of PBDEs (283 ng/kg ww) (Schecter *et al*., 2006) than Belgian chicken breast sample (31 ng/kg ww) (Voorspoels *et al*., 2007b). BDE-209 accounted for about 48.5 ng/kg ww in the U.S. study (Schecter *et al*., 2006), whereas it was not included in the Belgian study (Voorspoels *et al*., 2007b). In general, the PBDE concentrations in meat were considerably lower than those in fish, with great variations being seen within the categories.

Dairy products, fats and oils

PBDEs are most abundant in lipid-rich products such as butter, cheese, fats and oils (2.0-810 ng/kg ww) (Schecter *et al*., 2006; Voorspoels *et al*., 2007b; Kiviranta *et al*., 2004; Bocio *et al*., 2003; Darnerud *et al*., 2006). Whilst solid milk products including butter and cheese contained fairly significant quantities of PBDEs (40 ng/kg ww) (Kiviranta *et al*., 2004), liquid milk products contained very low PBDE levels (2.0 ng/kg ww) (Kiviranta *et al*., 2004). ΣPBDE concentrations in the U.S. and Europe seem to be similar; nevertheless, the quantity of information for this food group is very limited. A U.S. and Spanish study suggested that BDE-47, 99 and 209 are the major congeners in dairy products and oils, respectively (Schecter *et al*., 2006; Gomara *et al*., 2006).

Vegetables and fruits

The PBDE content in vegetables and fruits is thought to be substantially lower than that in other food types as a consequence of the low fat content, greater water content and the primary level in food chain or food web. Low PBDE concentrations in this food group are confirmed by the studies of Kiviranta *et al*. (2004) and Bocio *et al*. (2003) where concentrations were found to lie in the range 8-17 ng/kg ww for European vegetables, and 4.2-6 ng/kg ww for European fruits. Nonetheless, far higher levels in Japanese vegetables were reported by Ohta *et al*. (2002) (Table 1.14). PBDE concentrations in spinach from Japan (134 ng/kg ww) exceeded those in many meats including pork, beef and chicken from the same area (6.3-64 ng/kg ww).

Other food types

This category represents several different items of products like beverages and fast food. In Belgium, levels of ΣPBDEs in fast food such as McDonalds Big Mac and Pizza Hut Super Supreme were in the range 110-160 ng/kg ww (Voorspoels *et al*., 2007b). The ΣPBDE concentrations in Belgian fast food were similar to those in meat products (ΣPBDEs: 31-160 ng/kg ww) from the same region (Voorspoels *et al*., 2007b).

Table 1.14 Summary of PBDE levels (ng/kg wet weight) in different food items

Matrix	Area/ country	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	Σ BDEs[a]	Notes	Reference
Fish and seafood												
Salmon	Catalonia, Spain	-	1,061	177	250	36	90	6.3	-	2,015	Mean levels	Domingo *et al*., 2006
Mackerel		-	400	155	140	33	81	7.9	-	1,124		
Sardine		-	319	22	163	11	13	1.3	-	710		
Tuna		-	227	37	89	18	37	4.3	-	558		
Mussel		-	134	63	55	4.8	5.5	4.9	-	350		
Squid		-	69	30	36	6.0	8.9	3.3	-	204		
Clam		-	20	16	5.9	3.4	4.2	3.8	-	79		
Shrimp		-	7.2	2.2	1.3	1.2	0.7	2.7	-	20		
Cuttlefish		-	4.2	1.2	2.2	0.6	0.5	1.9	-	16		
Snubnose pompano	China	25.8	214	34.9	42	18.6	34	ND[b]	ND[b]	426	Median levels	Meng *et al*., 2007
Hairtail		10.3	142	25	30.1	10.3	25.6	ND[b]	ND[b]	272		
Red drum		18.6	118	9.7	22.2	5.8	13.5	ND[b]	ND[b]	224		
Fish		24.3	126	12.9	18.9	8.7	16.1	3.4	70.8	231	Mean of medians	
Salmon	Spain	6.21	148	40.3	31	5.63	10.2	NA[c]	NA[c]	251	Median levels & upper bound levels	Gomara *et al*., 2006
Fatty fish		1.89	122	8.51	41	0.75	0.79	0.36	9.53	211		
Lean fish		1.61	100	13.5	16.6	6.91	8.32	1.33	4.72	157		
Salmon	USA	142	2,081	147	353	36.6	142	ND[b]	ND[b]	3,082		Schecter *et al*., 2006
Sardines		53.6	2,748	358	257	51.9	139	ND[b]	ND[b]	3,726		
Trout		49.3	826	128	198	24.7	61.3	2.5	ND[b]	1,319		
Shrimp		3.6	75.6	9.4	14.3	1.2	2.6	0.2	ND[b]	108		
Fish and seafood		26.2	603	166	126	21	49.3	2.08	91.8	1,120	Mean of means	
Mussel	UK	-	1,640	1,410	400	<100	<100	-	-	-		Harrad *et al*., 2004
Fish	Sweden	-	478	-	-	-	-	-	-	634	Mean levels	Darnerud *et al*., 2006
Fish	Finland	-	-	-	-	-	-	-	-	850	Upper bound level	Kiviranta *et al*., 2004

Table 1.14 Summary of PBDE levels (ng/kg wet weight) in different food items (continued)

Matrix	Area/ country	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	Σ BDEs[a]	Notes	Reference
Fresh salmon	Belgium	-	-	-	-	-	-	-	-	1,580	Average levels & upper bound levels	Voorspoels *et al.*, 2007b
Smoked salmon		-	-	-	-	-	-	-	-	1,030		
Trout		-	-	-	-	-	-	-	-	280		
Sardines		-	-	-	-	-	-	-	-	110		
Shrimp		-	-	-	-	-	-	-	-	70		
Fish and seafood		-	-	-	-	-	-	-	-	480	Mean of means	
Blue fish	Catalonia , Spain	-	-	-	-	-	-	-	-	1,019		Bocio *et al.*, 2003
Tinned fish		-	-	-	-	-	-	-	-	260		
White fish		-	-	-	-	-	-	-	-	88		
Shellfish		-	-	-	-	-	-	-	-	88		
Fish and shellfish		-	-	-	-	-	-	-	-	334	Mean of means	
Young yellowtail	Japan	-	-	-	-	-	-	-	-	1,643	Mean levels	Ohta *et al.*, 2002
Salmon		-	-	-	-	-	-	-	-	836		
Yellow tuna		-	-	-	-	-	-	-	-	20.8		
Short-necked clam		-	-	-	-	-	-	-	-	52.4		
Meat products												
Chicken breast	USA	0.5	60.5	128	17.1	12.0	10.8	3.2	48.5	283		Schecter *et al.*, 2006
Beef tenderloin		ND[b]	35.1	40.3	6.9	4.9	3.7	3.8	ND[b]	105		
Pork		ND[b]	6.9	16.3	1.8	1.0	1.2	1.3	11.7	41		
Meatloaf	Belgium	-	-	-	-	-	-	-	-	160	Average levels & upper bound levels	Voorspoels *et al.*, 2007b
Pork chop		-	-	-	-	-	-	-	-	120		
Beef steak		-	-	-	-	-	-	-	-	31		
Chicken breast		-	-	-	-	-	-	-	-	31		
Pork and pork products	Catalonia , Spain	-	-	-	-	-	-	-	-	172		Bocio *et al.*, 2003
Beef and beef products		-	-	-	-	-	-	-	-	42		
Chicken		-	-	-	-	-	-	-	-	10		
Pork	Japan	-	-	-	-	-	-	-	-	63.6	Mean levels	Ohta *et al.*, 2002
Beef		-	-	-	-	-	-	-	-	16.2		
Chicken		-	-	-	-	-	-	-	-	6.25		
Meat	Sweden	-	18	-	-	-	-	-	-	46	Mean levels	Darnerud *et al.*, 2006

Table 1.14 Summary of PBDE levels (ng/kg wet weight) in different food items (continued)

Matrix	Area/ country	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	Σ BDEs[a]	Notes	Reference
Eggs and dairy products												
Cream cheese	USA	<1.8	97.8	77.1	12.2	5.96	2.84	<5.6	481.4	683		Schecter *et al*., 2006
Chicken eggs		0.20	22.5	36.6	5.93	3.63	2.56	0.68	10.32	85		
Butter		1.3	165	172	40.4	16.8	12.6	5.3	66.2	485		
Eggs	Belgium	-	-	-	-	-	-	-	-	170	Average levels & upper bound levels	Voorspoels *et al*., 2007b
Cheese		-	-	-	-	-	-	-	-	220		
Butter		-	-	-	-	-	-	-	-	810		
Eggs	Catalonia , Spain	-	-	-	-	-	-	-	-	64		Bocio *et al*., 2003
Liquid milk products	Finland	-	-	-	-	-	-	-	-	2.0	Upper bound levels	Kiviranta *et al*., 2004
Solid milk products		-	-	-	-	-	-	-	-	40		
Eggs	Sweden	-	14	-	-	-	-	-	-	42	Mean levels	Darnerud *et al*., 2006
Fats and oils												
Oils	Spain	0.85	21.6	13.9	4.12	5.38	1.82	0.97	24.9	119	Median levels & upper bound levels	Gomata *et al*., 2006
Vegetable oils and fats	Catalonia , Spain	-	-	-	-	-	-	-	-	804		Bocio *et al*., 2003
Fats	Sweden	-	30	-	-	-	-	-	-	159	Mean levels	Darnerud *et al*., 2006
Fats	Finland	-	-	-	-	-	-	-	-	220	Upper bound levels	Kiviranta *et al*., 2004

Table 1.14 Summary of PBDE levels (ng/kg wet weight) in different food items (continued)

Matrix	Area/ country	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	Σ BDEs[a]	Notes	Reference
Vegetables												
Spinach	Japan	-	-	-	-	-	-	-	-	134	Mean levels	Ohta *et al*., 2002
Potato		-	-	-	-	-	-	-	-	47.6		
Carrot		-	-	-	-	-	-	-	-	38.4		
Vegetables	Catalonia , Spain	-	-	-	-	-	-	-	-	8		Bocio *et al*., 2003
Vegetables	Finland	-	-	-	-	-	-	-	-	17	Upper bound levels	Kiviranta *et al*., 2004
Fruits												
Fruits	Catalonia , Spain	-	-	-	-	-	-	-	-	6		Bocio *et al*., 2003
Fruits and berries	Finland	-	-	-	-	-	-	-	-	4.2	Upper bound levels	Kiviranta *et al*., 2004
Fast food												
McDonalds Filet-O-Fish	Belgium	-	-	-	-	-	-	-	-	110	Average levels & upper bound levels	Voorspoels *et al*., 2007b
McDonalds Mc Chicken		-	-	-	-	-	-	-	-	110		
McDonalds Big Mac		-	-	-	-	-	-	-	-	160		
Pizza Hut Super Supreme		-	-	-	-	-	-	-	-	130		

[a] The total PBDE concentrations.
[b] ND = not detected.
[c] NA = not analyzed.

1.6.2 Inhalation and dust ingestion exposure

As stated in section 1.4 and 1.6.1, dietary intake alone does not appear to account for the PBDE body burdens estimated in the U.S. (Schecter *et al*., 2006; Wu *et al*., 2007). Indoor environments (dust, air) have been recently regarded as important sources of human exposure to PBDEs (Johnson-Restrepo and Kannan, 2009; Allen *et al*., 2008b; Wu *et al*., 2007; Schecter *et al*., 2006; Harrad, *et al*., 2006, 2004; Harrad and Diamond, 2006; Jones-Otazo *et al*., 2005; Wilford *et al*., 2005, 2004; Stapleton *et al*., 2005; Sjodin *et al*., 2004a; Alcock *et al*., 2003). House dust contributes to 82% and 77% of the U.S. adult and toddler PBDE exposure (Lorber, 2008; Johnson-Restrepo and Kannan, 2009), and contributes more than 80% of exposure for Canadian children (Wilford *et al*., 2005, 2004; Jones-Otazo *et al*., 2005). Toddlers and children likely are at the greatest risk from ingestion and inhalation exposure because they sit, crawl or roll on floors and place objects in their mouths (hand-to-mouth behaviour) (Lorber, 2008; Frederiksen *et al*., 2009). For instance, ingestion of contaminated dust can result in 100 times greater exposure than average for a toddler living in a home in which elevated PBDE levels are present (Jones-Otazo *et al*., 2005). Fischer *et al*. (2006) found the highest PBDE concentrations in blood drawn from the youngest child (18-month-old son) of an American family of four. This supports the hypothesis that younger children are more exposed to PBDEs than adults. Karlsson *et al*. (2007) revealed a positive relationship for the sum BDE levels in house dust and blood plasma. A study by Wu *et al*. (2007) showed the statistically significant, positive correlations between PBDE concentrations (excluding BDE-209) in human milk and domestic dust. Recently published data reported significant associations between the levels of BDE-99 in indoor air and breast milk and BDE-153 in dust and BDE-183 in human milk (Toms et *al*., 2009a).

1.6.3 Occupational exposure

Occupational exposure can be substantial for people working in the manufacture, disposal or recycling of PBDE-containing materials. They are often subject to high occupational exposures through air inhalation, dust ingestion and dermal absorption (Chen *et al*., 2008; Deng *et al*., 2007; Cahill *et al*., 2007; Julander *et al*., 2005; Pettersson-Julander *et al*., 2004; Sjodin *et al*., 2001). Occupational exposure may be most important in developing countries such as China, India, Pakistan, Vietnam, the Philippines and Nigeria, where approximately 50-80% of the electronic waste generated by industrialised countries is illegally exported for recycling and discarded (Bi *et al*., 2007; Wong *et al*., 2007; Nnorom and Osibanjo, 2008). Median serum levels of deca-BDE (BDE-209) in residents from an electronic waste dismantling region in South China (310 ng/g lipid weight) are 50 to 200-fold higher than reported for any other occupationally exposed population (Bi *et al*., 2007). In Sweden, occupational exposure to PBDEs has been monitored in clerks working full-time at computer screens and personnel at an electronics-dismantling plant, with hospital cleaners as a control group. The highest median PBDE levels in the serum were observed in dismantlers (37 pmol/g lw; 26 ng/g lw), followed by clerks (7.1 pmol/g lw; 4.1 ng/g lw) and cleaners (5.4 pmol/g lw; 3.3 ng/g lw) (Sjodin *et al.*, 1999). Occupational exposure has also been investigated among computer technicians whose median serum concentrations of BDE-47 (2.7 pmol/g lw; 1.4 ng/g lw), BDE-153 (4.1 pmol/g lw; 2.6 ng/g lw), BDE-154 (0.93 pmol/g lw; 0.6 ng/g lw), BDE-183 (1.3 pmol/g lw; 0.98 ng/g lw) and BDE-209 (1.6 pmol/g lw; 1.5 ng/g lw) were five times greater than those previously reported among computer clerks and hospital cleaners (Jakobsson *et al*., 2002). Another study of workers at a Swedish electronics recycling plant showed a significant decrease in occupational exposure to BDE-183 and BDE-209 because of industrial hygiene improvements (Thuresson *et al*., 2006). Occupational exposure has also been studied for incinerator workers in Korea (Lee *et al*., 2007). The mean total PBDE level in blood is 16.84 ±7.48 ng/g lipid, which is somewhat higher than in other countries except North America and Canada. Concentrations of PBDEs were measured in plasma samples from Norwegian electronic recycling workers whose exposure seems to be less significant in this occupational setting owing to the safe workplace conditions including proper respirators and ventilation systems (Thomsen *et al*., 2001; Sjodin *et al*., 2003).

1.7 Toxicity of PBDEs

The toxicity of PBDEs displays considerable congener-specificity. On the whole, acute toxicity is low and the lower brominated congeners appear more toxic than the higher brominated classes. For example, penta-BDE (with five bromine atoms) and octa-BDE (with eight bromine atoms) are more toxic than deca-BDE (with ten bromine atoms) (ATSDR, 2004; Birnbaum and Staskal, 2004; Darnerud, 2003). This different toxicity is probably associated with the preferential accumulation of the lighter brominated mixtures in animal and human tissues (ATSDR, 2004). Studies on experimental animals showed an opposite correlation between the degree of bromination and uptake efficiency or bioaccumulation

(Darnerud *et al*., 2001). BDE-209 is poorly absorbed by ingestion, rapidly eliminated and does not bioaccumulate, whereas the lower brominated varieties like tri- to hexa-formulations are almost completely absorbed, slowly eliminated, highly bioacumulative and much more bioactive than deca-BDE (Hooper and McDonald, 2000; McDonald, 2002; U.S. EPA, 2006). Therefore, the lighter PBDEs tend to persist in humans and are widespread in the environment. The tetrabrominated BDE-47 and the pentabrominated BDE-99 are believed to be the most widely observed mixtures in human and animal tissues such as adipose, adrenal glands and liver (Hooper and McDonald, 2000; U.S. EPA, 2006).

Numerous studies demonstrate that PBDEs impair liver, endocrine systems, thyroid hormones, neurobehavioural development and male fertility as well as possibly causing cancer (ATSDR, 2004; Darnerud, 2003, 2008; Branchi *et al*., 2003; McDonald, 2002; Hooper and McDonald, 2000; Akutsu *et al*., 2008). The most sensitive populations are likely to be pregnant women, developing fetuses, and infants (McDonald, 2002).

The U.S. EPA has classified deca-BDE as a possible human carcinogen based on rodent carcinogenicity bioassay data, whilst PBDEs with fewer bromine contents than deca-BDE are listed by the U.S. EPA as not classifiable as to human carcinogenicity because of the lack of animal and human cancer studies (ATSDR, 2004; MBH and MDEP, 2005). A study by Turyk *et al*. (2008) revealed that PBDEs were related to increased thyroid hormones thyroxine (T_4) and increased thyroglobulin antibodies in the U.S. adult male sport fish consumers, while BDE-47 exposure was positively related to testosterone concentrations. Recently, a correlation has been reported between reduced thyroxine concentrations and prenatal exposure to PBDEs (Herbstman *et al*., 2008). PBDE levels in breast milk were associated with congenital cryptorchidism and were also positively associated with serum luteinizing hormone (LH) (Main *et al*., 2007). Furthermore, a prenatal toxicity study on PBDEs reports permanent effects of penta-BDE on the developing brain and, thus, on behaviour (Eriksson *et al*., 1999). Prenatal exposure to high doses of deca-BDE led to delayed hardening of skull bones in foetuses, while wider ranging developmental effects on the foetus were reported after administering rats with much lower doses of octa-BDE and commercial mixtures of hexa-, hepta- and octa-BDE (Santillo *et al*., 2001). Neonatal BDE-99 exposure during a sensitive period of foetal brain development impaired the spontaneous behaviour of offspring, as well as learning and memory functions in the adult animals. Neonatal exposure to BDE-47 and 99 caused permanent aberrations in spontaneous motor behaviour which worsened with age (de Wit, 2002). A pilot study on the correlation between male serum PBDEs and sperm quality suggested that there were strong negative relationships between male serum level of 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153) and sperm level and testis size (Akutsu *et al.*, 2008).

Ecotoxicological studies in birds also suggest that environmentally relevant doses of lighter brominated groups of PBDEs result in oxidative stress, immunosuppression, diminished thyroid function and reduced vitamins A and E. BDE-47 and BDE-99 were noted to have detrimental effects on the development and reproduction of the invertebrate, while BDE-209 is essentially nontoxic to invertebrates (Kierkegaard, 2007; Birnbaum and Staskal, 2004).

Table 1.15 presents exposure guidelines, including the reference dose (RfD), health-based limit values (HBLVs), LOELs and oral LD-50 for the critical effects of PBDEs. Based on reported LOELs and oral LD-50, penta-BDE appears to be the most toxic of the PBDEs, with LOELs of 2 mg/kg bw/day and 1 mg/kg/day and a LD-50 of 0.5-5 g/kg body weight.

Table 1.15 Exposure guidelines for PBDEs

Compound	Exposure guideline	Toxicity endpoint	Reference
Commercial Penta-BDE[a]	LOEL = 2 mg/kg bw/day	Liver histopathology: subchronic dietary study (rat)	Health Canada, 2004
Commercial Octa-BDE[b]	LOEL = 5 mg/kg bw/day	Liver weight: subchronic dietary study (rat)	Health Canada, 2004
Commercial Deca-BDE[c]/ Deca-BDE	LOEL = 2.22 mg/kg bw/day	Developmental behavioural (mouse)	Health Canada, 2004
Penta-BDE	LOEL = 1 mg/kg/day	-	Hellstrom, 2000
Octa-BDE	LOEL = 2 mg/kg/day	-	Hellstrom, 2000
Deca-BDE	LOEL = 100 mg/kg/day	-	Hellstrom, 2000
Penta-BDE	Oral LD-50 = 0.5-5 g/kg bw	Reduced growth, diarrhoea & piloerection (rat)	Darnerud, 2003
Octa-BDE	Oral LD-50 = >2 & >28 g/kg bw	Low skin & eye irritation (rat)	Darnerud, 2003
Deca-BDE	Oral LD-50 = 2 & 5 g/kg bw	Skin irritation & negative chloracnegenic activity	Darnerud, 2003
BDE-99	HBLV = 0.23-0.30 ng/kg bw/day	-	Bakker *et al.*, 2008
BDE-209	RfD (oral exposure) = 7 µg/kg bw/day	-	U.S. EPA, 2008

Note: - = no information given

[a] Commercial Penta-BDE (44-45% penta-BDEs, 41-42% tetra-BDEs & 6-7% hexa-BDEs) (Alaee *et al*., 2003).

[b] Commercial Octa -BDE (>40% BDE-183 & > 30% octa-BDEs) (La Guardia *et al*., 2006).

[c] Commercial Deca-BDE (97-98% BDE-209) (Alaee *et al*., 2003).

1.8 Objectives of this study

PBDEs are of environmental and human health concern due to their potential toxicity, both in humans and animals. They can migrate from the products in which they are used and enter indoor air and dust (ODHS, 2009). Since PBDEs have been extensively used in indoor applications, their levels in indoor environments significantly exceed those outdoors (Wilford *et al.*, 2004; Hazrati and Harrad, 2006). Indoor environments have been recognised recently as important sources of human exposure to PBDEs (Johnson-Restrepo and Kannan, 2009; Jones-Otazo *et al.*, 2005; Wilford *et al.*, 2005, 2004) with toddlers and children experiencing higher exposures than adults owing to their greater ingestion of dust. Individuals who work in jobs like electronics recycling or in manufacturing or disposal of goods containing PBDEs are also at risk of PBDE exposure. Given these concerns, this study will investigate concentrations of PBDEs in a wide variety of home and workplace outdoor/indoor environments in Thailand and the U.K. The overall hypothesis tested in this study is that the application of PBDEs in consumer products and materials is resulting in contamination of indoor environments at concentrations that may be deleterious to human health. The primary objectives of this study are:

- to elucidate potential emission sources of PBDEs existing in UK homes, and in Thai e-waste storage facilities, homes and cars to elucidate the factors influencing levels of PBDEs in indoor environments.
- to investigate the evidence for debromination of PBDEs present in dust.
- to assess the absolute magnitude and relative significance of occupational and non-occupational exposure to PBDEs via air inhalation and dust ingestion within Thai e-waste storage facilities, homes and cars for both adults and children as appropriate.
- to study the extent of within-room, and within-house spatial and temporal variability in concentrations of PBDEs in house dust, and the implications of such variability for source attribution and human exposure.
- to evaluate the hypothesis that at higher dust loadings (g dust per unit surface area), PBDE concentrations in dust are lower.

CHAPTER 2

Sampling and analytical methodology

2.1 Synopsis

In this chapter, the sampling methods and analytical techniques used in the collection, extraction, purification and quantification of the samples studied in this thesis are described, along with the quality control (QC) and quality assurance (QA) measures employed as part of the determination of PBDEs in outdoor air, indoor air and indoor dust.

2.2 Sampling and sample preparation for air samples

2.2.1 Collection of air samples

A total of 18 air samples were collected from 5 electronic waste storage facilities and 3 homes in various provinces in Thailand using PUF (polyurethane foam) disk passive air samplers. The advantages of using passive air samplers are that they are far smaller than high-volume air samplers, more cost-effective than active samplers, reusable, simple to deploy as well as unobtrusive and silent as no pump or power source is required for sampling (Nothstein *et al*., 2000). These attributes of passive samplers enable their widespread deployment in ambient, residential and workplace environments without disrupting day-to-day activities.

PUF disk passive air samplers treated with 10 ng of sampling efficiency standard (SES; PCB 147) were deployed to take outdoor and indoor air samples from electronic waste storage facilities and homes in Thailand during a 47-58 day period in December 5, 2007-February 2, 2008. Each passive air sampler used comprises a PUF disk (approximately 14 cm diameter, 1.2 cm thickness, 360.6 cm^2 surface area, 3.11 g weight, 184 cm^3 volume and 0.01685 g cm^{-3} density) housed within two different size stainless steel chambers to lessen particle deposition and wind effects (Figure 2.1) (Hazrati and Harrad, 2007). Prior to site deployment, the containers were cleaned and hexane rinsed to eliminate contamination. The disks were pre-cleaned via soxhlet extraction with HPLC grade CH_2Cl_2 for 16 hours before air drying at room temperature. PUF disks were wrapped in hexane rinsed aluminium foil and sealed in a polyethylene zip bag before and after deployment. Harvested disks were stored at -18 ^{o}C until analysis.

Figure 2.1 PUF disk passive air sampler*

Note: * Photograph taken at an e-waste storage facility in Ayutthaya Province, Thailand.

On completion of sampling, indoor and outdoor air sampling questionnaires were completed by a researcher. The questionnaire recorded details of the facility or home, sampling location and sampling room specifications (i.e. wind direction and ambient temperature obtained from directly measured meteorological data, room ventilation system, types of room floor, categories of electronic wastes in sampling rooms and any other observations considered relevant). A copy of these questionnaires is provided in Appendix A.

2.2.2 Extraction and purification of air samples

Air samples were extracted and purified using methods described previously (Harrad *et al*., 2006; Harrad and Hunter, 2006). PUF disks were treated with known quantities (10 ng) of each PBDE internal standard ($^{13}C_{12}$-BDEs-28, 47, 99 and 153) and then hot soxhlet extracted with roughly 350 mL of HPLC grade hexane for 8 hours or until 32 cycles of the soxhlet apparatus has been achieved, which is regarded as sufficient to ensure reliable recovery of organic compounds including PBDEs (Erickson, 1997). Following extraction, the crude extracts were reduced in volume to approximately 0.5 mL using a Turbovap^{TM} apparatus. The extracts were then transferred to finger vials and the Turbovap^{TM} tubes rinsed three times with 2 mL of HPLC grade hexane (in total). To eliminate lipid content, extracts were treated with 2 mL concentrated sulfuric acid (Aldrich Chemistry, 99.999%) and shaken twice for 2 minutes. The mixtures were placed in the refrigerator overnight (approximately 24 hours) to facilitate full separation of the hexane from sulfuric acid. To eliminate remaining polar compounds, and as a final purification stage, the hexane layer extracts were eluted through a column containing 1 g of pre-extracted Florisil (Acros Organics; 60-100 mesh, for column chromatography) topped with 1 g of pre-extracted anhydrous sodium sulfate (Fisher Scientific, Analytical reagent grade) with 20 mL of hexane. The eluate was evaporated to incipient dryness by a gentle nitrogen stream, transferred to GC vials and then dissolved in 10 µL of PCB 129 (1 ng/µL in nonane) used as a recovery determination standard (RDS) prior to GC/MS analysis in EI SIM mode.

2.3 Sampling and sample preparation for dust samples

2.3.1 Collection of dust samples

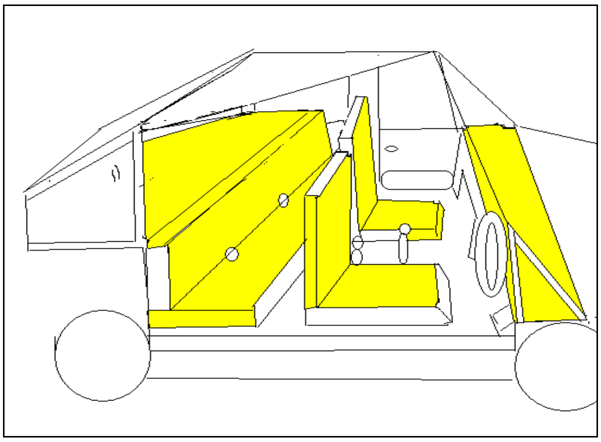
Indoor dust samples were collected from Thai electronic waste storage facilities (n=25), Thai homes (n=53), Thai cars (n=30) and U.K. homes (n=112) using a Hitachi CV-BL16 1600 W (for Thai dust sampling) and a Nilfisk Sprint Plus 1600 W vacuum cleaner (for U.K. dust sampling). The vacuum cleaners were deployed to sample dust into a 25 µm pore size nylon sock and were cleaned between sample collections to prevent cross contamination. In each facility and home, four m^2 of bare floor or one m^2 of carpeted floor was thoroughly and evenly vacuumed for exactly 4 or 2 minutes respectively (Figure 2.2). Also in each car, the front and rear seats, parcel shelf and dashboard (Figure 2.3) were thoroughly and evenly vacuumed for exactly 2 minutes. After collection, samples were stored at -18^{o}C. All dust samples were passed through a pre-cleaned and hexane rinsed 500 µm mesh sieve, homogenized thoroughly, weighed and immediately transferred to clean, hexane rinsed glass vials prior to analysis. Furthermore, indoor dust sampling questionnaires were used to collect basic information about the electronic waste storage facilities, homes, cars and sampling rooms (i.e., car manufacturer, room ventilation, room flooring and types of electronic wastes in the sampling rooms). A copy of these questionnaires is presented in Appendix A.

The data recorded in the questionnaires were used in subsequent chapters. For example, room characteristics including floor type as well as number and type of electrical and electronic equipment in rooms monitored were used in the temporal and spatial variability studies described in Chapter 5.

Figure 2.2 Indoor dust sampling*

Note: * Photograph taken at an e-waste storage facility in Nontaburi Province, Thailand.

Figure 2.3 Dust sampling areas (highlighted in yellow) within a car*



Note: * If present, the child seats were removed before sampling.

Source: Goosey, 2009.

2.3.2 Extraction and purification of dust samples

The extraction and purification method employed in this study is based on that developed previously by Harrad *et al.* (2006), with some minor modifications to enhance recovery of PBDEs. Accurately weighed 0.15-0.25 g aliquots of each dust sample were extracted with HPLC grade hexane by pressurised liquid extraction (Dionex ASE300) system, using a 66 mL cell filled from the bottom with 1.5 g of pre-extracted Florisil, pre-extracted Hydromatrix (a solid support for extractions and purifications; Varian Inc.), dust sample spiked with 10 ng of each PBDE internal standard ($^{13}C_{12}$-BDEs-28, 47, 99 and 153) and pre-extracted Hydromatrix. Extraction conditions were: temperature 100 ^{0}C, pressure 1500 psi, heat time 5 minutes, static time 4 minutes, flush volume 60%, purge time 60 seconds, static cycles 3. Following extraction, the crude extracts were purified by the same methods used for air sample purification. Briefly, the extracts were reduced in volume to 0.5 mL on a Turbovap^{TM} apparatus and treated with 2 mL of concentrated sulfuric acid prior to elution through a column containing 1 g of pre-extracted Florisil, topped with 1 g of pre-extracted anhydrous sodium sulfate with 20 mL of HPLC grade hexane. The eluate was reduced under a gentle stream of nitrogen to incipient dryness before addition of 20 µL of n-nonane containing 10 ng of PCB 129 as recovery determination standard (RDS). The samples were reduced under nitrogen to 25 µL with 1 µL injected onto the GC/MS.

2.4 GC/MS analysis of PBDEs

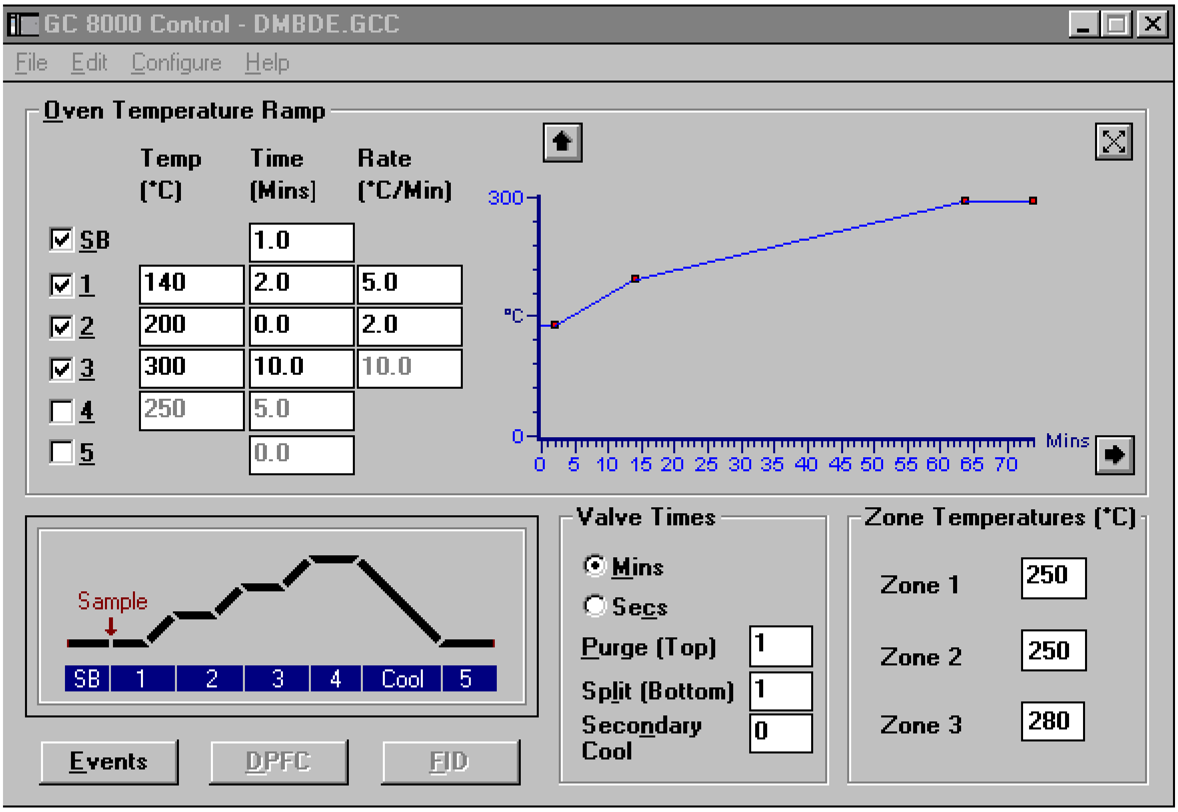
In this study, air samples as well as house and car dust samples were investigated for ten PBDE congeners (Σ_{10}PBDEs; BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154); whilst twenty-one PBDE congeners (Σ_{21}PBDEs = Σ_{10}PBDEs + BDEs 181, 183, 184, 191, 196, 197, 203, 206, 207, 208 and 209), decabromodiphenylethane (DBDPE) and decabromobiphenyl (BB 209) were determined in workplace dust samples (n=25).

GC-MS measurement of tri- to hexa-BDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154; Σ_{10}PBDEs) was carried out as for air and dust samples at University of Birmingham. Quantification of hepta- to deca-BDEs (BDEs 181, 183, 184, 191, 196, 197, 203, 206, 207, 208 and 209), DBDPE and BB 209 in workplace dust samples (n=25) was conducted by scientists at the University of Antwerp, Belgium in accordance with previously published analytical methods (Covaci *et al*., 2005).

At the University of Birmingham, all PBDE analyses were performed on a Fisons GC8000 gas chromatograph coupled to a Fisons MD800 mass spectrometer equipped with an AS800 autosampler. The MS was run in electron impact ionization (EI^+) mode and helium used as carrier gas. Before analysis of each batch of samples, the MS was manually tuned using perfluorotributylamine ($C_{12}F_{27}N$; PFTBA; Heptacosa) as a reference compound over the mass range of 69, 219, 264 and 502 amu to obtain optimum sensitivity, resolution and performance by varying certain parameters including ion energy, ion energy ramp, ion repeller, lens voltage as well as high and low mass resolution. These tuning parameters were adjusted to achieve relative abundances of about 100, 40, 10 and 2% for the masses 69, 219, 264 and 502 amu, respectively.

The Fisons' MD-800 GC/MS system was fitted with a 60 m factorFour VF5 MS column (Varian, Inc; 0.25mm id, 0.25 µm film thickness) consisting of a 5% Phenyl Methyl Siloxane stationary phase. A 1µL aliquot of prepared sample extract was injected onto the column in splitless mode at an injector and interface temperature of 280 ^{0}C. Helium head pressure of 180 kpa was applied, yielding a linear flow rate of 22 to 27 cm s^{-1} during an oven temperature program of 140 ^{0}C for 2 minutes; 5 ^{0}C minute^{-1} ramp to 200 ^{0}C; 2 ^{0}C minute^{-1} to 300 ^{0}C and held for 10 minutes, as illustrated in Figure 2.4. The MS was operated in 5 acquisition groups in EI selected ion monitoring (SIM) mode (ionization voltage, 70 eV; ion source temperature = 200 ^{0}C) to monitor the two most abundant ions from each PBDE homologue group and QA/QC standards, 20 ions in total (for BDE-17, -28 and $^{13}C_{12}$-BDE-28: 405.8, 407.8, 417.8 and 419.8; BDE-47, -49, -66 and $^{13}C_{12}$-BDE-47: 485.8, 487.8, 495.8, 497.8; BDE-85, -99, -100 and $^{13}C_{12}$-BDE-99: 403.8, 405.8, 415.8, 417.8; and BDE-153, -154 and $^{13}C_{12}$-BDE-153: 481.7, 483.7, 493.7, 495.7; plus for QA/QC PCB standards 147 (sampling efficiency standard; SES) and 129 (recovery determination standard; RDS): 255.95, 257.95, 359.9 and 361.9) (Table 2.1).

Figure 2.4 GC temperature program for PBDE analysis



Oven Temperature Ramp

	Temp (°C)	Time (Mins)	Rate (°C/Min)
☑ SB		1.0	
☑ 1	140	2.0	5.0
☑ 2	200	0.0	2.0
☑ 3	300	10.0	10.0
☐ 4	250	5.0	
☐ 5		0.0	

Valve Times

● Mins
○ Secs
Purge (Top) 1
Split (Bottom) 1
Secondary Cool 0

Zone Temperatures (°C)

Zone 1 250
Zone 2 250
Zone 3 280

Table 2.1 Mass ions monitored in SIM for PBDE analysis

PBDEs	Molecular weight		Ions monitored from molecule cluster			
			Quantification ion		Secondary ion (abundance %)	
Tri-BDEs (BDEs 17 & 28)	Native	404	405.8	$(M+2)^+$	407.8 (97)	$(M+4)^+$
	Labeled	414	417.8		419.8	
Tetra-BDEs (BDEs 47, 49 & 66)	Native	482	485.8	$(M+2)^+$	487.8 (71)	$(M+2)^+$
	Labeled	492	495.8		497.8	
Penta-BDEs (BDEs 85, 99 & 100)	Native	560	403.8	$(M+2-Br_2)^+$	405.8 (98)	$(M+4-Br_2)^+$
	Labeled	570	415.8		417.8	
Hexa-BDEs (BDEs 153 & 154)	Native	638	481.7	$(M+2-Br_2)^+$	483.7 (77)	$(M+4-Br_2)^+$
	Labeled	648	493.7		495.7	
Hexa-CB (PCB 147) (Sampling Efficiency Standard; SES)	Native	360	255.95	$(M)^+$	257.95 (97)	$(M+2)^+$
Hexa-CB (PCB 129) (Recovery Determination Standard; RDS)	Native	360	359.9	$(M)^+$	361.90 (80)	$(M+2)^+$

Source: Modified from Hazrati, 2006.

A total of 10 PBDE congeners were analysed in each sample, and Σ_{10}PBDEs was defined as the sum of BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154. The most abundant ion for each homologue group was used for the peak integration, whilst the second ion peak was used as a check.

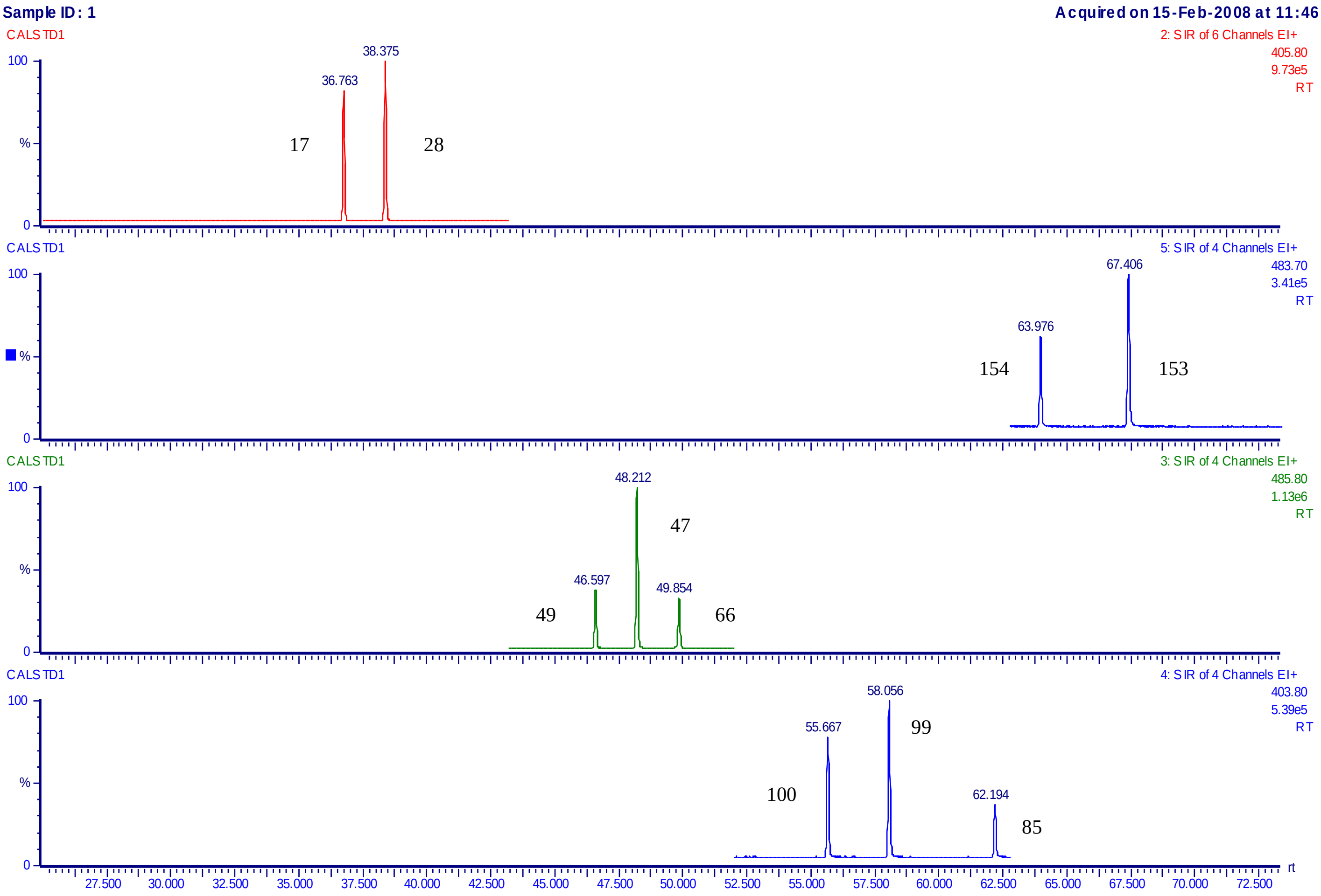
In order to assess the linearity of the MS response over the concentration range of PBDEs in air and dust samples, a full 6-point calibration was carried out prior to analysis of each batch of samples. Apart from the IS ($^{13}C_{12}$-BDEs-28, 47, 99 and 153), SES (PCB 147) and RDS (PCB 129) congeners kept constant at 500 pg μL^{-1} through all of the 6 points, each calibration standard comprised 10 native PBDE congeners (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154) at 18, 180, 250, 500, 1000 and 2000 pg μL^{-1}.

Additionally, a single point calibration (500 pg μL^{-1}) was conducted at the beginning and end of each sample batch for PBDE quantification in that sample batch and for calculation of relative response factor (RRF) values for each congener. This standard solution consisted of the 4 ISs, SES and RDS congeners as well as the PBDE native BDEs 17, 28, 49, 47, 66, 100, 99, 85, 154 and 153; based on retention time order.

As a quality control/quality assurance (QC/QA) measures, chromatographic peaks were only accepted as PBDEs for quantification if the following criteria were met:

1. The signal to noise ratios (S/N) for the least abundant ion exceeded 3:1
2. The bromine isotope ratios for peaks were within ± 20% of those obtained for the two calibration standards run in the same batch as the samples.
3. The relative retention time (RRT) of the peak in the sample was within ± 0.2% of the average value determined for same congener in the 2 calibration standards conducted for that sample batch. When the standard was not available, the congeners were identified and quantified via literature-derived relative retention times, as shown in Figure 2.5.

Figure 2.5 Chromatogram showing elution of target PBDE congener standards



2.5 Quantification of PBDE congeners using the internal standard technique

2.5.1 Internal standard (IS)

Standard solutions of PBDE congeners were used to evaluate the efficiency of the method as well as to quantify PBDEs in the collected air and dust samples. These congeners were chosen for various reasons. It was important that they were representative of the homologue group, that they gave well-resolved chromatographic peaks and that they were not present in environmental samples. In this study, congeners used as standards are exhibited in Table 2.2.

Since the quantification methods with the use of isotope-labelled internal standard solutions employed in this study intrinsically correct for any losses of target PBDE congeners, no correction of concentrations for recovery are needed. Four isotopically labelled congeners, $^{13}C_{12}$-BDEs-28, 47, 99 and 153, were chosen to act as internal/surrogate standards for quantification of tri-, tetra-, penta- and hexa-BDEs respectively (Table 2.2). Each IS was representative of a PBDE homologue group or similar physicochemical properties.

Table 2.2 Congeners used as IS, RDS and SES for PBDE analysis

Congener	Bromine/chlorine position	Standard Use
$^{13}C_{12}$-BDE-28	2, 4, 4’	IS for tri-BDEs (BDEs 17 & 28)
$^{13}C_{12}$-BDE-47	2, 4, 2’, 4’	IS for tetra-BDEs (BDEs 47, 49 & 66)
$^{13}C_{12}$-BDE-99	2, 4, 5, 2’, 4’	IS for penta-BDEs (BDEs 85, 99 & 100)
$^{13}C_{12}$-BDE-153	2, 4, 5, 2’, 4’, 5’	IS for hexa-BDEs (BDEs 153 & 154)
PCB 129	2, 3, 4, 5, 2’, 3’	RDS for $^{13}C_{12}$-BDEs-28, 47, 99 and 153
PCB 147	2, 3, 5, 6, 2’, 4’	SES for all PBDEs

Source: Modified from Hazrati, 2006.

Quantification of individual PBDE congeners in collected environmental samples such as air and dust samples was carried out in relation to the IS of the appropriate homologue group. All air and dust samples were spiked with 10 ng of IS before soxhlet and pressurized liquid extraction respectively. Loss of individual PBDE congeners during extraction and purification of these samples was assumed to be the same as that of the IS congener of the appropriate homologue group owing to the similarity in physicochemical properties, especially vapour pressure among congeners of the same homologue group.

To determine concentrations of PBDEs, relative response factors (RRFs) were calculated for each congener contained in the calibration standard which was run at the beginning and end of each batch of samples via equation 2.1.

$$RRF = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{IS}}{C_{NAT}} \qquad \text{(Equation 2.1)}$$

Where A_{NAT} is the peak area for the target (native) PBDE congener in the standard; A_{IS} is the peak area of the corresponding internal standard congener in the standard; C_{IS} is the concentration of the internal standard congener in the standard; and C_{NAT} is the concentration of the target (native) PBDE congener in the standard. Once the RRFs had been calculated, concentration of PBDEs in each sample was then determined using equation 2.2.

$$Concentration = \frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS} \qquad \text{(Equation 2.2)}$$

Where A_{NAT} is the peak area of the target (native) PBDE congener in the sample; A_{IS} is the peak area of the internal standard in the sample; RRF is the relative response factor for the target (native) PBDE congener obtained from the calibration standard (Equation 2.1); M_{IS} is the mass of the internal standard added to sample (pg) and SS is the sample size (m^3 for air samples and g for dust samples and standard reference materials (SRMs)). The sample size for PUF passive air samples was defined as equivalent volume of air sampled by the PUF disks for each PBDE congener during the sampling period. Based on the previously published studies relating to sampling rates of similar PUF disk passive air samplers, sampling rates of $1.66\ m^3\ d^{-1}$ and $4\ m^3\ d^{-1}$ were used to calculate PBDE concentrations in indoor and outdoor air respectively (Hazrati and Harrad, 2007; Jaward *et al*., 2004).

2.5.2 Sampling efficiency standard (SES)

To evaluate any losses of PBDEs during air sampling period and sample preparation prior to addition of IS and soxhlet extraction, 10 ng of sampling efficiency standard (SES)-PCB 147 was added to each PUF disk passive air sampler before site deployment. PCB 147 (hexachlorobiphenyl) represented loss of tri through hexabrominated diphenyl ethers. In view of the fact that the use of the SES was solely for QA/QC purposes rather than for quantification, one SES congener was assumed sufficient.

2.5.3 Recovery determination standard (RDS)

Total losses of both IS and SES congener during sample preparation or sampling were determined by comparing the IS and SES against the RDS (recovery determination standard) contained PCB 129 (hexachlorobiphenyl). A known amount (accurately known and usually 10 ng) of the RDS- PCB 129 was added immediately to all air and dust samples at the final stage prior to GC/MS analysis so that any losses following the addition of the SES and IS can be evaluated. PCB 129 was used to compare loss of all PBDE congeners in the IS and SES (e.g. $^{13}C_{12}$-BDEs-28, 47, 99 and 153). The RDS was assumed to suffer zero loss because it was added at the final clean up stage before GC/MS analysis. The recoveries of ISs for each sample were calculated by equation 2.3.

$$\%Recovery = \left[\left(\frac{A_{IS}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{IS}}\right)_{STD}\right] \times \left[\left(\frac{C_{IS}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{IS}}\right)_S\right] \times 100 \qquad \text{(Equation 2.3)}$$

Where $(A_{IS}/A_{RDS})_S$ is the ratio of the IS peak area to RDS peak area in the sample; $(A_{RDS}/A_{IS})_{STD}$ is the ratio of the RDS peak area to IS peak area in the calibration standard (the average of values obtained for both calibration standards carried out for a batch of samples was used); $(C_{IS}/C_{RDS})_{STD}$ is the concentration ratio of the IS to RDS in the calibration standard; and $(C_{RDS}/C_{IS})_S$ is the concentration ratio of the RDS to IS in the sample.

For air sampling, the recoveries of SESs were subsequently calculated using equation 2.4.

$$\%SES \;\; Recovery = \left[\left(\frac{A_{SES}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{SES}}\right)_{STD} \times \left(\frac{C_{SES}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{SES}}\right)_S\right] \times 100 \qquad \text{(Equation 2.4)}$$

Where $(A_{SES}/A_{RDS})_S$ is the ratio of the SES peak area to RDS peak area in the sample; $(A_{RDS}/A_{SES})_{STD}$ is the ratio of the RDS peak area to SES peak area in the calibration standard (the average of values obtained for both calibration standards conducted for a batch of samples was used); $(C_{SES}/C_{RDS})_{STD}$ is the concentration ratio of the SES to RDS in the calibration standard; and $(C_{RDS}/C_{SES})_S$ is the concentration ratio of the RDS to SES in the sample (assuming 100% recovery).

For air sampling again, the percentage recovery during sampling only (%S Recovery) could be examined via equation 2.5.

$$\%S\ Recovery = \frac{Rec_{SES}}{Rec_{IS}} \times 100 \qquad \text{(Equation 2.5)}$$

Where Rec_{SES} is the SES recovery given by equation 2.4 and Rec_{IS} is the IS recovery given by equation 2.3.

2.6 Validation of analytical protocols

2.6.1 Standard reference material (SRM)

In this study, aliquots of SRM 2585 indoor dust reference material from the U.S. Department of Commerce, National Institute of Standards and Technology (NIST) were used to determine the accuracy and precision of the method for tri- through hexa-BDEs at the University of Birmingham. The results of twelve replicates along with the certified values for selected PBDE congeners in SRM 2585 are provided in Table 2.3. The data presented here indicate good agreement between measured values and those certified for SRM 2585. Very low levels of RSDs obtained for measured PBDE congeners (on average 9.1%) underline the precision of the method. Furthermore, low deviations from certified values (on average 8.6%) given as $\left[\left(\left|Measured - Certified\right| / Certified\right) \times 100\right]$ for PBDEs underline good accuracy for the analytical method. Nevertheless, the method was found to overestimate concentrations of BDE 17.

Table 2.3 Concentrations (ng g^{-1} d.w.) of PBDE congeners determined at the Univeristy of Birmingham in SRM 2585 (house dust) compared to the certified values

Congener/ sample	17	28	49	47	66	100	99	85	154	153
SRM 2585-1	11	45	48	429	31	141	754	41	81	110
SRM 2585-2	12	43	47	444	34	129	781	44	101	131
SRM 2585-3	16	43	58	465	32	131	831	46	86	100
SRM 2585-4	16	43	57	404	34	153	781	39	98	120
SRM 2585-5	16	48	60	409	33	135	792	38	86	115
SRM 2585-6	12	45	47	423	36	168	902	41	83	100
SRM 2585-7	16	46	57	454	34	103	808	38	92	128
SRM 2585-8	15	49	55	479	27	153	814	36	89	138
SRM 2585-9	18	50	64	437	35	139	880	38	77	103
SRM 2585-10	16	49	59	467	36	152	834	43	86	120
SRM 2585-11	17	45	55	427	35	146	885	44	84	117
SRM 2585-12	19	51	62	485	32	125	847	32	95	110
Average-SRM	15.3	46.4	55.9	443.4	33.2	139.6	825.7	39.9	88.1	115.9
SD	2.4	2.8	5.6	26.8	2.5	16.9	46.3	3.8	7.0	12.3
RSD (%)	15.5	6.1	10.1	6.0	7.5	12.1	5.6	9.6	7.9	10.6
Deviation from certified values (%)	33.0	-1.1	4.5	-10.8	-	-3.7	-7.4	-8.9	5.5	-2.6
Certified average	11.5	46.9	53.5	497	na	145	892	43.8	83.5	119
Certified SD	1.2	4.4	4.2	46	na	11	53	1.6	2	1
Certified RSD (%)	10.4	9.4	7.9	9.3	-	7.6	5.9	3.7	2.4	0.84

Note: na = no data available.

At the University of Antwerp, aliquots of SRM 2584 indoor dust reference material were used to measure the accuracy and precision of the method for hepta- and deca-BDEs. Method accuracy and precision is indicated by the good agreement between measured values (n=10) and those indicative for SRM 2584 (Table 2.4). Very low levels of RSDs obtained for measured PBDE congeners (on average 9.5%) and very low deviations from indicative values (on average 4.9%) given as $\left[\left(\left|Measured - Indicative\right| / Indicative\right)\times 100\right]$ for PBDEs underline the precision of the method and the good accuracy for the analytical method respectively.

Table 2.4 Concentrations (ng g^{-1} d.w.) of BDE-183 and BDE-209 determined at the University of Antwerp in SRM 2584 (indoor dust) compared to the indicative values

Congener/sample	183	209
SRM 2584-1	38	2493
SRM 2584-2	30	2211
SRM 2584-3	31	2089
SRM 2584-4	31	1969
SRM 2584-5	38	1895
SRM 2584-6	31	2383
SRM 2584-7	33	2151
SRM 2584-8	31	2502
SRM 2584-9	32	2000
SRM 2584-10	35	2081
Average-SRM	33	2177
SD	3.0	216
RSD (%)	9.0	10
Deviation from indicative values (%)	3.1	-6.6
Indicative average	32	2330
Indicative SD	4.0	210
Indicative RSD (%)	12.5	9.0

Note: Indicative values in SRM 2584 are reported by Stapleton *et al*. (2005b).

2.6.2 Recoveries of SESs and ISs

As described previously in section 2.5, all PUF disk passive air samplers as well as air and dust samples were spiked with 10 ng of SES and IS congeners before field sampling and extraction, respectively. Given that they are used for QA/QC purposes, the percentage recoveries of ISs and SESs were determined by equations 2.3 and 2.4. The results obtained for outdoor and indoor air as well as for indoor dust samples are shown in Table 2.5 and 2.6 respectively. The percentage recoveries of SESs and ISs for air samples were typically 60% and 70%, while the percentage recoveries of ISs for dust samples were typically 73%, suggesting overall good recoveries of PBDEs from both passive air and indoor dust samples.

Table 2.5 Recoveries of SESs and ISs for air samples (n=21)

	Congener				
	PCB 147[a]	**$^{13}C_{12}$-BDE-28**[b]	**$^{13}C_{12}$-BDE-47**[b]	**$^{13}C_{12}$-BDE-99**[b]	**$^{13}C_{12}$-BDE-153**[b]
Average	60	69	72	73	66
SD	14	11	10	15	9
Min	38	53	58	54	50
Max	93	91	92	108	83
RSD	24	16	14	21	14

[a] = SES
[b] = IS

Table 2.6 Recoveries of ISs for indoor dust samples (n=223)

	$^{13}C_{12}$-BDE congener (IS)			
	28	**47**	**99**	**153**
Average	70	74	77	71
SD	14	14	15	14
Min	41	31	13	25
Max	93	99	105	92
RSD	20	19	19	19

2.6.3 Field and method blank analysis

In order to estimate transport and field handling bias in air sampling technique (Vonderheide, 2009), field blanks (n=3) comprising a PUF disk (treated in identical fashion to those used for sampling and also transported to/from sampling locations, except that no air was aspirated through them) were found to contain levels of tri- to hexa-BDEs no higher than 5% of the levels detected in the corresponding air samples (Table 2.7). Moreover, a method blank (n=45) consisting of 1 g of pre-extracted sodium sulfate (treated and analyzed with the same method as the real samples) was run with each batch of 5 samples to evaluate the response of entire laboratory analytical system for the dust analysis procedures (Vonderheide, 2009). The method blanks were typically found to contain less than 5% of the PBDE concentrations in the majority of indoor dust samples (Table 2.8). Hence, the data reported in this study were not corrected for blank concentrations.

Table 2.7 Mass (pg) of PBDEs in field blanks (n=3)

PBDE congener	Average	SD	Min	Max
17	nd	nd	nd	nd
28	0.04	0.07	nd	0.12
47	0.59	0.55	nd	1.09
49	nd	nd	nd	nd
66	nd	nd	nd	nd
85	0.34	0.58	nd	1.01
99	0.83	0.94	nd	1.85
100	nd	nd	nd	nd
153	0.04	0.08	nd	0.13
154	nd	nd	nd	nd

nd = Not detectable (the detection limit for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 was 0.1 pg m^{-3}).

Table 2.8 Mass (pg) of PBDEs in method blanks (n=45)

PBDE congener	Average	SD	Min	Max
17	0.06	0.15	nd	0.47
28	0.07	0.20	nd	0.83
47	0.65	1.03	nd	2.91
49	0.08	0.37	nd	1.89
66	0.17	0.54	nd	2.60
85	0.42	1.26	nd	3.55
99	1.01	1.59	nd	6.12
100	0.19	0.68	nd	2.27
153	0.23	1.11	nd	4.06
154	0.12	0.72	nd	3.34

nd = Not detectable (the detection limit for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 in workplace dust and house and car dust was 0.5 and 0.03 ng g^{-1} dust respectively).

2.7 Data and statistical analysis

Throughout the study, statistical tests were conducted using SPSS version 17.0 for Windows at a significance level of $\alpha = 0.05$. Probability values less than 0.05 ($p<0.05$) were considered as statistically significant. A one-way analysis of variance (ANOVA), simple linear regression analysis, Kolmogorov-Smirnov (KS) test, t-test analysis and principal component analysis (PCA) was used for statistical analysis of a data set.

CHAPTER 3

Concentrations of PBDEs and the other brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand

3.1 Synopsis

This chapter presents concentrations of tri- to hexa-BDEs in outdoor and indoor air as well as tri- to deca-BDEs and the selected other brominated flame retardants (BFRs) in indoor dust samples collected from 5 Thai electronic waste (e-waste) storage facilities. The hypothesis tested in this chapter is that BFRs present in the stored e-waste will migrate into the surrounding environment, leading to elevated concentrations in air and dust, with concomitant impications for occupational exposure. Relationships between the type of e-waste stored in a room or facility and the BFRs detected in associated air and dust samples will also be explored. Ten PBDE congeners (Σ_{10}PBDEs) present predominantly in the penta-BDE formulation (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154) were measured in air samples; while dust samples were monitored for decabromodiphenylethane (DBDPE), decabromobiphenyl (BB209) and twenty-one PBDE congeners (Σ_{21}PBDEs = Σ_{10}PBDEs + BDEs 181, 183, 184, 191, 196, 197, 203, 206, 207, 208 and 209). Comparison data from studies of outdoor air, indoor air and indoor dust from other countries is also provided. Furthermore, occupational exposure to PBDEs via air inhalation and dust ingestion is estimated based on concentrations detected in the investigated air and dust samples, respectively.

3.2 Sampling protocol and locations

PUF (polyurethane foam) disk passive air samplers (Figure 3.1a and 3.1b) treated with 10 ng of sampling efficiency standard (SES; PCB 147) were deployed to take 10 outdoor air samples both upwind and downwind of 5 electronic waste storage facilities in Thailand (see Figure 3.2). Additionally, one indoor air sample was taken at each of these facilities. Both indoor and outdoor air samples were taken over a 49-58 day period in December 2007-February 2008. As well as these air samples, indoor dust samples (n=25) were collected from facilities 1-3 in Ayutthaya Province and facility 4 in Nonthaburi Province (Figure 3.2) using a

Hitachi CV-BL16 1600 W vacuum cleaner via a methodology previously described in Chapter 2. Meanwhile, the sampling questionnaires for outdoor air, indoor air and indoor dust (see Questionnaire 1-3 in Appendix A) were filled-out by the researcher. All samples were shipped to Birmingham for analysis. GC-MS determination of tri- to hexa-BDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154; Σ_{10}PBDEs) was conducted as for air and dust samples at University of Birmingham. Analysis of other BFRs (hepta- to deca-BDEs; BDEs 181, 183, 184, 191, 196, 197, 203, 206, 207, 208 and 209, DBDPE and BB 209) in dust samples was conducted by researchers at the University of Antwerp in accordance with previously published methods (Covaci *et al.*, 2005). Details of the monitored air and dust samples are given in Appendix B.

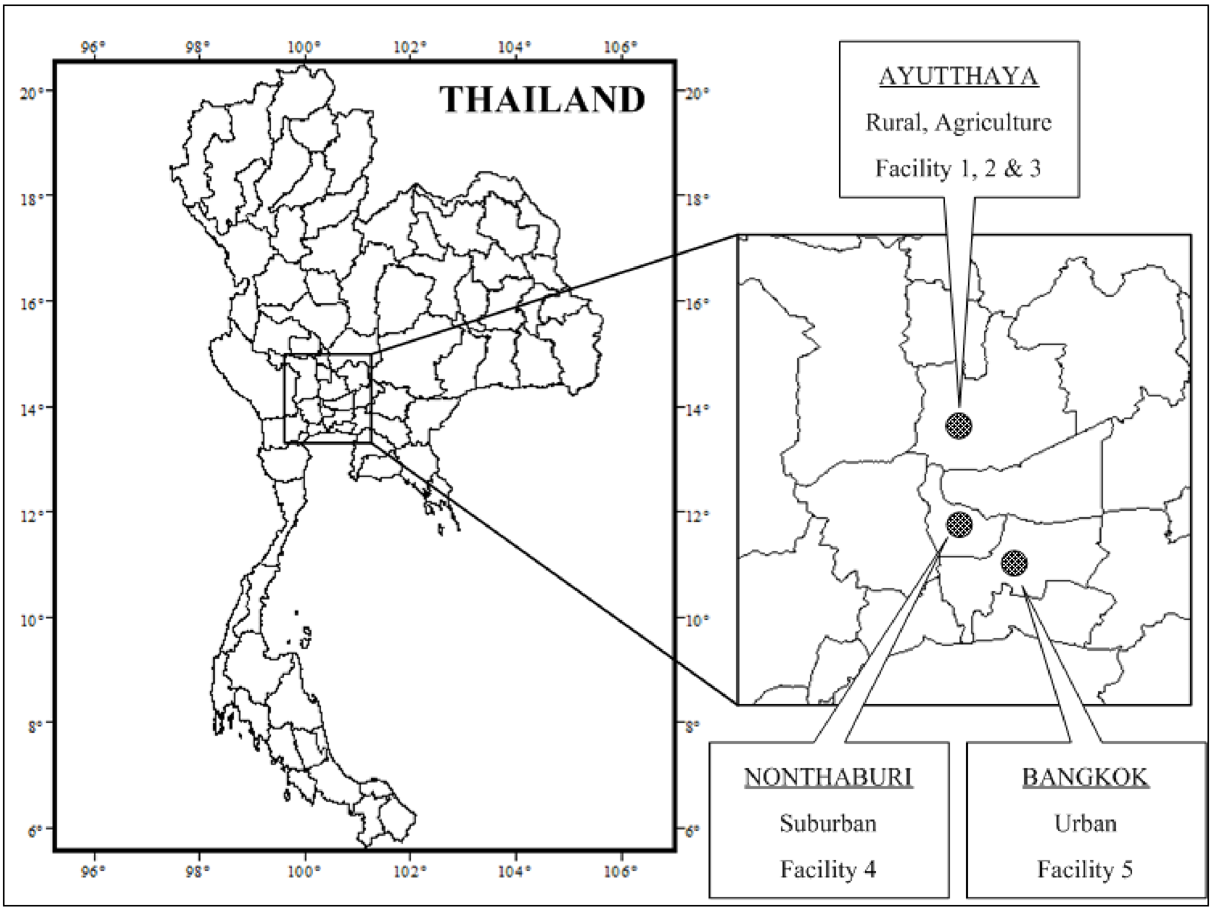
Figure 3.1a PUF disk sampler deployed at outdoor air location*

Note: * Photograph taken at an e-waste storage facility in Ayutthaya Province, Thailand.

Figure 3.1b PUF disk sampler deployed at indoor air location*

Note: * Photograph taken at an e-waste storage facility in Nontaburi Province, Thailand.

Figure 3.2 Map of air and dust sampling locations in Thailand



3.3 Results and discussion

3.3.1 Concentrations of tri- to hexa-BDEs (Σ_{10}PBDEs) in air samples

Passive air sampling rates of 1.66 m^3 d^{-1} and 4 m^3 d^{-1} were used to determine PBDE concentrations for indoor and outdoor air based on previously reported sampling rates of PBDEs by identical PUF disk sampler configurations (Hazrati and Harrad, 2007; Jaward *et al*., 2004). Concentrations of Σ_{10}PBDEs in outdoor air samples in the vicinity of e-waste storage facilities ranged from 8 to 150 pg m^{-3} (Table 3.1). Indoor air concentrations ranged from 46 to 350 pg m^{-3}, with the highest concentration detected in a room storing personal computer (PC) and printer waste at an e-waste storage facility. The most abundant congeners in both outdoor and indoor air samples were BDE-47 and BDE-99. The PBDE concentrations in outdoor and indoor air reported here were substantially lower than those observed in Swedish and American electronic recycling facilities as well as Chinese electronic waste recycling sites (Table 3.1) (Chen *et al*., 2008; Cahill *et al*., 2007; Deng *et al*., 2007; Julander *et al*., 2005; Pettersson-Julander *et al*., 2004; Sjodin *et al*., 2001). Outdoor and indoor air in these other studies was sampled using active air samplers and included the particle-bound phase. As PUF disk passive air samplers sample the particle phase ineffectively (Batterman *et al*., 2009), and the proportion of tetra- to hexa-BDEs associated with the particle phase of indoor air varies between 14% and 80% (Harrad *et al*., 2004); the lower concentrations in this study may to some extent be attributable to the fact that the PUF disk samplers used underestimated particle-bound PBDEs. Nevertheless, it is noted that these samplers also collect to some degree particle-phase PBDEs (Hazrati and Harrad, 2007), that the prevailing temperatures in this study would favour partition to the vapour phase, and that the levels in this study exceeded those reported for urban background UK outdoor and indoor air using the same sampler configuration (Harrad *et al*., 2006; Harrad and Hunter, 2006). It is believed that the far lower atmospheric PBDE levels in this study are partly because of the much lower use in Asia of the Penta-BDE product compared to North America (BSEF, 2001), and partly owing to the fact that unlike in the other studies, in the facilities studied here, e-waste was only stored and not dismantled.

It is hypothesised that concentrations of Σ_{10}PBDEs in indoor air at e-waste storage plants would exceed substantially those in outdoor air as a consequence of volatilisation of PBDEs from the indoor stored e-wastes. The results show that indoor concentrations are generally higher than those outdoors, although the difference is not dramatic for these facilities (Table 3.1). This could possibly be ascribed to meteorological and physical facility conditions, which might affect the concentrations of PBDEs in indoor and outdoor air. In this respect, almost all of the e-waste storage plants use open barns with a varying number of walls, which resulted in good air ventilation and substantial outdoor-indoor air exchange. High average ambient temperatures (26.3-28.4 ^{0}C) during the sampling campaign (December 2007-February 2008) may also cause wide distribution of PBDEs throughout the studied areas owing to high volatilization. Moreover, some outdoor air sampling locations for facilities 2, 4 and 5 were located close to the PBDE emission sources.

Based on wind direction data directly measured during the sampling period for the e-waste sites monitored (Meteorological Department, 2010; Pollution Control Department (PCD), 2011), the downwind concentrations at two e-waste storage facilities (facilities 1 and 3) exceed those analyzed upwind, indicating that these facilities represent a source of PBDEs to the outdoor environment. Interestingly, the Σ_{10}PBDE levels at the other 3 plants are lower at the downwind sites than the upwind sites. Possible reasons for this are: (a) the upwind sampling location for facility 4 is the drop off point where all used electronic and electrical device donations arrive, and is located close to a fridge and washing machine waste storage room; and (b) the upwind sampling locations for plants 2 and 5 are near e-waste piles. In both instances, the outdoor sampling locations are likely to be influenced strongly by their proximity to e-waste point sources.

Table 3.1 Concentrations of PBDEs (pg m^{-3}) in air samples from Thai e-waste storage facilities and other relevant microenvironments

Congener/Location	17	28	47	49	66	85	99	100	153	154	Σ_{10} PBDEs[a]
Thailand, this study, Indoor & outdoor air, E-waste storage facilities, n=15											
Facility 1, Indoor air (PC & printer wastes)	0.80	2.6	13	1.4	0.34	0.05	11	0.60	14	3.0	46
Facility 1, Outdoor air, Upwind	0.93	1.4	12	0.13	1.6	0.05	4.9	2.2	0.71	0.52	24
Facility 1, Outdoor air, Downwind	0.59	3.8	20	3.4	1.3	3.9	11	5.5	20	5.0	75
Facility 2, Indoor air (Portable TV wastes)	0.55	1.8	9.8	0.26	0.71	0.22	15	4.3	9.9	9.3	52
Facility 2, Outdoor air, Upwind	0.29	0.74	5.0	0.21	0.47	0.80	3.5	0.70	0.32	<0.1	12
Facility 2, Outdoor air, Downwind	0.29	1.1	2.9	0.19	0.29	0.12	1.4	0.17	1.0	0.59	8
Facility 3, Indoor air (PC & TV wastes)	2.2	8.9	49	4.6	3.3	2.6	31	8.5	18	13	140
Facility 3, Outdoor air, Upwind	0.82	3.1	17	3.8	1.9	0.70	23	9.4	0.93	0.77	61
Facility 3, Outdoor air, Downwind	0.86	5.8	46	5.9	3.1	2.3	29	1.1	8.1	5.3	110
Facility 4, Indoor air (PC & printer wastes)	0.99	5.3	84	6.2	4.4	7.2	170	30	20	18	350
Facility 4, Outdoor air, Upwind	0.66	2.8	40	3.2	2.1	4.2	73	12	7.2	6.6	150
Facility 4, Outdoor air, Downwind	0.41	1.5	13	1.7	0.87	2.4	27	4.7	2.9	2.5	57
Facility 5, Indoor air (PC wastes)	2.4	9.5	14	3.7	2.6	3.9	5.2	1.8	1.8	1.5	46
Facility 5, Outdoor air, Upwind	0.36	1.2	9.6	0.71	1.1	0.25	6.8	8.5	3.1	1.7	33
Facility 5, Outdoor air, Downwind	0.25	0.93	3.8	0.82	0.66	0.71	8.8	3.8	1.6	1.3	23
Average[b]	0.82	3.4	23	2.4	1.6	2.0	28	6.3	7.3	4.6	79
σ^{b}_{n}	0.64	2.8	22	2.1	1.2	2.1	43	7.6	7.3	5.1	85
Median[b]	0.66	2.6	13	1.7	1.3	0.80	11	4.3	3.1	2.5	52
Minimum	0.25	0.74	2.9	0.13	0.29	0.05	1.4	0.17	0.32	<0.1	8
Maximum	2.4	9.5	84	6.2	4.4	7.2	169	30	20	18	350
Percentile 5[b]	0.28	0.87	3.5	0.17	0.33	0.05	2.9	0.47	0.59	0.38	11
Percentile 95[b]	2.2	9.1	59	6.0	3.6	5.1	101	18	20	14	210
Guangzhou, China, Indoor air, Workplace office, n=6 (Chen *et al*., 2008)											
Average	-	151	1329	-	73	15	473	85	45	24	-
σ_{n}	-	165	1974	-	108	20	657	118	81	32	-
Median	-	79	230	-	30	5.4	128	19	12	8.6	-
Minimum	-	20	77	-	13	2.7	48	6.8	4.7	6.3	-
Maximum	-	429	4925	-	290	54	1717	298	210	89	-
Guiyu, China, Diurnal air, E-waste dismantling region (Chen *et al*., 2009)											
Average	-	-	2748	-	-	-	1656	-	-	-	-

Table 3.1 Concentrations of PBDEs (pg m^{-3}) in air samples from Thai e-waste storage facilities and other relevant microenvironments (continued)

Congener/ Location	17	28	47	49	66	85	99	100	153	154	Σ_{10} PBDEs[a]
<u>U.S., Indoor air, E-waste dismantling hall, n=4 (Cahill *et al*., 2007)</u>											
Average	93	330	2400	2400	570	230	2500	340	7800	3400	-
σ_n	14	52	490	490	180	38	770	99	950	2000	-
<u>Sweden, Indoor air, E-waste dismantling hall, n=12 (Sjodin *et al*., 2001)</u>											
Average	-	-	1200	-	-	170	2600	250	3900	570	-
Minimum	-	-	350	-	-	100	540	63	880	130	-
Maximum	-	-	2100	-	-	240	5500	520	11000	1000	-
<u>Sweden, Indoor air (inhalable dust fraction), Electronics recycling facility, n=12 (Julander *et al*., 2005)</u>											
Arithmetic mean	100	170	1310	1010	340	100	1970	200	1570	370	-
<u>Sweden, Personal air, E-waste dismantlers, n=11 (Pettersson-Julander *et al*., 2004)</u>											
Average	300	500	5100	600	1200	400	8000	900	4000	990	-
Minimum	10	30	600	10	40	30	900	200	200	70	-
Maximum	1500	2700	16000	2700	6300	1300	25000	2600	11000	2700	-
<u>Guangzhou, China, Outdoor air, n=9 (Chen *et al*., 2008)</u>											
Average	-	67	332	-	52	9.9	222	29	73	30	-
σ_n	-	39	309	-	41	8.3	203	27	86	27	-
Median	-	70	184	-	51	6.1	191	20	37	14	-
Minimum	-	23	78	-	10	2.0	49	4.4	7.3	7.9	-
Maximum	-	128	1000	-	133	25	630	83	277	80	-
<u>Guiyu, China, Ambient air, E-waste recycling site, n=30 (Deng *et al*., 2007)</u>											
Average	-	486	6456	-	1782	-	5519	481	811	247	-
σ_n	-	289	1942	-	528	-	2751	181	333	80	-

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[b] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.1 pg m^{-3}).

3.3.2 Concentrations and sources of BFRs in dust samples

Concentrations of Σ_{21}PBDEs, DBDPE and BB-209 in dust from e-waste storage facilities were 320-290,000 ng g^{-1}, 43-8,700 ng g^{-1} and <20-2,300 ng g^{-1} respectively (Table 3.2). The PBDE congener profile in all dust samples (average contribution to Σ_{21}PBDEs) was dominated by BDE-209 (74%)>> BDE-183 (5.5%)> BDE-206 (3.6%)~ BDE-207 (3.2%)~ BDE-99 (2.9%)> BDE-197 (2.5%)> BDE-47 (1.8%)> BDE-208 (1.4%). DBDPE was also among the most dominant BFRs present in all dust samples, but at levels typically an order of magnitude lower than those of BDE-209. With the exception of BDE-209 in US and UK dust samples, the dust PBDE concentrations received from this study are not surprisingly typically at least an order of magnitude higher than those detected in UK and New Zealand homes and UK offices (Table 3.3). They are also slightly higher than those in Canadian homes, but are lower than the results seen in U.S. residences (Harrad *et al*., 2008a,b). Additionally, PBDE levels in this study are, on average, slightly higher but within the range of those reported previously for a small number (n=5) of dust samples from the floor of an e-waste recycling workshop in Fengjiang town, Taizhou, eastern China (Ma *et al*., 2009).

The highest concentration of Σ_{21}PBDEs, BDE-209 and DBDPE (290,000, 250,000 and 8,700 ng g^{-1}) was found in dust sampled from a room used to house waste TVs, stereos and radios, while the highest BB-209 level (2,300 ng g^{-1}) was detected in dust collected from a room used to store waste personal computers and printers. Detailed analysis of any relationships between the type of e-waste stored and the concentrations and pattern of dust contamination demonstrated no discernible trends (Figure 3.3). This is likely to be a function of the heterogeneous nature of the e-waste stored across locations, and that the BFRs used to treat specific e-waste types (i.e. PCs) are not limited to one particular BFR formulation.

Table 3.2 and Figure 3.4 present percentage ratios of BDE-208:BDE-183 and BDE-208:BDE-209 in dust samples. It has been reported recently that the former ratio in the Octa-BDE and the latter ratio in the Deca-BDE formulation do not exceed 0.45% and 0.08% respectively (La Guardia *et al*., 2006). In all dust samples studied here, these ratios are exceeded substantially, suggesting that debromination of BDE-209 to BDE-208 has occurred. While it is possible that some of this debromination may have occurred in the dust following emission from the e-waste, it is important to note the recent report of elevated values of such ratios in TV/PC display casings, and PC components sampled in South China that the authors attributed to the decomposition of higher brominated PBDEs during the process of manufacturing, use and/or recycling of PBDE-containing products (Chen *et al*., 2010). Specifically, the ratios of average concentrations of BDE-208: average concentrations of BDE-209 in TV and PC housing were 5.4% and 2.8% respectively. Likewise, the ratios of average concentrations of BDE-208: average concentrations of BDE-183 in TV and PC housings were 329% and 7.5% respectively (Chen *et al*., 2010). It hence seems plausible that the elevated abundances of BDE-208 and of the other nona-BDEs (BDE-206 and 207) in the dust samples studied here arise largely due to direct migration from stored e-waste, rather than degradation post-emission.

Table 3.2 Concentrations of selected BFRs (ng g^{-1}) in dust samples from Thai e-waste storage facilities

Sample #/ facility #	Waste Category	28	47	99	100	153	154	183	197	206	207	208	209	Σ_{10}PBDEs[a]	Σ_{21}PBDEs[b]	DBDPE	BB-209	%208:209	%208:183
1/1	PC + printer	0.51	6.9	10	5.9	4.6	1.8	68	74	38	19	16	990	36	1300	1900	<20	1.6	23.5
2/1	PC + printer	0.52	8.5	18	12	7	<0.5	19	8	17	12	13	540	48	670	1500	<20	2.4	68.4
3/1	PC + printer	0.63	13	30	6.5	7.5	3.1	11	5	31	19	23	1000	72	1200	3000	<20	2.3	209.1
4/1	PC + printer	0.92	11	27	9.8	9.7	9.6	18	8	24	16	17	900	70	1100	1500	<20	1.9	94.4
5/2	TV	<0.5	27	15	2.4	5.1	3	13	5	<10	<10	<10	250	56	320	56	<20	2.0	38.5
6/2	TV	<0.5	21	19	4.2	2.6	0.72	17	7	11	<10	<10	350	49	450	43	<20	1.4	29.4
7/3	PC + TV	5.3	150	380	56	37	37	75	57	1900	550	700	26000	720	30000	1100	<20	2.7	933.3
8/3	PC + TV	1.5	27	16	4.6	11	5.7	110	75	240	110	120	7000	87	7900	580	<20	1.7	109.1
9/4	PC + printer	7.3	700	1300	180	290	130	3000	1900	530	830	170	11000	2700	22000	1400	190	1.5	5.7
10/4	PC + printer	7.1	540	980	140	230	100	3100	1800	1000	1200	250	18000	2100	29000	510	320	1.4	8.1
11/4	PC + printer	7.7	460	910	140	220	97	2700	840	220	470	75	11000	1900	19000	800	89	0.7	2.8
12/4	PC + printer	6.6	610	1500	210	230	120	3500	1900	820	1000	240	12000	2700	24000	890	320	2.0	6.9
13/4	PC + printer	8.1	550	1000	160	470	210	1800	640	910	1100	240	20000	2500	28000	1000	230	1.2	13.3
14/4	PC + printer	15	730	300	50	610	190	3000	830	1700	2000	360	56000	1900	66000	2200	140	0.6	12.0
15/4	PC + printer	10	600	1100	170	460	160	2000	660	2400	2600	700	35000	2700	47000	1000	860	2.0	35.0
16/4	PC + printer	9.8	550	1100	160	690	260	3300	1000	3000	2500	910	36000	2500	50000	750	2300	2.5	27.6
17/4	PC + printer	18	1800	4500	680	1500	960	3500	1100	1700	3000	520	25000	1900	46000	620	90	2.1	14.9
18/4	PC + printer	25	1800	4600	680	3300	1100	2100	640	6500	9500	1700	110000	2600	140000	1300	150	1.5	81.0
19/4	Fridge + washing machine	33	780	1300	190	260	250	1600	950	320	210	140	13000	2800	20000	160	<20	1.1	8.8
20/4	TV + Video recorder	16	160	410	52	85	45	1600	770	2000	1200	760	31000	9600	39000	1300	350	2.5	47.5
21/4	TV + fan	3.9	57	180	25	50	20	1500	440	820	580	400	20000	12000	25000	150	140	2.0	26.7
22/4	TV, fan + microwave	5.3	92	310	41	130	34	1700	540	5100	3000	2300	100000	3000	120000	71	65	2.3	135.3
23/4	TV, stereo + radio	6.8	230	950	120	700	140	6700	2100	14000	8600	5100	250000	840	290000	8700	240	2.0	76.1
24/4	Rice cooker + photocopier	5.6	140	310	44	100	49	1200	320	1600	1300	510	27000	360	33000	840	50	1.9	42.5
25/4	Typewriter + Video recorder	12	150	360	49	130	48	2000	990	1900	1700	610	21000	650	30000	760	790	2.9	30.5
Average[c]	-	8.3	410	870	130	380	160	1800	710	1900	1700	640	33000	2200	43000	1300	260	1.9	83
σ_n[c]	-	8.1	500	1200	180	700	280	1600	660	3000	2400	1100	53000	2900	62000	1700	480	0.58	184
Median[c]	-	6.8	160	380	52	130	49	1700	640	910	1000	250	20000	1900	28000	890	90	2.0	31
Minimum	-	<0.5	6.9	10	2.4	2.6	<0.5	11	5	<10	<10	<10	250	36	320	43	<20	0.64	2.8
Maximum	-	33	1800	4600	680	3300	1100	6700	2100	14000	9500	5100	250000	12000	290000	8700	2300	2.9	933

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 (tri- to hexa-BDEs were analysed at University of Birmingham).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153, 154, 181, 183, 184, 191, 196, 197, 203, 206, 207, 208 and 209 (other BFRs were analysed by researchers at University of Antwerp).

[c] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 28 and 154 dl = 0.5 ng g^{-1}; for PBDEs 206, 207, and 208 dl = 10 ng g^{-1}; for BB-209 dl = 20 ng g^{-1}).

Table 3.3 Summary of concentrations (ng g^{-1}) of selected BFRs in dust samples from this and selected other studies

Location (reference)	**Statistical parameter/ compound**	**BDE-28**	**BDE-47**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**	**BDE-183**	**BDE-206**	**BDE-207**	**BDE-209**	**Σtri-hexa-BDE**[a]	**ΣBDE**[b]	**DBDPE**
Thailand, This study, Four e-waste storage facilities, n=25	Average	8.3	410	870	130	380	160	1,800	1,900	1,700	33,000	2,000	43,000	1,300
	Median	6.8	160	380	52	130	49	1,700	910	1,000	20,000	840	28,000	890
	Minimum	<0.5	6.9	10	2.4	2.6	<0.5	11	<10	<10	250	36	320	43
	Maximum	33	1,800	4,600	680	3,300	1,100	6,700	14,000	9,500	250,000	12,000	290,000	8,700
Fengjiang town, Taizhou, eastern China, e-waste recycling workshop floor, n =5 (Ma *et al.*, 2009)	Average	85	310	270	29	65	18	-	-	-	30,000	-	31,000	-
	Minimum	11	70	24	15	23	12	-	-	-	5,600	-	6,300	-
	Maximum	170	530	510	42	110	28	-	-	-	81,000	-	82,000	-
Birmingham, UK, Homes, n=30[c] (Harrad *et al.*, 2008b)	Average	0.70	15	36	5.6	14	4.4	71	-	-	260,000	77	260,000	270
	Median	<0.5	10	20	3.4	5.0	2.8	4.2	-	-	8,100	46	8,500	24
	Minimum	<0.5	1.2	2.8	<0.5	<0.5	<0.5	<2.0	-	-	<3.0	7.1	12	<5.0
	Maximum	2.1	58	180	17	110	16	550	-	-	2,200,000	250	2,200,000	3,400
Birmingham, UK, Offices, n=18[d] (Harrad *et al.*, 2008b)	Average	1.8	67	120	16	16	10	11	-	-	30,000	250	31,000	170
	Median	<0.5	23	65	3.2	8.7	5.1	8.3	-	-	6,200	100	7,400	99
	Minimum	<0.5	2.6	4.2	<0.5	<0.5	<0.5	<2.0	-	-	620	16	790	<5.0
	Maximum	11	380	490	79	99	38	24	-	-	280,000	1,100	280,000	860
Birmingham, UK, Cars, n=20[e] (Harrad *et al.*, 2008b)	Average	6.1	720	990	220	150	160	19	-	-	410,000	2,300	340,000	400
	Median	<0.5	54	100	17	11	11	7.8	-	-	100,000	190	57,000	100
	Minimum	<0.5	19	23	<0.5	<0.5	<0.5	<2.0	-	-	12,000	54	140	<5.0
	Maximum	43	7,500	8,000	2,300	1,500	1,900	67	-	-	2,600,000	22,000	2,600,000	2,900
Canada, Homes, n=10[f] (Harrad *et al.*, 2008a)	Average	6.6	300	510	120	71	69	13	-	-	670	1,100	1,400	-
New Zealand, Homes, n=20 (Harrad *et al.*, 2008a)	Average	0.86	36	87	16	9.8	8.7	-	-	-	-	-	-	-
USA, Homes, n=20[g] (Harrad *et al.*, 2008a)	Average	25	810	1,400	240	240	240	28	-	-	1,600	3,000	4,800	-
USA, Homes (main living area), n=19 (Stapleton *et al.*, 2008b)	Geometric mean	-	-	-	-	-	-	-	-	-	-	-	-	138
Japan, Offices, n=14 (Suzuki *et al.*, 2006)	Average	7.1	110	170	30	34	16	81	-	-	2,400	-	-	-
Japan, Two homes (Takigami *et al.*, 2009a)	Average	<0.03	2.5	2.8	0.54	2.0	0.99	-	-	-	390	-	-	-
Japan, TV interiors, n=5 (Takigami *et al.*, 2008)	Average	-	5,700	8,800	18	3,600	490	900	15,100	6,000	240,000	-	-	-
Sweden, Homes, n=5 (Karlsson *et al.*, 2007)	Average	2.2	51	79	24	4.9	3.9	4.8	22	16	470	-	-	47
Australia, Homes, n=10 (Toms *et al.*, 2009a)	Average	-	91	184	38	23	-	100	-	-	380	-	-	-
Australia, Homes & offices, n=9 (Toms *et al.*, 2009b)	Average	-	54	77	15	13	7.3	25	-	-	620	-	-	-
Germany, Homes, n=34 (Fromme *et al.*, 2009)	Average	3.4	24	35	6.5	5.0	3.6	9.2	-	-	350	-	-	-
USA, Cars, n=60 (Lagalante *et al.*, 2009)	Average	150	1,200	2,000	350	550	190	240	-	-	270,000	-	-	-

[a] Sum of PBDEs 28, 47, 49, 66, 85, 99, 100, 153 and 154, plus BDE-17 (this study only).

[b] Sum of PBDEs 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203 and 209, plus BDEs-17, 181, 184, 191, 206, 207 and 208 (this study only).

[c] Thirty samples analyzed for tri-hexa-BDEs; eighteen samples analyzed for ΣBDE and DBDPE.

[d] Eighteen samples analyzed for tri-hexa-BDEs; fifteen samples analyzed for ΣBDE and DBDPE.

[e] Twenty samples analyzed for tri-hexa-BDEs; nine samples analyzed for ΣBDE and DBDPE.

[f] Ten samples analyzed for tri-hexa-BDEs; seven samples analyzed for ΣBDE.

[g] Twenty samples analyzed for tri-hexa-BDEs; seventeen samples analyzed for ΣBDE.

Figure 3.3 Variation of concentrations (ng g^{-1}) of BDE-209, BDE-183 (x 10), tri-hexa-BDEs (x 10), DBDPE (x 10) and BB-209 (x 10) in dust samples from areas of an e-waste storage facility (facility 4) housing different e-waste categories (N.B. VDO = video recorder)

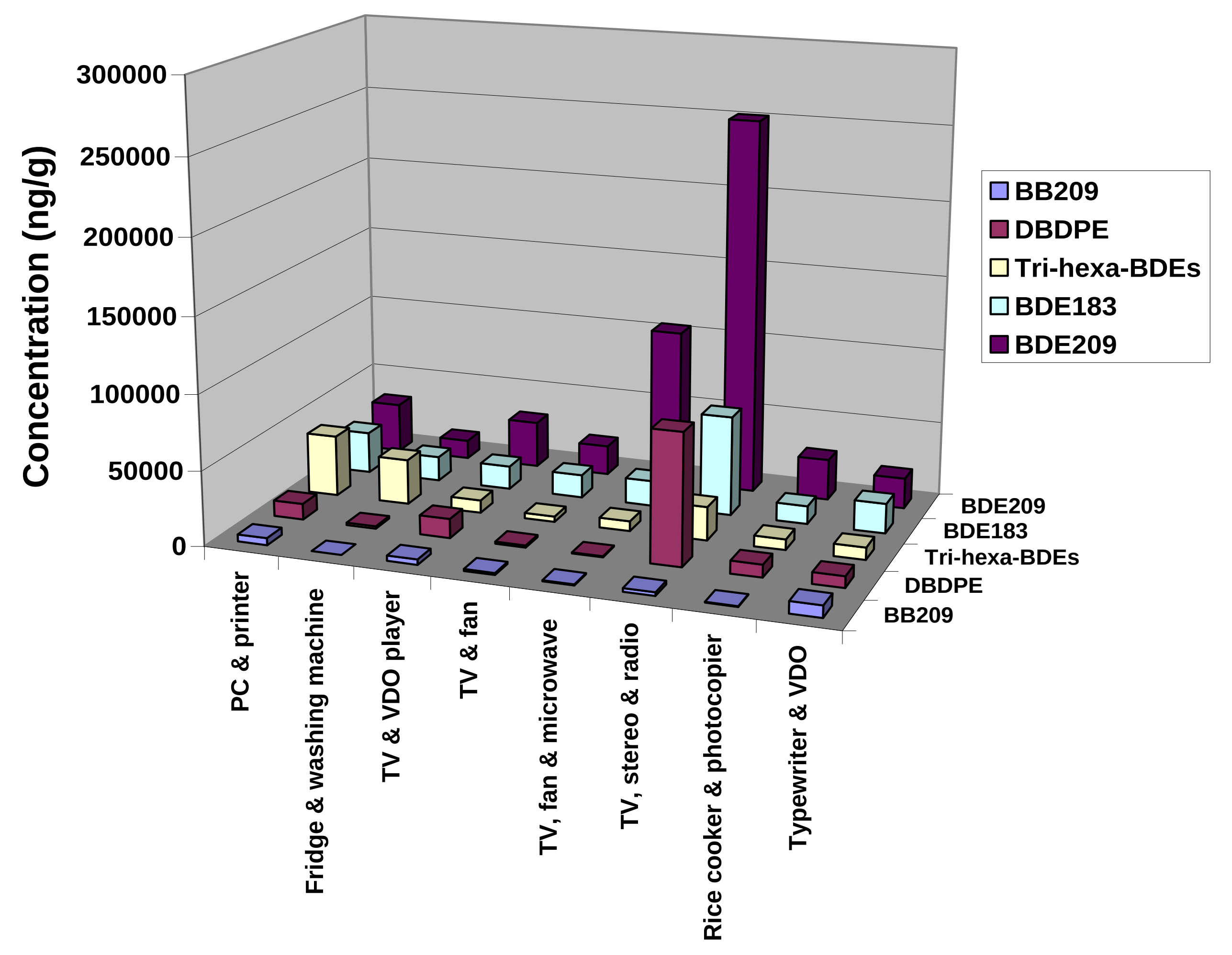


Figure 3.4 Ratios of %BDE-208:BDE-209 (x 100) and %BDE-208:BDE-183 in dust samples from Thai e-waste storage facilities

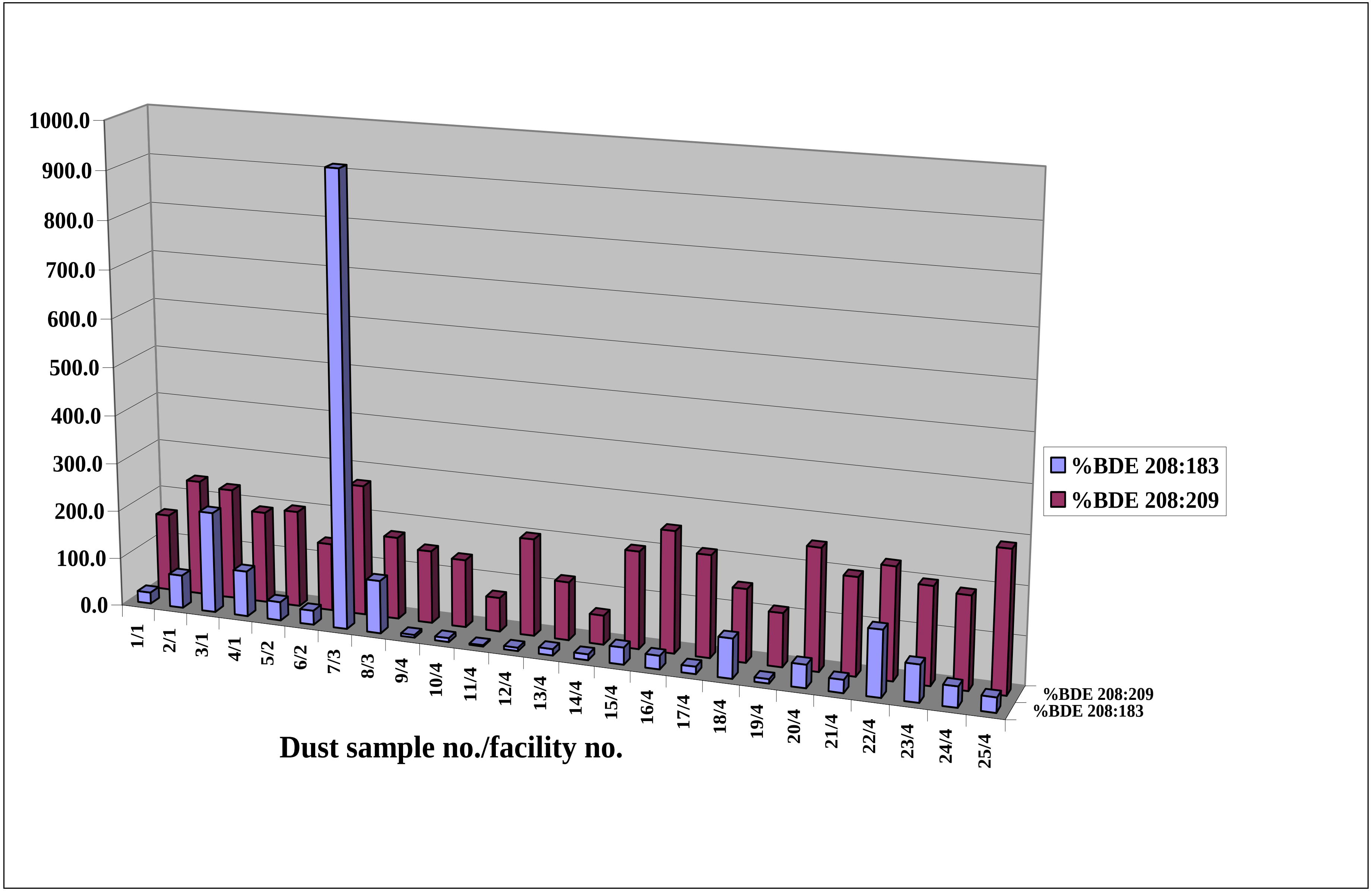


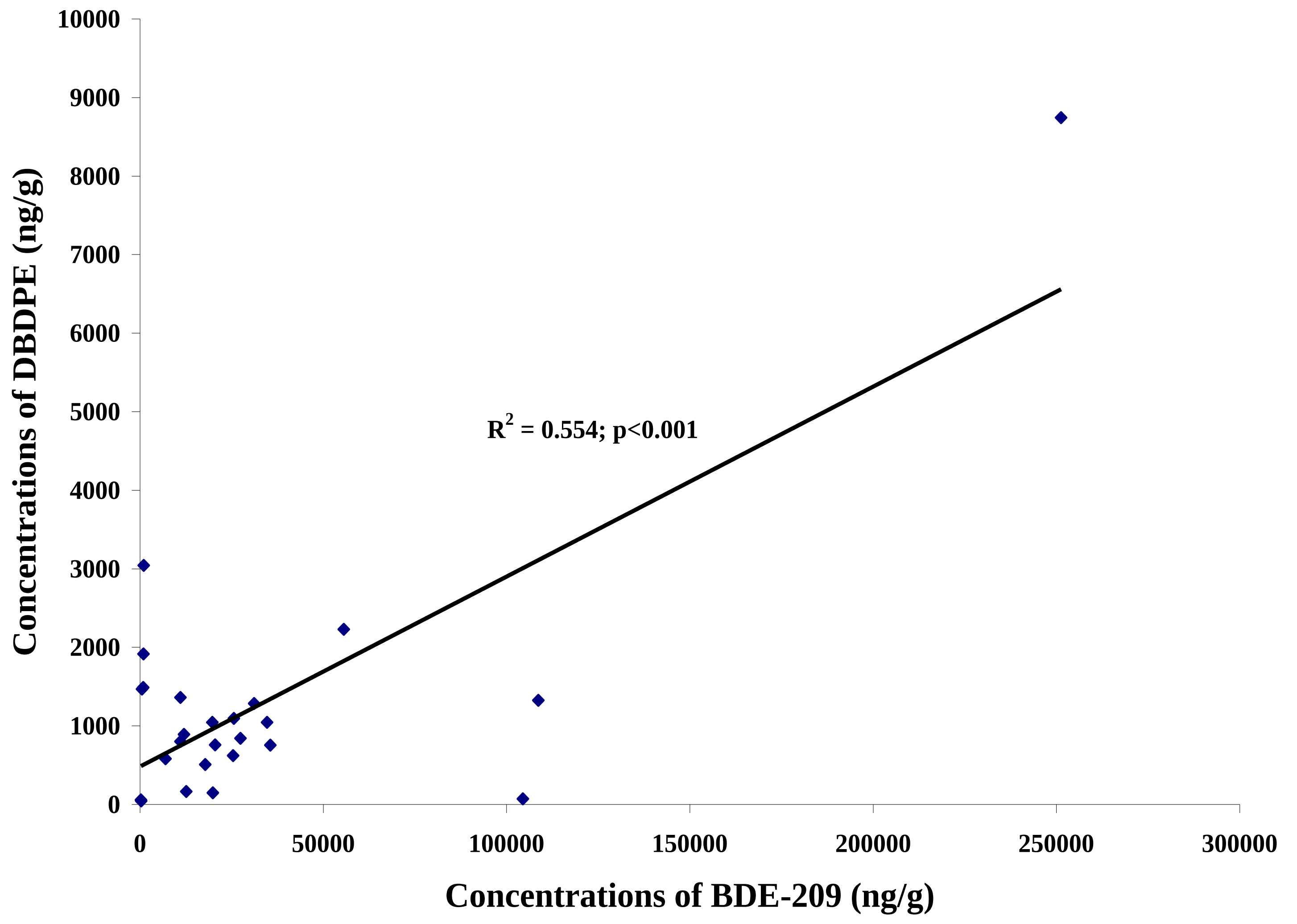
Table 3.3 reveals that the ratio of median concentrations of BDE-183:BDE-99 in samples from this study (4.5) is substantially higher than those observed in dust from the other studies cited (all <1). This implies a high contribution of contamination from the Octa-BDE formulation. Inspection of this ratio in individual dust samples however, did not reveal any conclusive link to the type of waste stored.

Examinations of linear correlations between concentrations of Σ_{10}PBDEs (equates to Penta-BDEs), BDE-183, BDE-209, DBDPE and BB-209 in dust from all four plants demonstrated a significant and positive association between levels of BDE-209 and DBDPE (r^2 = 0.554, p <0.001) (Figure 3.5), but no other associations. This suggests that BDE-209 and DBDPE have similar emission sources, and is consistent with the use of DBDPE as a Deca-BDE "replacement". In samples from plant 1, the ratio of DBDPE:BDE-209 much exceeded those in samples from other plants. Closer inspection shows that the high ratios in the plant 1 samples are driven by very low levels of BDE-209, with levels of DBDPE similar to those in other dust samples in this study. This reveals that the high ratios observed are a consequence of low Deca-BDE contamination of e-waste stored in plant 1, rather than unusually elevated use of DBDPE.

Few studies have monitored indoor dust concentrations of DBDPE. The DBDPE levels in Swedish domestic dust ranged from not detected to 121 ng g^{-1} (Karlsson *et al.*, 2007), while those in household dust from Boston, USA ranged from <10-11,070 ng g^{-1} with geometric means of 39.4, 138 and 154 ng g^{-1} depending on sample origin (living area, bedroom or vacuum cleaner bag) (Stapleton *et al.*, 2008b). In another study, the concentrations of DBDPE in UK indoor dust were between not detected to 3,400 ng g^{-1} with median values of 24, 99 and 100 ng g^{-1} for homes, offices and cars respectively (Harrad *et al.*, 2008b). In a recent study, the DBDPE levels in dust from a Japanese hotel were also lower (<30-210 ng g^{-1}) than those measured in this study (Takigami *et al.*, 2009b). Overall, the DBDPE concentrations in dust from this study exceed those found in Japan and Sweden, and are more in line with those reported for the UK and the USA.

Although levels of PBDEs in outdoor and indoor air from Thai e- waste storage facilities were lower than those in Swedish and American electronic recycling facilities, as well as Chinese electronic waste recycling sites (Sjodin *et al.*, 2001; Pettersson-Julander *et al.*, 2004; Julander *et al*., 2005; Cahill *et al*., 2007; Deng *et al*., 2007; Chen *et al*., 2008, 2009), the levels of DBDPE and PBDEs in indoor air and dust from the Thai e-waste storage facilities in this study however indicate that such workplace environments may constitute sources of occupational exposure to BFRs. Consequently, the potential of these environments to cause adverse effects on the respective workers and on the surrounding environment should be investigated. Despite the fact that no *dismantling* of e-waste occurs at these waste storage facilities, the elevated concentrations detected raise concerns that concentrations at e-waste dismantling facilities may be much higher. These findings also suggest that contamination by BFRs (i.e., PBDEs, DBDPE and BB-209) in e-waste dismantling plants obviously need future investigation.

Figure 3.5 Correlation between concentrations of BDE-209 and DBDPE in dust samples from Thai e-waste storage facilities



3.3.3 Occupational exposure to PBDEs via air inhalation and dust ingestion

It has been reported that PBDEs may adversely affect workers exposed occupationally via air inhalation and dust ingestion (Julander *et al*., 2005; Sjodin *et al*., 2001). Therefore, in order to assess occupational exposure to PBDEs within the Thai e-waste storage facilities, 100% absorption of intake has been assumed. Assuming that dust ingestion occurs only during waking hours (average 16 hrs per day), average adult air inhalation and dust ingestion figures of 0.83 $m^3 hr^{-1}$ (feasible at the higher activity rates during working time) and 1.25 mg hr^{-1}, and high dust ingestion figures for adults of 3.13 mg hr^{-1} have been used (Jones-Otazo *et al*., 2005). Average male and female adult weights for the Thai population of 68.9 kg and 57.4 kg also have been used (SizeThailand, 2010), and assumed that occupational exposure occurs for 8 hours daily. Based on these assumptions, a number of exposure scenarios have been generated. These variously estimate exposure at average and high-end dust ingestion rates and where exposure is assumed to be due to air and dust contaminated at the median, 5th or 95th percentile concentrations reported here. Table 3.4 provides these occupational exposure assessments of both male and female workers to BDE-99 and BDE-209 via air inhalation and dust ingestion.

These values are compared with currently available health-based limit values (HBLVs) for PBDEs. For BDE-99, a preliminary HBLV of 0.23–0.30 ng/kg bw/day has been derived by Netherlands researchers (Bakker *et al*., 2008). Moreover, for BDE-209, the U.S. EPA's Integrated Risk Information System (IRIS) Toxicological Evaluation recommends a reference dose (RfD) of daily oral exposure to BDE-209 of 7 μg/kg bw/day that is considered to be without appreciable risk of deleterious effects (U.S. EPA, 2008). The exposure estimates for BDE-99 calculated from the Thai dust (0.56-1.69 ng/kg bw/day) exceeded the HBLV cited above when the dust to which exposure occurred was contaminated at or above the 95th percentile concentration (3,900 ng g^{-1}), regardless of the assumed dust ingestion rate. By comparison all exposure estimates for BDE-209 were lower than the U.S. EPA's RfD.

Table 3.4 Estimated exposures (ng/kg bw/day) of male and female workers in Thai e-waste storage facilities to BDE-99 and BDE-209 via air inhalation and dust ingestion

Exposure pathway	BDE-99		BDE-209	
	Male	Female	Male	Female
Air inhalation				
- 5th percentile concentration	0.00028	0.00034	-	-
- Median concentration	0.0011	0.0013	-	-
- 95th percentile concentration	0.0098	0.012	-	-
Average dust ingestion rate[a]				
- 5th percentile concentration	0.0022	0.0026	0.0566	0.0679
- Median concentration	0.05	0.07	2.87	3.44
- 95th percentile concentration	0.56	0.68	15.7	18.8
High-end dust ingestion rate[b]				
- 5th percentile concentration	0.0055	0.0065	0.1417	0.1701
- Median concentration	0.14	0.16	7.2	8.63
- 95th percentile concentration	1.41	1.69	39.2	47.1
Health-based limit value	0.23-0.30[c]	0.23-0.30[c]	7,000[d]	7,000[d]

[a] 1.25 mg hr^{-1}.
[b] 3.13 mg hr^{-1}.
[c] Bakker *et al.*, 2008.
[d] U.S. EPA, 2008.

3.4 Conclusion and recommendation

This chapter reports contamination by selected BFRs (PBDEs, DBDPE and BB-209) in Thai e-waste storage facilities. Airborne PBDE levels are substantially lower than those reported for e-waste treatment facilities in China, the U.S. and Sweden. However, dust concentrations of the selected BFRs are comparable to those reported for UK, New Zealand, Canadian, U.S. and Swedish homes, UK offices and cars, a Japanese hotel and a Chinese e-waste recycling workshop. Furthermore, levels in dust in some instances exceed those reported for homes and offices in other countries. The PBDE congener profile for both outdoor and indoor air samples was dominated by BDE-47 and BDE-99, while BDE-209, 183, 206, 207, 99, 197, 47, 208 and DBDPE were the principal BFRs detected in all dust samples, revealing that open storage of e-waste may be constitute a source of BFRs to the environment. However, while both absolute concentrations and congener patterns of BFRs in dust varied between locations sampled; no systematic relationship was discernible between the level and pattern of BFR contamination and the type of e-waste stored. The significant postive corretaion between concentrations of BDE-209 and DBDPE, are consistent with the hypothesis that the latter is findig increasing use as a replacement for the former. Finally, under some high-end but plausible scenarios, estimated occupational exposures of both male and female workers to BDE-99 via dust ingestion at the Thai e-waste storage facilities studied here, exceed a health-based limit value proposed recently by Netherlands researchers.

Whilst there is a growing database related to the environmental occurrence, fate, and behaviour of BFRs, there remains an urgent need to characterise BFR contamination of workers involved in the processing of e-waste. Specific issues that require addressing include: the importance of indoor air inhalation and dust ingestion as occupational exposure pathways; the factors influencing BFR contamination of workplace environments; the influence of indoor contamination on concentrations in outdoor air; and the potential health impacts of occupational exposure to BFRs.

CHAPTER 4

Concentrations of PBDEs in indoor air and dust from homes and cars in Thailand: an assessment of human air inhalation and dust ingestion exposures

4.1 Synopsis

In this chapter, concentrations of tri- to hexa-BDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154) in indoor air samples (n=3), house dust samples (n=53) and car dust samples (n=30) collected from various provinces in Thailand are reported and compared with those observed for indoor air and dust in other studies. Potential sources of indoor contamination with PBDEs and PBDE congener profiles in indoor air and dust are also discussed. In addition, human air inhalation and dust ingestion exposures are estimated based on concentrations found in the monitored indoor air and dust samples, respectively. These exposure estimates are compared against a proposed health based limit value for BDE 99, thereby providing a preliminary risk assessment.

4.2 Sampling protocol and locations

PUF (polyurethane foam) disk passive air samplers spiked with 10 ng of sampling efficiency standard (SES-PCB 147) were deployed to take 3 indoor air samples (Figure 4.1) at different homes in Thailand over a 47-51 day period in December 2007-January 2008. Moreover, 53 house (Figure 4.2) and 30 car dust samples (Figure 4.3) were collected from 28 homes and 30 cars in various provinces of Thailand using a Hitachi CV-BL16 1600 W vacuum cleaner via the sampling protocol described in Chapter 2. Sampling questionnaires for indoor air, house dust and car dust samples (see Questionnaire 2-4 in Appendix A) were completed by the householders, car owners or researcher. All samples were sent to the laboratory at the Public Health Building, Division of Environmental Health and Risk Management, University of Birmingham, the United Kingdom for PBDE quantification. Sampling locations for all indoor air and dust samples are shown in Figure 4.4, whilst details of the investigated indoor air, house and car dust samples are presented in Appendix C.

Figure 4.1 Indoor air sampling*

Note: * Photograph taken at a home in Phuket Province, Thailand

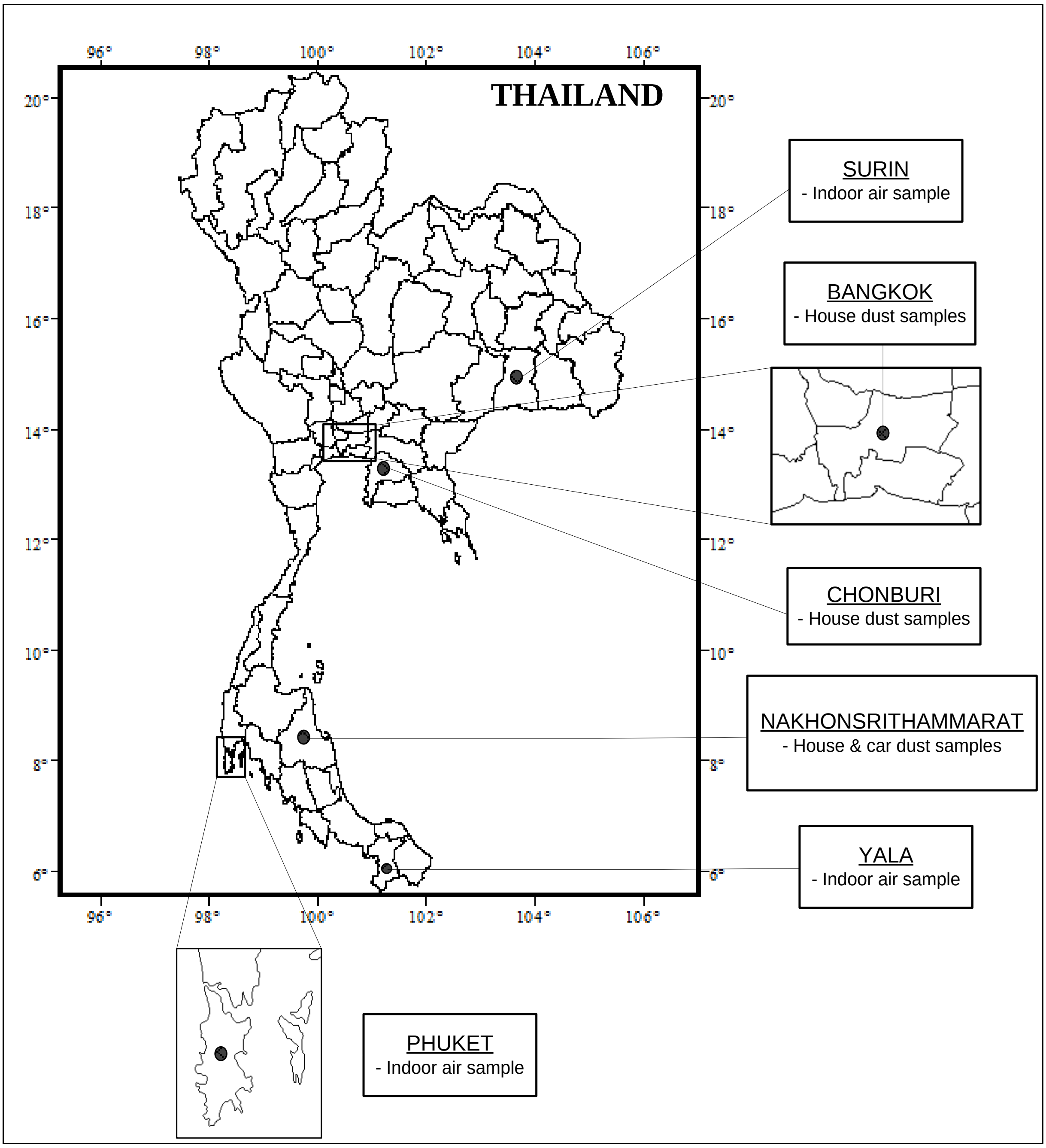
Figure 4.2 House dust sampling*

Note: * Photograph taken at a home in Nakhonsrithammarat Province, Thailand

Figure 4.3 Car dust sampling*

Note: * Photograph taken at a car care centre in Nakhonsrithammarat Province, Thailand

Figure 4.4 Map of indoor air and dust sampling locations in Thailand



4.3 Results and discussion

4.3.1 Concentrations of tri- to hexa-BDEs (Σ_{10}PBDEs) in indoor air samples from Thai homes

Based on a previously published study relating to sampling rate of similar PUF disk samplers, a passive air sampling rate of 1.66 m^3 d^{-1} was selected to calculate airborne PBDE concentrations in indoor air (Hazrati and Harrad, 2007). Concentrations of Σ_{10}PBDEs in domestic indoor air ranged from 23 to 72 pg m^{-3} (Table 4.1). The household indoor air concentrations in this study were higher than those reported previously in Kuwait and Japan (Gevao *et al*., 2006b; Takigami *et al*., 2009a). Nevertheless, the PBDE levels in indoor air reported here were lower than those found previously in Germany, Sweden, Canada, Australia and the U.S. (Fromme *et al*., 2009; Karlsson *et al*., 2007; Wilford *et al*., 2004; Toms *et al*., 2009a,b; Batterman *et al*., 2009). The predominant congeners in indoor air samples were BDE 47 and 99. The ratios of BDE 47:99 in indoor air samples ranged from 1.3-5.5 (average of 2.3, median of 3.7 that exceeds the values of 1.0 and 0.7 found in Penta-BDE formulations Bromkal 70-5DE (Sjodin *et al*., 1998) and DE-71 respectively (Hoh and Hites, 2005)). The lowest BDE 47:99 ratio was seen in indoor air taken from a home located in Phuket Province (Table 4.1). Interestingly, the 47:99 ratios in indoor air presented here exceeded those observed in UK homes (average = 1.4, median = 1.0), UK indoor microenvironments overall (31 homes, 33 offices, 25 cars and 3 public microenvironments) (median = 1.2), German (average = 2.0, median = 3.5), Australian (average = 1.5, median = 0.78) and Kuwait homes (average = 2.1, median = 1.5) (Hazrati and Harrad, 2006; Fromme *et al*., 2009; Toms *et al*., 2009a; Gevao *et al*., 2006b). However, the 47:99 ratios in this study were lower than those reported for domestic indoor air in Ottawa (average = 3.8, median = 4.4), and similar to those found in Japanese houses (average = 2.4) (Wilford *et al*., 2004; Takigami *et al*., 2009a). Although firm conclusions are hard to reach in view of the very small sampler numbers in this study, the different 47:99 ratios in Thai indoor air may be attributable to the application of different PBDE formulations in Thailand compared to the UK, Germany, Australia, Kuwait and Canada.

Table 4.1 Concentrations of PBDEs (pg m^{-3}) in indoor air samples from Thai homes and selected other studies

Congener/ Location	17	28	47	49	66	85	99	100	153	154	ΣPBDEs	BDE47:99 ratio
Thailand, this study, Homes, n=3												
Home 1 (Phuket Province)	1.7	6.1	5.9	1.4	0.52	0.85	4.5	0.36	1.3	0.96	23^a	1.3
Home 2 (Yala Province)	0.54	1.3	17	<0.1	<0.1	0.72	3.0	0.63	0.22	0.22	23^a	5.5
Home 3 (Surin Province)	1.8	6.1	29	3.4	2.1	8.5	15	6.0	0.50	0.25	72^a	1.9
Average^b	1.3	4.5	17	1.6	0.88	3.3	7.5	2.3	0.67	0.48	40^a	2.3
σ_n^b	0.68	2.7	11	1.7	1.1	4.4	6.5	3.2	0.56	0.42	28^a	-
Median^b	1.7	6.1	17	1.4	0.52	0.85	4.5	0.63	0.50	0.25	23^a	3.7
Minimum	0.54	1.3	5.9	<0.1	<0.1	0.72	3.0	0.36	0.22	0.22	23^a	1.3
Maximum	1.8	6.1	29	3.4	2.1	8.5	15	6.0	1.3	0.96	72^a	5.5
Canada, Homes, n=74 (Wilford *et al*., 2004)												
Mean	12	24	160	-	2.9	0.72	42	10	1.6	1.9	-	3.8
Median	6.1	11	66	-	<dl	<dl	15	4.2	<dl	<dl	-	4.4
Minimum	<dl	<dl	<dl	-	<dl	<dl	<dl	<dl	<dl	<dl	-	-
Maximum	160	310	1600	-	98	32	890	160	74	57	-	-
Birmingham, UK, Homes, n=31 (Harrad *et al*., 2006)												
Average	-	7.5	18	2.8	1.8	0.8	13	3.5	1.7	1.0	52^c	1.4
Median	-	3.8	6.1	0.6	0	0	6.0	1.1	0	0	24^c	1.0 (1.2^d)
Minimum	-	0	1.9	0	0	0	0	0	0	0	4^c	-
Maximum	-	61	107	40	28	15	80	27	21	17	245^c	-
Germany, Homes, n=34 (Fromme *et al*., 2009)												
Mean	-	5.6	19	-	0.59	-	9.7	1.9	1.2	0.62	-	2.0
Median	-	4.2	9.4	-	0.31	-	2.7	0.54	0.27	0.20	-	3.5
Minimum	-	1.1	3.2	-	<0.02	-	<0.52	<0.23	<0.08	<0.06	-	-
Maximum	-	17	169	-	4.9	-	189	33	23	11	-	-

Table 4.1 Concentrations of PBDEs (pg m^{-3}) in indoor air samples from Thai homes and selected other studies (continued)

Congener/ Location	17	28	47	49	66	85	99	100	153	154	ΣPBDEs	BDE47:99 ratio
Australia, Homes, n=10 (Toms *et al*., 2009a)												
Mean	-	-	55	-	-	-	36	6.4	n.d.	-	-	1.5
σ_n	-	-	81	-	-	-	15	1.8		-	-	-
Median	-	-	25	-	-	-	32	6.4		-	-	0.78
Australia, Homes, n=6 (Toms *et al*., 2009b)												
Average	-	-	45	-	-	-	20	4.9	2.5	1.2	-	2.3
Kuwait, Homes, n=46 (Gevao *et al*., 2006b)												
Mean	-	1.0	9.1	-	-	-	4.4	0.9	0.2	0.2	-	2.1
Median	-	0.4	3.6	-	-	-	2.4	0.5	0.2	0.2	-	1.5
Maximum	-	7.6	101	-	-	-	36	10	0.9	1.5	-	-
σ_n	-	1.5	16	-	-	-	7.2	1.8	0.2	0.3	-	-
Sweden, Homes, n=4 (Karlsson *et al*., 2007)												
Average	-	15	109	-	3.6	-	n.d.	n.d.	n.d.	n.d.	-	-
Japan, Homes, n=4 (Takigami *et al*., 2009a)												
Average	-	3.0	1.8	-	0.4	-	0.76	0.16	<0.1	<0.1	-	2.4
USA, 12 homes (Batterman *et al*., 2009)												
Mean	240[e]	200[e]	2,500[e]	150[e]	51[e]	10[e]	760[e]	180[e]	32[e]	20[e]	-	3.3
Median	160[e]	140[e]	1,400[e]	11[e]	3[e]	1[e]	410[e]	110[e]	10[e]	6[e]	-	3.4
Maximum	800[e]	590[e]	7,200[e]	1200[e]	250[e]	75[e]	4,500[e]	970[e]	260[e]	110[e]	-	-

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[b] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.1 pg m^{-3}).

[c] Sum of PBDEs 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[d] The 47:99 ratio in all indoor air samples collected from 31 homes, 33 offices, 25 cars and 3 public microenvironments.

[e] Concentrations (vapour phase).

4.3.2 Concentrations of tri- to hexa-BDEs (Σ_{10}PBDEs) in house dust samples from Thailand

Concentrations of Σ_{10}PBDEs in dust from homes were 0.59-260 ng Σ_{10}PBDE g^{-1} (Table 4.2). The congener profile in all house dust samples was dominated by BDE 99 and 47. Levels of all BDE congeners detected in household dust in this study were lower than the levels reported in many countries around the world including the United Kingdom, the United States, Canada, Germany, Sweden, Portugal, Australia, New Zealand, Kuwait and Singapore (Table 4.3) (Harrad *et al*., 2008a,b; Stapleton *et al*., 2005b; Meeker *et al*., 2009; Allen *et al*., 2008a; Sjodin *et al*., 2008a; Zota *et al*., 2008; Wu *et al*., 2007; Wilford *et al*., 2005; Fromme *et al*., 2009; Karlsson *et al*., 2007; Cunha *et al*., 2010; Toms *et al*., 2009a,b; Gevao *et al*., 2006a; Tan *et al*., 2007). Nonetheless, the concentrations of BDE-28, 47, 99, 100 and 154 reported here exceed those observed in homes in Japan (Takigami *et al*., 2009a). The reasons for the low PBDE concentrations in domestic dust in this study are most likely due to greater use of BFRs like TBBP-A in Thailand, as well as differences in use patterns and household characteristics such as furnishings, non-carpeted rooms/floor and the small number of electronic and electrical items (especially personal computers and laptops) in rural Thai homes that account for 89% of total dust sampling sites. The ratios of BDE 47:99 in residential dust samples were not constant and ranged from 0.14-2.6 (average of 0.55, median of 0.55) (Table 4.2), with the lowest BDE 47:99 ratio found in a dust sample collected from a home located in Nakhonsrithammarat Province (sample TH-17). This unusual congener profile may be due to the fact that the sampled room contained several items of electronic equipment (TVs and stereo).

Table 4.2 Concentrations of PBDEs (ng g^{-1}) in house dust samples from Thailand

Congener/ Sample	17	28	47	49	66	85	99	100	153	154	Σ_{10}PBDEs^{a}	BDE47:99 ratio
TH-HD 1	0.32	0.55	13	0.51	0.19	1.8	14	3.7	17	5.9	58	0.94
TH-HD 2	0.09	0.31	2.2	0.11	0.04	2.4	6.1	2.5	4.0	1.9	20	0.35
TH-HD 3	0.07	0.11	3.6	0.13	0.34	4.6	13	4.1	10	3.9	40	0.28
TH-HD 4	0.06	0.12	2.2	0.37	0.22	0.41	2.9	0.72	4.6	2.7	14	0.77
TH-HD 5	0.19	0.21	6.3	3.2	2.1	3.7	6.7	2.9	5.0	3.4	34	0.95
TH-HD 6	<0.03	0.23	2.7	0.40	0.82	2.7	6.9	2.4	4.1	2.9	23	0.39
TH-HD 7	<0.03	0.31	3.0	0.52	0.39	2.4	5.6	1.9	1.6	0.32	16	0.54
TH-HD 8	0.04	0.55	59	1.8	<0.03	5.3	138	21	14	18	257	0.43
TH-HD 9	<0.03	<0.03	9.8	4.6	0.97	1.8	15	1.2	5.3	9.8	49	0.65
TH-HD 10	<0.03	0.26	1.5	0.09	0.08	0.20	4.4	0.23	0.74	1.1	8.6	0.35
TH-HD 11	<0.03	0.08	0.92	0.06	0.03	0.21	1.8	0.38	0.12	0.08	3.7	0.51
TH-HD 12	<0.03	<0.03	0.52	0.06	<0.03	0.06	0.47	0.08	0.15	0.12	1.5	1.1
TH-HD 13	<0.03	<0.03	0.30	0.09	0.13	0.05	0.58	0.06	0.74	0.66	2.6	0.52
TH-HD 14	0.11	0.09	1.3	0.05	0.07	1.1	2.5	1.1	1.2	1.2	8.7	0.51
TH-HD 15	0.18	0.10	1.9	0.46	0.89	0.59	1.7	0.80	0.90	0.58	8.1	1.1
TH-HD 16	<0.03	<0.03	0.29	0.08	0.06	<0.03	1.1	0.28	0.11	0.08	2.0	0.27
TH-HD 17	<0.03	0.06	1.3	0.51	<0.03	1.5	9.1	4.6	0.80	0.20	18	0.14
TH-HD 18	<0.03	0.18	1.5	6.0	5.0	1.5	3.9	1.1	1.1	0.92	21	0.39
TH-HD 19	0.05	0.05	0.63	0.48	0.35	0.70	3.2	0.91	0.43	0.15	6.9	0.20
TH-HD 20	0.04	0.05	7.2	2.3	0.24	0.22	2.8	0.19	1.3	0.48	15	2.6
TH-HD 21	<0.03	0.04	0.94	0.08	0.71	1.3	3.7	2.9	0.28	0.17	10	0.25
TH-HD 22	0.05	0.17	5.7	2.4	1.7	0.58	7.2	0.65	1.4	0.88	21	0.79
TH-HD 23	<0.03	<0.03	1.2	0.87	0.29	0.49	2.3	1.0	0.78	0.76	7.7	0.50
TH-HD 24	<0.03	0.07	0.84	0.13	0.11	0.22	1.6	0.26	0.33	0.29	3.8	0.54
TH-HD 25	0.04	0.05	0.13	0.10	<0.03	0.09	0.52	0.28	0.34	0.32	1.9	0.25
TH-HD 26	<0.03	0.04	0.22	<0.03	<0.03	0.17	0.30	0.22	0.06	<0.03	1.1	0.73
TH-HD 27	<0.03	0.12	0.75	<0.03	0.04	0.04	0.84	0.05	<0.03	<0.03	1.9	0.89
TH-HD 28	<0.03	0.15	1.4	0.05	0.06	0.37	2.6	0.47	0.23	0.07	5.4	0.52
TH-HD 29	<0.03	<0.03	0.21	<0.03	0.04	<0.03	0.19	<0.03	0.12	<0.03	0.65	1.1
TH-HD 30	<0.03	0.04	0.12	<0.03	<0.03	<0.03	0.19	<0.03	0.11	0.05	0.59	0.63
TH-HD 31	<0.03	<0.03	1.3	0.16	0.07	0.64	2.5	1.6	0.91	0.81	8.0	0.54
TH-HD 32	<0.03	<0.03	2.2	0.09	0.13	1.0	8.1	2.0	<0.03	<0.03	14	0.27

Table 4.2 Concentrations of PBDEs (ng g^{-1}) in house dust samples from Thailand (continued)

Congener/ Sample	17	28	47	49	66	85	99	100	153	154	Σ_{10} PBDEs[a]	BDE47:99 ratio
TH-HD 33	0.09	0.12	1.0	0.32	0.47	2.2	6.5	2.6	0.94	<0.03	14	0.15
TH-HD 34	<0.03	0.15	4.9	0.17	0.12	0.28	3.5	1.3	1.7	0.69	13	1.4
TH-HD 35	<0.03	0.20	3.8	0.31	<0.03	0.67	5.7	0.82	3.0	2.1	17	0.67
TH-HD 36	0.03	0.16	0.84	0.64	0.06	0.06	1.0	0.30	0.31	<0.03	3.4	0.82
TH-HD 37	<0.03	0.07	0.41	0.11	0.10	<0.03	2.0	0.04	0.18	<0.03	2.9	0.21
TH-HD 38	0.06	0.12	0.75	0.09	0.08	0.10	1.4	0.10	0.68	0.64	4.0	0.53
TH-HD 39	0.04	0.07	2.1	0.34	0.10	0.06	3.1	0.09	0.52	0.13	6.5	0.70
TH-HD 40	0.09	0.19	4.8	0.84	0.07	0.09	3.0	0.21	1.9	1.1	12	1.6
TH-HD 41	0.14	0.25	2.3	0.64	0.19	0.38	3.6	0.73	2.1	1.8	12	0.63
TH-HD 42	<0.03	<0.03	1.3	0.48	0.19	0.20	2.7	0.55	<0.03	<0.03	5.5	0.47
TH-HD 43	0.07	0.54	8.6	<0.03	0.78	0.67	11	0.96	1.1	0.86	25	0.76
TH-HD 44	<0.03	0.04	2.0	<0.03	0.45	0.22	2.1	0.27	0.94	0.39	6.5	0.93
TH-HD 45	0.04	0.08	0.97	0.35	0.29	0.08	1.6	0.11	<0.03	<0.03	3.5	0.62
TH-HD 46	0.14	0.32	4.7	3.4	0.74	0.65	5.0	1.0	<0.03	<0.03	16	0.94
TH-HD 47	0.05	0.08	1.4	0.20	0.09	0.28	5.1	0.65	<0.03	<0.03	7.9	0.27
TH-HD 48	0.12	0.22	7.0	1.7	1.0	0.94	8.3	1.4	2.2	1.9	25	0.84
TH-HD 49	0.20	0.36	3.4	1.9	0.53	0.30	4.1	0.41	3.0	<0.03	14	0.82
TH-HD 50	<0.03	0.26	3.9	0.12	0.25	0.15	4.1	0.38	2.6	2.3	14	0.95
TH-HD 51	<0.03	0.04	1.9	0.06	0.32	0.25	3.4	0.34	1.0	0.68	8.0	0.55
TH-HD 52	<0.03	0.04	4.2	0.20	0.05	0.51	4.5	0.91	1.6	0.72	13	0.92
TH-HD 53	0.06	0.19	2.4	0.95	0.10	0.75	4.5	0.97	1.1	0.36	11	0.53
Average[b]	0.05	0.14	3.7	0.73	0.40	0.85	6.7	1.4	1.9	1.4	17	0.55
σ_n[b]	0.06	0.14	8.3	1.2	0.76	1.2	19	2.9	3.3	2.9	36	0.41
Median[b]	0.015	0.10	1.9	0.20	0.13	0.38	3.4	0.72	0.91	0.48	10	0.55
Minimum	<0.03	<0.03	0.12	<0.03	<0.03	<0.03	0.19	<0.03	<0.03	<0.03	0.59	0.14
Maximum	0.32	0.55	59	6.0	5.0	5.3	138	21	17	18	257	2.6
Percentile 5[b]	0.015	0.015	0.22	0.015	0.015	0.015	0.40	0.05	0.015	0.015	1.3	0.20
Percentile 95[b]	0.18	0.43	9.1	3.3	1.3	3.1	13	3.8	7.3	4.7	43	1.2

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[b] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

Table 4.3 Summary of PBDE concentrations (ng g^{-1}) in house dust samples from this and selected other studies

Location (reference)	Statistical parameter/ congener	17	28	47	49	66	85	99	100	153	154	Σ_{10} PBDEs[a]
Various locations, Thailand, this study, Thirty homes, n=53	Average[b]	0.05	0.14	3.7	0.73	0.40	0.85	6.7	1.4	1.9	1.4	17
	σ_n[b]	0.06	0.14	8.3	1.2	0.76	1.2	19	2.9	3.3	2.9	36
	Median[b]	0.015	0.10	1.9	0.20	0.13	0.38	3.4	0.72	0.91	0.48	10
	Minimum	<0.03	<0.03	0.12	<0.03	<0.03	<0.03	0.19	<0.03	<0.03	<0.03	0.59
	Maximum	0.32	0.55	59	6.0	5.0	5.3	138	21	17	18	257
Birmingham, UK, n=30 (Harrad *et al*., 2008b)	Average	-	0.70	15	-	-	-	36	5.6	14	4.4	-
Toronto, Canada, n=10 (Harrad *et al*., 2008a)	Average	-	6.6	300	-	-	-	510	120	71	69	-
Ottawa, Canada, n=74 (Wilford *et al*., 2005)	Mean	4.3	15	1100	-	37	190	1800	490	470	380	-
	Median	1.0	3.0	300	-	4.7	17	430	73	49	37	-
Wellington, New Zealand, n=20 (Harrad *et al*., 2008a)	Average	-	0.86	36	-	-	-	87	16	9.8	8.7	-
Amarillo & Austin, TX, USA, n=20 (Harrad *et al*., 2008a)	Average	-	25	810	-	-	-	1400	240	240	240	-
Washington DC, USA, n=17 (Stapleton *et al*., 2005b)	Mean	8.9	-	1220	-	29	83	1700	274	181	156	-
	Median	4.2	-	644	-	13	33	676	119	64	73	-
Massachusetts, USA, n=24 (Meeker *et al*., 2009)	Geometric mean	-	-	577	-	-	-	809	220	-	-	-
Boston, MA, USA, Main living area, n=20 (Allen *et al*., 2008a)	Geometric mean	1.4	-	1865	30	17	-	2460	436	234	183	-
	Minimum	<0.1	-	445	0.3	0.2	-	331	71	28	27	-
	Maximum	112	-	16840	372	287	-	24510	4274	2377	2061	-
Atlanta, GA, USA, n=10 (Sjodin *et al*., 2008a)	Median	-	-	430	-	-	-	880	150	140	80	-
California, USA, n=49 (Zota *et al*., 2008)	Median	-	-	2700	-	-	-	3800	684	-	-	-
Boston, USA, n=11 (Wu *et al*., 2007)	Median	-	-	670	-	<dl	<dl	1010	174	107	93	-
Hokkaido, Japan, n=2 (Takigami *et al*., 2009a)	Average	-	<0.03	2.5	-	-	-	2.8	0.54	2.0	0.99	-
Sweden, n=5 (Karlsson *et al*., 2007)	Average	-	2.2	51	-	3.3	-	79	24	4.9	3.9	-
Brisbane, Queensland, Australia, n=10 (Toms *et al*., 2009a)	Average	-	-	91	-	-	-	184	38	23	-	-
South East Queensland, Australia, n=5 (Toms *et al*., 2009b)	Average	-	-	2.4	-	-	-	36	7.0	6.8	4.0	-
Munich, Germany, n=34 (Fromme *et al*., 2009)	Average	-	3.4	24	-	0.55	-	35	6.5	5.0	3.6	-
Various locations, Germany, n=10 (Sjodin *et al*., 2008a)	Median	-	-	<14	-	-	-	10	<6	<6	-	-
	Minimum	-	-	<14	-	-	-	<4	<6	<6	<6	-
	Maximum	-	-	22	-	-	-	28	7	22	-	-
Portugal, Sieved fraction, n=11 (Cunha *et al*., 2010)	Average	-	0.40	25	21	2.9	n.d.	9.8	1.9	2.5	0.60	-
Kuwait, n=17 (Gevao *et al*., 2006a)	Average	-	0.35	6.6	-	-	0.72	6.0	1.2	1.3	1.4	-
	Median	-	0.12	2.7	-	-	0.40	3.4	0.68	0.72	0.85	-
Singapore, n=31 (Tan *et al*., 2007)	Mean	-	1.2	110	-	-	-	340	65	76	43	-
	Median	-	0.6	20	-	-	-	24	4.2	6.9	3.5	-

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[b] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

4.3.3 Concentrations of tri- to hexa-BDEs (Σ_{10}PBDEs) in car dust samples from Thailand

Concentrations of Σ_{10}PBDEs in car dust were 0.68-38 ng g^{-1} (Table 4.4) and were much lower than those detected previously in the United Kingdom, the United States and Portugal (Harrad *et al*., 2008b; Lagalante *et al*., 2009; Cunha *et al*., 2010). BDEs 99 and 47 were the most abundant congeners in all samples. The ratios of BDE 47:99 in vehicle dust samples were not constant and ranged from 0.003-6.5 (average of 0.62, median of 0.55) (Table 4.4). Interestingly, the 47:99 ratios in car dust samples reported here were in line with previous results from the UK (average = 0.73, median = 0.54), the US (average = 0.62, median = 0.78) and Portugal (average = 0.60, median = 0.70) (Harrad *et al*., 2008b; Lagalante *et al*., 2009; Cunha *et al*., 2010), suggesting that Thai, UK, American and Portuguese vehicles are treated with similar commercial PBDE products.

A very few studies are available addressing factors affecting PBDE levels in automobiles. The study of Hazrati (2006) reported no statistically significant correlations between car age and concentrations of PBDEs in vehicle air. Additionally, the U.S. and Portuguese study showed no relationships between dust PBDE concentrations and vehicle variables including the extent of car use (as inferred by the mileometer reading), car age (calculated from the date of manufacture), year of production, mark and number of times cleaned (Lagalante *et al*., 2009; Cunha *et al*., 2010). This study did not examine the associations between vehicle age and PBDE levels in car dust owing to the lack of data on vehicle age. However, given the non-linear relationship between year of vehicle manufacture and the extent of PBDE use in vehicles, it is thought unlikely that a straightforward relationship would exist.

Table 4.5 and Figure 4.5 illustrate how concentrations of tri-hexa-BDEs (Σ_{10}PBDEs) in dust samples from thirty automobiles vary with the different car manufacturers. The highest average concentration of Σ_{10}PBDEs (11 ng g^{-1}) was found in car dust collected from Nissan vehicles (n=2), while the lowest average level (1.8 ng g^{-1}) was found in automobile dust sampled from Mitsubishi cars (n=2). A one-way ANOVA test revealed no significant difference between concentrations of Σ_{10}PBDEs in vehicle dust samples from different car manufacturers ($p = 0.521$). This could possibly be ascribed to the small sample size for some car manufacturers such as Honda (n=1) and Ford (n=1).

Kolmogorov-Smirnov (KS) statistical analysis indicated that the concentrations of Σ_{10}PBDEs and all PBDE congeners in domestic and vehicle dust samples taken in this study deviate significantly from a normal distribution. Therefore, a t-test was conducted on log-transformed concentrations to elucidate any differences in average concentrations of PBDEs between household and car dust. The results showed that Σ_{10}PBDE levels in residential dust were significantly greater than those in automobile dust ($p = 0.001$). Moreover, concentrations of all congeners studied, except for BDE-28, were significantly higher in house dust than in car dust (p = <0.001-0.004), implying more extensive use of the Penta-formulation in homes. This finding contrasts with the studies of Cunha *et al.* (2010) and Harrad *et al*. (2008b) who reported that levels of ΣPBDEs and Σtri-hexa-BDEs are greater in automobiles than in residences in Portugal and the UK respectively. However, it is consistent with a U.S. study that found vehicle dust generally contained lower levels (statistical significance of this was not reported) of all 21 target congeners except for BDE-206, 207, 208 and 209 as compared to domestic dust (Batterman *et al*., 2009). The findings presented here revealed that house dust is more contaminated with tri- to hexa-BDEs than car dust, and indicate that more investigation is needed to characterise PBDE contamination and its sources in Thai houses and vehicles.

Table 4.4 Concentrations of PBDEs (ng g^{-1}) in car dust samples from Thailand and selected other studies

Congener/ location	**17**	**28**	**47**	**49**	**66**	**85**	**99**	**100**	**153**	**154**	**Σ_{10}PBDEs^{a}**	**BDE47:99 ratio**
Thailand, this study, Cars, n=30												
TH Car 1-Nissan	<0.03	<0.03	0.38	<0.03	<0.03	2.0	2.1	0.85	4.3	0.63	10	0.18
TH Car 2-Isuzu	<0.03	<0.03	0.49	<0.03	<0.03	0.35	1.4	0.23	<0.03	<0.03	2.6	0.34
TH Car 3-Isuzu	<0.03	<0.03	1.1	<0.03	<0.03	<0.03	0.49	<0.03	1.3	0.78	3.8	2.3
TH Car 4-Toyota	<0.03	<0.03	0.66	<0.03	<0.03	0.14	0.37	0.15	0.34	0.25	2.0	1.8
TH Car 5-Isuzu	0.30	6.8	16	5.7	6.4	<0.03	2.4	<0.03	<0.03	<0.03	38	6.5
TH Car 6-Mitzubishi	<0.03	<0.03	1.7	<0.03	<0.03	<0.03	1.1	<0.03	<0.03	<0.03	2.9	1.6
TH Car 7-Isuzu	<0.03	<0.03	0.68	<0.03	<0.03	<0.03	2.5	<0.03	<0.03	<0.03	3.3	0.28
TH Car 8-Isuzu	<0.03	0.33	11	0.37	<0.03	0.29	22	3.3	0.98	<0.03	38	0.48
TH Car 9-Isuzu	<0.03	<0.03	1.1	0.06	0.11	0.18	1.3	0.18	0.74	0.79	4.4	0.86
TH Car 10-Isuzu	<0.03	<0.03	0.62	<0.03	0.11	0.04	0.40	0.13	0.49	0.26	2.1	1.6
TH Car 11-Ford	<0.03	<0.03	1.5	<0.03	0.11	0.13	2.8	0.49	0.26	<0.03	5.3	0.52
TH Car 12-Toyota	<0.03	<0.03	3.4	<0.03	<0.03	1.3	11	2.4	0.79	0.71	19	0.32
TH Car 13-Isuzu	<0.03	<0.03	0.23	<0.03	0.05	0.10	0.87	0.13	0.68	0.18	2.3	0.26
TH Car 14-Toyota	<0.03	<0.03	0.23	<0.03	<0.03	0.09	0.18	0.16	0.32	0.47	1.5	1.3
TH Car 15-Toyota	<0.03	<0.03	0.52	<0.03	<0.03	0.07	0.73	0.11	0.28	0.25	2.0	0.71
TH Car 16-Toyota	<0.03	<0.03	1.3	<0.03	<0.03	0.20	2.1	0.52	0.92	0.84	6.0	0.62
TH Car 17-Toyota	0.36	1.6	6.1	0.06	<0.03	0.20	14	2.5	0.78	0.63	26	0.45
TH Car 18-Honda	<0.03	<0.03	0.57	<0.03	<0.03	0.10	0.65	0.32	0.19	<0.03	1.9	0.88
TH Car 19-Toyota	<0.03	<0.03	1.3	<0.03	<0.03	<0.03	0.23	<0.03	<0.03	<0.03	1.6	5.6
TH Car 20-Isuzu	<0.03	<0.03	0.53	<0.03	<0.03	<0.03	0.26	<0.03	<0.03	<0.03	0.91	2.0
TH Car 21-Isuzu	<0.03	0.59	1.9	0.66	0.24	0.12	1.6	0.10	0.25	<0.03	5.5	1.1
TH Car 22-Toyota	<0.03	<0.03	0.80	<0.03	<0.03	0.21	2.2	0.15	<0.03	<0.03	3.5	0.36
TH Car 23-Isuzu	<0.03	<0.03	0.58	<0.03	<0.03	0.27	0.86	0.24	0.13	0.17	2.3	0.67
TH Car 24-Toyota	<0.03	<0.03	0.18	<0.03	<0.03	0.04	0.59	0.12	0.15	<0.03	1.2	0.31
TH Car 25-Isuzu	<0.03	<0.03	0.48	<0.03	<0.03	0.10	0.53	0.09	0.14	0.20	1.6	0.91
TH Car 26-Toyota	<0.03	<0.03	0.09	<0.03	<0.03	<0.03	0.89	<0.03	<0.03	<0.03	1.1	0.10
TH Car 27-Isuzu	<0.03	<0.03	<0.03	<0.03	<0.03	1.0	4.9	<0.03	<0.03	<0.03	6.1	0.003
TH Car 28-Isuzu	<0.03	<0.03	0.41	<0.03	<0.03	0.21	2.1	0.17	<0.03	<0.03	3.0	0.19
TH Car 29-Mitzubishi	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.54	<0.03	<0.03	<0.03	0.68	0.03
TH Car 30-Nissan	<0.03	<0.03	1.4	<0.03	<0.03	0.19	8.1	0.93	0.42	0.36	11	0.17
Average^{b}	0.04	0.32	1.8	0.24	0.25	0.25	3.0	0.45	0.45	0.23	7.0	0.62
σ_n^{b}	0.08	1.3	3.4	1.0	1.2	0.44	4.8	0.82	0.80	0.29	10	-
Median^{b}	0.015	0.015	0.64	0.015	0.015	0.11	1.2	0.14	0.22	0.015	3.0	0.55
Minimum	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.18	<0.03	<0.03	<0.03	0.68	0.003
Maximum	0.36	6.8	16	5.7	6.4	2.0	22	3.3	4.3	0.84	38	6.5
Percentile 5^{b}	0.015	0.015	0.05	0.015	0.015	0.015	0.24	0.015	0.015	0.015	1.0	-
Percentile 95^{b}	0.17	1.1	8.7	0.53	0.18	1.2	12	2.5	1.2	0.79	32	-

Table 4.4 Concentrations of PBDEs (ng g^{-1}) in car dust samples from Thailand and selected other studies (continued)

Congener/ location	**17**	**28**	**47**	**49**	**66**	**85**	**99**	**100**	**153**	**154**	**Σ_{10}PBDEs[a]**	**BDE47:99 ratio**
Birmingham, UK, Cars, n=20 (Harrad *et al*., 2008b)												
Average	-	6.1	720	-	-	-	990	220	150	160	-	0.73
σ_n	-	13	2000	-	-	-	2400	560	360	440	-	-
Median	-	<0.5	54	-	-	-	100	17	11	11	-	0.54
Minimum	-	<0.5	19	-	-	-	23	<0.5	<0.5	<0.5	-	-
Maximum	-	43	7500	-	-	-	8000	2300	1500	1900	-	-
USA, Cars, n=60 (Lagalante *et al*., 2009)												
Average	-	154	1233	-	-	-	1989	345	552	194	-	0.62
Median	-	118	880	-	-	-	1130	211	163	105	-	0.78
Minimum	-	<3.2	139	-	-	-	201	32	43	21	-	-
Maximum	-	763	13600	-	-	-	22900	3870	16600	2050	-	-
Portugal, Car dust (sieved fraction), n=9 (Cunha *et al*., 2010)												
Average	-	8.8	387	26	8.4	56	650	161	148	110	-	0.60
σ_n	-	14	621	16	12	119	1028	301	301	225	-	-
Median	-	4.0	88	26	3.0	6.0	126	23	23	12	-	0.70
Minimum	-	<dl	26	9.0	<dl	<dl	13	2	1	2	-	-
Maximum	-	46	1549	57	37	368	3104	914	937	697	-	-

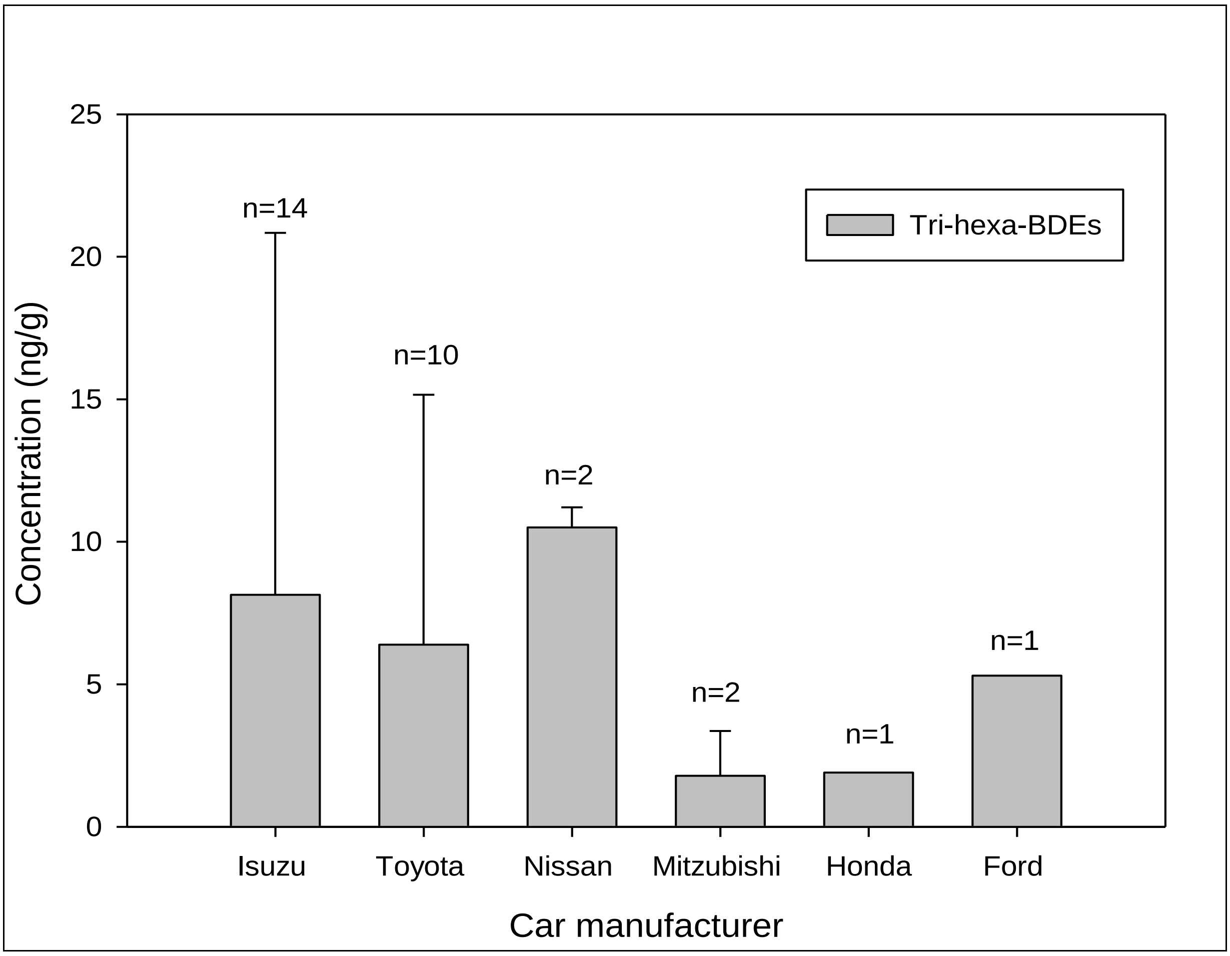
[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[b] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

Table 4.5 PBDE concentrations (range in parentheses) in car dust samples (ng g^{-1}) from different car manufacturers

Car manufacturer	Car dust concentrations of Σ_{10}PBDEs (ng g^{-1})		
	Number	Average	SD
Isuzu	14	8.1 (0.91-38)	13
Toyota	10	6.4 (1.1-26)	8.8
Nissan	2	11 (10-11)	0.71
Mitzubishi	2	1.8 (0.68-2.9)	1.6
Honda	1	1.9	-
Ford	1	5.3	-

Figure 4.5 Variation of concentrations (ng g^{-1}) of tri-hexa-BDEs (Σ_{10}PBDEs) in car dust samples from different car manufacturers



4.3.4 PBDE congener patterns in indoor dust

In order to investigate congener patterns of PBDEs in indoor dust in more detail, PBDE congener profiles were systematically compared between Thai house and car dust and also between Thai and UK house dust using Principal Component Analysis (PCA). This multi-variate technique reduces complex datasets from a great number of variables (in this context individual PBDE congeners) to a lesser number of Principal Components (PCs)/factors (ordinarily 3-4 PCs/factors), and in consequence, it facilitates pattern identification within the dataset and underlines similarities and dissimilarities between different categories of samples.

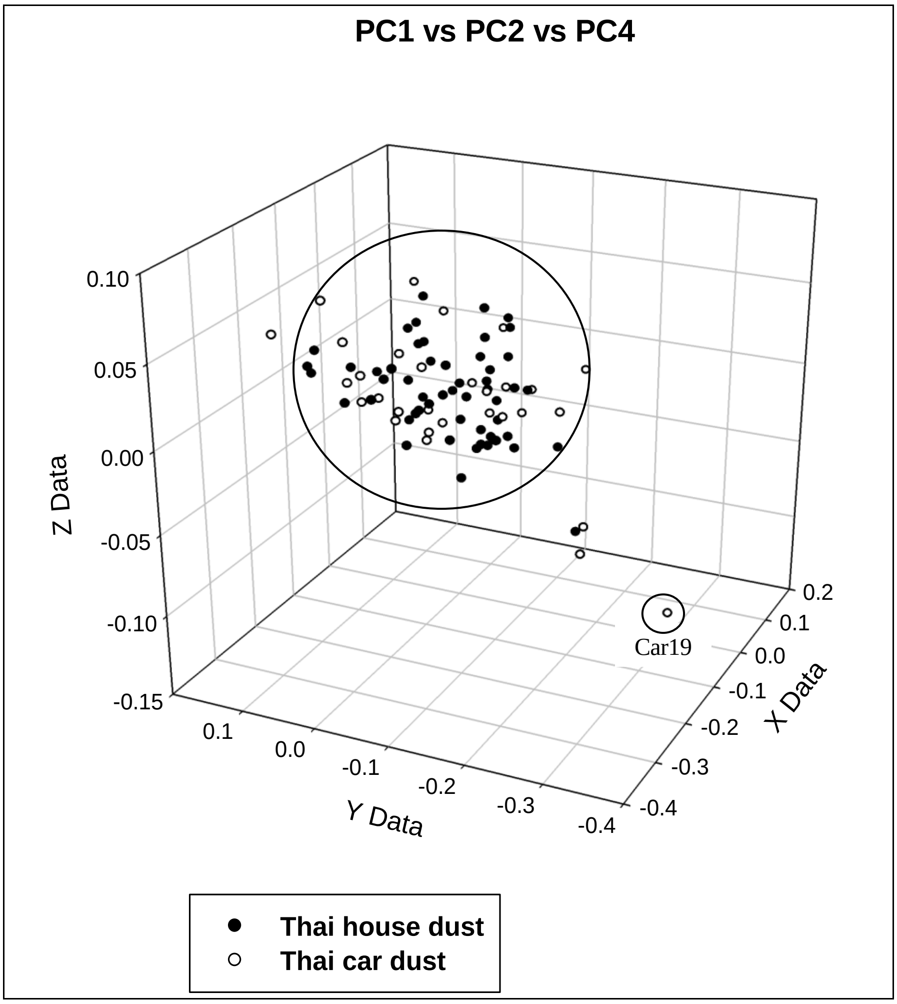
To examine the data via PCA, the relative fractional contribution of PBDE congeners (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154) to ΣPBDEs was calculated for each monitored sample and entered as a variable into the statistical analysis.

4.3.4.1 PBDE congener patterns in Thai house and car dust

The PCA evaluation of the whole dataset comprising Thai house (n=53) and car dust samples (n=30) resulted in 10 Principal Components (PCs)/factors with Eigenvalues of four PCs exceeding 1. These first four extracted PCs accounted for 75% of the variance within the data. Factor scores of PC1, PC2, PC3 and PC4 were calculated for all investigated samples included in the PCA. PC1 was mainly driven in a positive direction by high proportions of individual hexa-BDE congeners (BDEs 153 and 154), and in a negative direction by elevated proportions of BDE 99. Conversely, PC2 was principally driven in a positive direction by high proportions of BDEs 85 and 100 (penta-BDE congeners), and in a negative direction by elevated proportions of BDE 47. PCs 3 and 4 were primarily driven in a positive direction by high proportions of tetra-BDE congeners (BDEs 49 and 66) and individual tri-BDE congeners (BDEs 17 and 28) respectively. Figure 4.6 plots the factor scores of PC1 versus PC2 versus PC4 for Thai house and car dust. Plots involving PC3 proved uninformative and so are not included.

As is clear from Figure 4.6, there were not any differences in PBDE congener patterns between Thai house and car dust. The vast majority of house and car dust samples lie in the same area and seem to hover in the centre of component space. This indicated that the tri- to hexa-BDEs detected in Thai house and car dust derive from similar sources. Nevertheless, the congener pattern in car dust appears more variable than in house dust, perhaps because cars vary more in terms of factors such as vehicle age, model, manufacturer, and country of manufacture, all of which may influence the type of flame retardant present in the vehicle. In contrast, in houses, emissions will essentially arise only from electronic and electrical goods, furniture and fabrics. Of particular interest is sample Car 19 which displays a particularly distinctive profile in the guise of an elevated BDE-47:99 ratio. This may imply a distinct source or sources of PBDEs in this vehicle. However, the concentrations in this dust sample are very low, with BDEs 47 and 99 the only two congeners above detection limits, so the significance of this distinctive profile may be overestimated.

Figure 4.6 Plot of scores for principal component 1 versus principal component 2 versus principal component 4 for Thai house and car dust

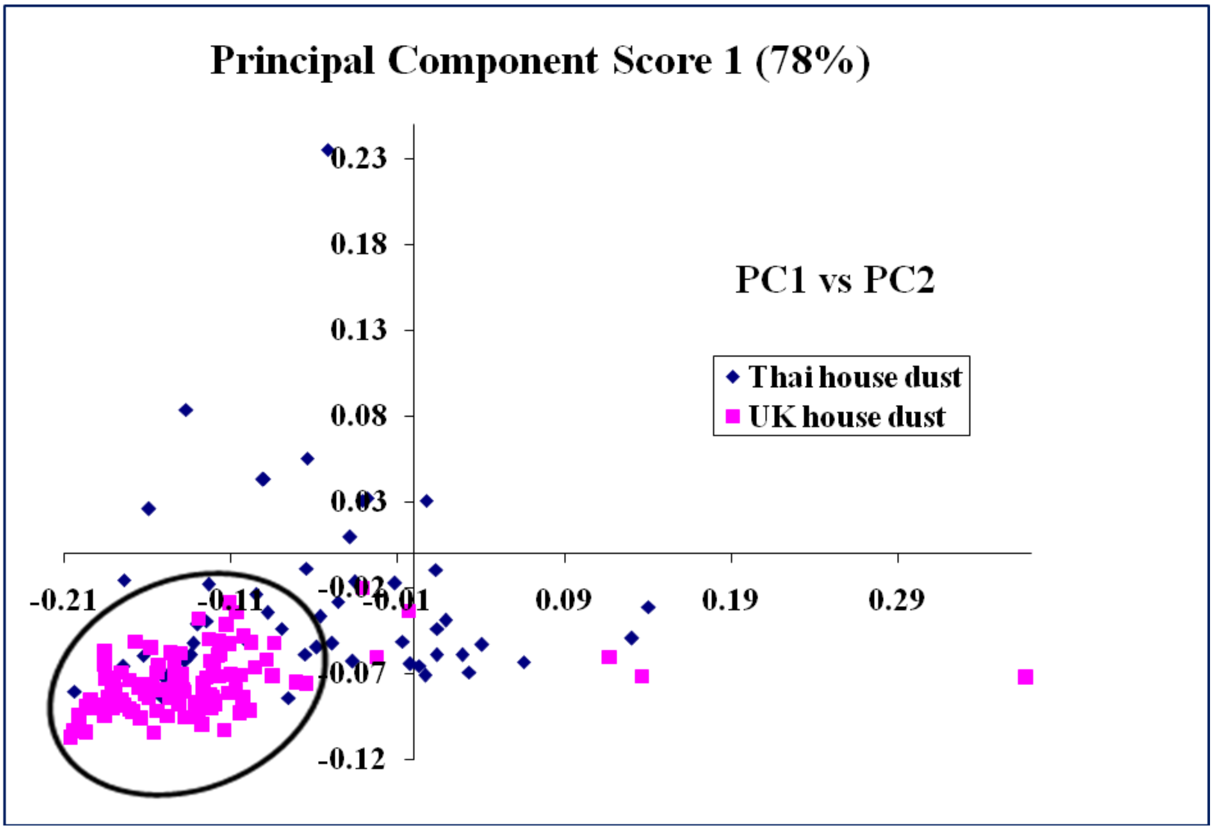


4.3.4.2 PBDE congener patterns in Thai and UK house dust

A similar comparison was carried out for PBDE congener profiles in Thai and UK house dust. Levels of BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 were normalized to levels of ΣPBDEs and subjected to PCA. Examination of the entire dataset constituting Thai (n=53) and UK house dust samples (n=112) yielded 10 PCs with eigenvalues of four PCs exceeding 1. The first four PCs - accounting for 78% of the total variance within the dataset - were extracted. PC1 was driven in a positive direction by elevated proportions of individual hexa-BDE congeners (BDEs 153 and 154), and in a negative direction by high proportions of BDE 99. PC2 and PC3 was principally driven in a positive direction by elevated proportions of tetra-BDE congeners (BDEs 49 and 66) and individual tri-BDE congeners (BDEs 17 and 28) respectively. Furthermore, PC4 was mainly driven in a positive direction by high proportions of BDEs 85 and 100 (penta-BDE congeners), and in a negative direction by elevated proportions of BDE 47. The scores for PC1 and PC2 were plotted against each other for Thai and UK house dust samples (Figure 4.7).

As Figure 4.7 shows, the residential dust samples in this study occupy a region of component space represented by a line stretching from the bottom far left corner controlled by BDE 99 (where almost all of the UK house dust samples sit), to the bottom far right governed by BDEs 153 and 154 (hexa-BDE congeners). Most of Thai dust samples sit along this line, the exceptions being eight samples, which sit in the top left region of component space and appear influenced by BDEs 49 and 66 (tetra-BDEs congeners). Figure 4.7 supports the idea that, whilst BDE 99 is the chief influence on UK house dust samples, Thai house dust samples are impacted by BDEs 49, 66, 99, 153 and 154. This supports the idea that the sources of PBDEs in Thailand differ from those in European countries such as the UK.

Figure 4.7 Plot of scores for principal component 1 versus principal component 2 for Thai and UK house dust



4.3.5 Non-occupational exposure to PBDEs via air inhalation and dust ingestion

Although diet is an important pathway of exposure to PBDEs for the general population (Frederiksen *et al*., 2009; Fromme *et al*., 2009; Gomara, *et al*., 2006; Watanabe and Sakai, 2003; Darnerud *et al*., 2001), there is mounting evidence that inhalation of indoor air and ingestion of indoor dust is also important (Wu *et al*., 2007; Jones-Otazo *et al*., 2005; Wilford *et al*., 2005; Sjodin *et al*., 2004). Hence, in order to assess non-occupational exposure to the Σtri-hexa-BDEs that represent the predominant congeners present in the Penta-BDE formulation, average adult and child air inhalation figures of 20 and 8.3 m^3 day^{-1} (Wilson *et al*., 2001) have been used. Average adult and child dust ingestion figures of 20 and 50 mg day^{-1}, and high dust ingestion figures for adults and children of 50 and 200 mg day^{-1} (Jones-Otazo *et al*., 2005) are utilised. Overall dust ingestion exposure estimates are calculated taking into account ingestion of both house and car dust. Dust ingestion is assumed to occur pro-rata to typical activity patterns (e.g. for adults and children 4.2% car and 95.8% home) (Harrad *et al*., 2008b). Assuming that the concentrations of PBDEs in microenvironments other than homes and cars are identical to those in homes, a number of air inhalation and dust ingestion exposure scenarios have been calculated using 5th percentile, average, median and 95th percentile concentrations in the indoor air and dust samples determined in this study. Additionally, the daily intake of dust has been estimated for three scenarios: namely low-end, typical and high-end exposures and the parameters used in each scenario are presented in Table 4.6. Table 4.7 provides these non-occupational exposure assessments of both adults and children to BDEs 47, 99, 100, 153, 154 and Σtri-hexa-BDEs via indoor air inhalation and dust ingestion. At median concentrations, for example, the ΣPBDE indoor air inhalation exposure is 0.46 and 0.19 ng day^{-1} for adults and children, while the average-high intake of ΣPBDEs from dust ingestion is 0.19-0.49 and 0.49-1.94 ng day^{-1} for adults and children respectively. Low, typical and high PBDE exposure levels for adults are 0.026, 0.19 and 2.13 ng day^{-1}, whilst those for children are 0.064, 0.49 and 8.51 ng day^{-1} respectively. In this study, the average-high dust ingestion estimates at median levels for both adults and children (0.19-0.49 and 0.49-1.94 ng day^{-1}) were lower than the estimates for the UK (0.36-8.71 and 4.8-17.4 ng day^{-1}), Singapore (4.8-116 and 64-232 ng day^{-1}) and Canada (7.5-180 and 99-360 ng day^{-1}) (Harrad *et al.*, 2006; Tan *et al.*, 2007; Wilford *et al.*, 2005). This is a result of the lower PBDE concentrations in residential dust in Thailand, particularly when compared with the contamination levels in Canada and the United States (Wilford *et al.*, 2005; Stapleton *et al.*, 2005; Allen *et al.*, 2008a). The median PBDE intake by the air inhalation pathway for Thai adults and children reported here (0.46 and 0.19 ng day^{-1}) exceeded figures reported for Kuwait (0.14 and 0.06 ng day^{-1}). However, the 95th percentile air inhalation intake of Σ PBDEs for adults and children (1.34 and 0.56 ng day^{-1}) were similar to and lower than the corresponding values in Kuwait (1.32 and 0.57 ng day^{-1}) and the UK (8.8 and 1.7 ng day^{-1}) respectively (Gevao *et al.*, 2006b; Harrad *et al.*, 2006). When compared with a health-based limit value (HBLV) for BDE-99 proposed recently by Netherlands researchers (0.23–0.30 ng/kg bw/day), all exposure estimates for Thai adults were well within the HBLV (Table 4.8). In contrast, for both male and female Thai children (assumed in this scenario to be 2 years old and weighing respectively 11.62 and 10.32 kg), the high-end exposure scenario estimate for BDE-99 was either very close to or slightly exceeding the exposure guideline.

Table 4.6 Parameters utilised in dust ingestion exposure scenarios

Scenario	Concentration	Dust ingestion rate
Low-end exposure	5th percentile	Average
Typical exposure	Median	Average
High-end exposure	95th percentile	High

Table 4.7 Estimated exposures to PBDEs (ng day^{-1}) via air inhalation and dust ingestion from this and other studies

Exposure pathway	BDE-47		BDE-99		BDE-100		BDE-153		BDE-154		ΣPBDEs[a]	
	Adults (ng day^{-1})	Children (ng day^{-1})	Adults (ng day^{-1})	Children (ng day^{-1})	Adults (ng day^{-1})	Children (ng day^{-1})	Adults (ng day^{-1})	Children (ng day^{-1})	Adults (ng day^{-1})	Children (ng day^{-1})	Adults (ng day^{-1})	Children (ng day^{-1})
Air inhalation, this study												
-average concentration	0.34	0.14	0.15	0.062	0.046	0.019	0.013	0.0056	0.0096	0.004	0.80	0.33
-median concentration	0.34	0.14	0.09	0.037	0.013	0.0052	0.01	0.0042	0.005	0.0021	0.46	0.19
-5th percentile concentration	0.14	0.058	0.064	0.027	0.0078	0.0032	0.005	0.0021	0.0044	0.0018	0.46	0.19
-95th percentile concentration	0.54	0.22	0.28	0.12	0.11	0.046	0.024	0.01	0.018	0.0074	1.34	0.56
Air inhalation exposure estimates from other studies												
-average concentration	-	-	-	-	-	-	-	-	-	-	2.1[b]	0.4[b]
-median concentration	-	-	-	-	-	-	-	-	-	-	0.82[b]	0.16[b]
-5th percentile concentration	-	-	-	-	-	-	-	-	-	-	0.18[b]	0.03[b]
-95th percentile concentration	-	-	-	-	-	-	-	-	-	-	8.8[b]	1.7[b]
-median concentration	-	-	-	-	-	-	-	-	-	-	0.14[c]	0.061[c]
-95th percentile concentration	-	-	-	-	-	-	-	-	-	-	1.321[c]	0.572[c]
Dust ingestion, this study												
-low-end exposure	0.0043	0.011	0.0079	0.02	0.00097	0.0024	0.0003	0.00075	0.0003	0.00075	0.026	0.064
-typical exposure	0.037	0.092	0.066	0.17	0.014	0.035	0.018	0.044	0.0092	0.023	0.19	0.49
-high-end exposure	0.45	1.82	0.65	2.59	0.19	0.75	0.35	1.41	0.23	0.91	2.13	8.51
Average-high dust ingestion rate, this study												
-median concentration	-	-	-	-	-	-	-	-	-	-	0.19-0.49	0.49-1.94
-5th percentile concentration	-	-	-	-	-	-	-	-	-	-	0.026-0.064	0.064-0.26
-95th percentile concentration	-	-	-	-	-	-	-	-	-	-	0.85-2.13	2.13-8.51
Average-high dust ingestion rate, exposure estimates from other studies												
-95th percentile concentration	-	-	-	-	-	-	-	-	-	-	2.4-58.7[b]	32.3-117.3[b]
-median concentration	-	-	-	-	-	-	-	-	-	-	0.36-8.71[b]	4.8-17.4[b]
-median concentration	-	-	-	-	-	-	-	-	-	-	4.8-116[d]	64-232[d]
-median concentration	-	-	-	-	-	-	-	-	-	-	7.5-180[e]	99-360[e]

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[b] Harrad *et al*., 2006 (sum of PBDEs 28, 47, 49, 66, 85, 99, 100, 153 and 154).

[c] Gevao *et al*., 2006b (sum of PBDEs 28, 47, 85, 99, 100, 153, 154 and 183).

[d] Tan *et al*., 2007 (sum of PBDEs 28, 47, 99, 100, 153, 154, 183 and 209).

[e] Wilford *et al*., 2005 (sum of PBDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209).

Table 4.8 Comparison of adult and child exposure to BDE-99 via air inhalation and dust ingestion (ng/kg bw/day) with exposure guideline

Exposure pathway	**BDE-99**		
	Adult[a]	**Male children**[b,d]	**Female children**[c,d]
Air inhalation			
Average concentration	0.0027	0.0053	0.006
Median concentration	0.0016	0.0032	0.0036
5th percentile concentration	0.0011	0.0023	0.0026
95th percentile concentration	0.005	0.0103	0.0116
Dust ingestion			
Low-end exposure	0.0001	0.0017	0.0019
Typical exposure	0.0012	0.0146	0.0165
High-end exposure	0.0116	0.2229	0.2510
Health-based limit value	0.23-0.30[e]	0.23-0.30[e]	0.23-0.30[e]

[a] Assumed adult weight of 56 kg (WHO, 2010).
[b] Assumed male child weight of 11.62 kg (Folk Doctor Foundation, 2009).
[c] Assumed female child weight of 10.32 kg (Folk Doctor Foundation, 2009).
[d] Two-year-old children were selected for exposure assessment as they are considered particularly prone to dust ingestion.
[e] Bakker *et al.*, 2008.

4.4 Conclusion and recommendation

The present study reports concentrations of tri-hexa-BDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154) in indoor air and dust samples collected from homes and cars in Thailand. PBDEs were detected in all household indoor air and dust samples although concentrations of these compounds in Thai domestic indoor air and dust appear at the low end of those reported elsewhere in the world. The congener pattern for indoor dust and air was dominated by BDE 99 and 47.

Principal Component Analysis (PCA) revealed no differences in PBDE congener profiles between Thai house and car dust. For Thai and UK domestic dust, the PCA suggested that, while BDEs 49, 66, 99, 153 and 154 are the main influences on Thai samples, the UK samples are principally governed by BDE 99.

PBDE levels in indoor air and dust as well as indoor air and dust ingestion exposure estimates are comparable to those reported in other countries including the United Kingdom, the United States, Canada, Australia, New Zealand, Germany, Sweden, Portugal, Kuwait, Japan and Singapore. Estimated non-occupational exposures of Thai adults to BDE-99 via air inhalation and dust ingestion were well within a health-based limit value proposed by Netherlands researchers. For young children aged 2 years, low-end and “typical” BDE-99 exposure estimates did not exceed the proposed HBLV. In contrast, under a high-end exposure scenario, the exposure to BDE-99 of such Thai children is either very close to or in exceedance of the HBLV. The findings presented here demonstrated that PBDEs are ubiquitous contaminants in Thai indoor environments such as homes and cars, and that the Thai population is continuously exposed to low concentrations of these chemicals via indoor air inhalation and dust ingestion. Further studies are required into the mechanism of non-occupational exposure to indoor PBDEs via air inhalation and dust ingestion as well as the factors playing a prominent role in exposure and in PBDE contamination of indoor environments.

CHAPTER 5

Intra-room temporal, intra-room, and intra-house spatial variability in concentrations of PBDEs in dust from two UK homes

5.1 Synopsis

This chapter provides the most detailed data to date concerning intra-room and intra-home spatial and intra-room temporal variation in concentrations of PBDEs in dust. Temporal variations in concentrations of tri- to hexa-BDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154) in dust samples (n=112) collected at monthly intervals from a number of rooms in two homes in Birmingham, United Kingdom are discussed and compared with concentrations in residential dust reported in other studies. Spatial variations in concentrations of these compounds are studied in: (a) samples taken from different rooms in the same house (intra-house variability), and (b) samples taken from different areas in the same room (intra-room variability). The most likely sources of indoor dust contamination with PBDEs, causes of observed PBDE congener patterns and factors governing PBDE levels in indoor dust are also discussed.

As stated in section 1.5, the overall hypothesis tested in this chapter is that temporal and spatial variability in indoor dust concentrations of PBDEs are of a magnitude sufficient to have important implications for source attribution and human exposure estimates (Harrad *et al.*, 2008b, 2010). Within-room spatial variation must be considered if the area vacuumed to obtain a dust sample is not the entire area of a room (Harrad, 2010). Under some circumstances, within-room spatial variation can occur, surpassing the combined analytical and sampling uncertainty, and in such situations, sampling the most-frequented area of the room is likely to provide the most “biologically relevant” sample (Harrad, 2010). Likewise, temporal variation may be significant given that assessments of exposure via dust ingestion have hitherto been based essentially on single grab samples. There have been three studies investigating such variability in PBDE levels in household dust. The US study of Allen *et al.* (2008a) reported a statistically significant difference in Octa-BDE levels but no significant change in Deca- and Penta-BDE levels in dust samples taken from the same rooms (20 main living rooms and 20 bedrooms in total in 20 houses) eight months apart. The same authors also mentioned that while Deca- and Penta-BDE concentrations were significantly higher in dust from the main living room than the bedroom; there was no significant difference for congeners associated with the Octa-BDE formulation.

The UK study of Harrad *et al.* (2008b) reported considerable temporal variation in PBDE concentrations in dust sampled monthly in three houses over a 9-10 month period. The same study reported that spatial variation in PBDE levels in dust within the same room were appreciably greater than that attributable to sampling and analytical variation. Another study in the US by Batterman *et al*. (2009) suggested that PBDE concentrations in dust vacuumed from twelve U.S. residences in two different seasons showed little consistency.

To the best of the author's knowledge, the data on within-room and within-home spatial variability in concentrations of PBDEs in dust reported in this chapter are the most comprehensive to date.

5.2 Sampling protocol and locations

A total of 112 domestic dust samples were collected from two homes in Birmingham, UK. Dust samples were taken at monthly intervals from 4 different rooms in Home 1 (n=80, sample ID: UK Dust 1-80) and from 2 different rooms in Home 2 (n=32, sample ID: UK Dust 81-112). All samples were collected using a Nilfisk Sprint Plus 1600 W vacuum cleaner via the sampling protocol described in Chapter 2 (Figure 5.1). Sample information questionnaires (see Questionnaire 3 in Appendix A) were completed for each sample by the researcher. All dust samples were transported to the laboratory for PBDE analysis. GC-MS determination of tri- to hexa-BDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154; Σ_{10}PBDEs) was carried out as described in Chapter 2. Details of the monitored household dust samples and room contents for these temporal and spatial variability studies are given in Appendix D and Table 5.1 respectively.

Figure 5.1 Dust sampling in a UK home

Table 5.1 Room contents in temporal and spatial variability studies

Room (# areas sampled within room)	Room ventilation	Floor type	# TVs	# Computers	# Sofas	# Foam chairs	# Beds	# Stereos	Other room contents
Home 1									
Living room (2)[a]	Natural	Carpet + 3 rugs	1[b]	0	2	0	0	0	Fire place
Bedroom 1 (1)	Natural	Carpet	1	1 (laptop)	0	1	1	0	Radio, hair dryer, iron, floor/desk lamp, alarm clock
Bedroom 2 (3)[c]	Natural	Carpet	1	1 (laptop)	0	0	1	1	Kettle
Bedroom 3 (4)[c,d,e]	Natural	Carpet	0	1 (PC)	0	0	1	1	
Home 2									
Bedroom 1 (3)[c,d]	Natural	Carpet	1	1 (laptop)	1	1	1	0	Radio, hair dryer, iron, floor/desk lamp, alarm clock
Bedroom 2 (1)[c]	Natural	Bare wood	1	1 (laptop)	0	0	1	1	Kettle

[a] Room located close to a kitchen.
[b] Unused TV.
[c] The room was located on the road frontage.
[d] The top floor room.
[e] The loft bedroom.

5.3 Results and discussion

5.3.1 Concentrations of tri- to hexa-BDEs (Σ_{10}PBDEs) in indoor dust samples from UK homes.

The following sections present data concerning: (a) within-room spatial variability; (b) within-home spatial variability; and (c) within-room temporal variability for the fourteen different areas monitored. Table 5.2 shows the concentrations of tri- to hexa-BDEs (Σ_{10}PBDEs) and individual congeners in dust from each area in the two homes studied, along with the relative standard deviations (RSDs) of these concentrations. Concentrations of Σ_{10}PBDEs in domestic dust samples from home 1 ranged from 21 to 280 ng g^{-1}, with the highest concentrations found in area 2 of bedroom 3 (H1B3/2), which was located on the top/carpeted floor (a loft bedroom) and adjoined a road. The levels detected suggest a PBDE emission source in the room. Σ_{10}PBDE levels in residential dust from home 2 were 20-1,000 ng g^{-1}, with the greatest levels observed in area 1 (H2B1/1) adjacent to TV, sofa and desk (with associated laptop and foam chair) in bedroom 1 located on the top/carpeted floor and a road frontage. In this study, the congener profile in all household dust samples was dominated by BDEs-99 and -47. The average levels of BDE-153 and BDE-154 determined in dust sampled from each area of home 1 were generally lower than the average levels reported previously for homes in Birmingham, the UK (Harrad *et al.*, 2008a,b). In contrast, average concentrations of BDE-154 in samples taken from each area of home 2 exceeded those reported for Birmingham homes (Harrad *et al.*, 2008a,b).

Table 5.2 PBDE concentrations (ng g^{-1}) in dust samples from UK homes

Congener #	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Range	Average[a]	SD[a]	RSD[a]
H1L/1: Home 1, Area 1 of Living Room												
17	1.8	<0.03	0.26	<0.03	0.06	0.39	0.18	0.04	<0.03-1.8	0.35	0.60	175
28	2.6	0.43	1.0	0.69	0.29	0.68	0.32	0.15	0.15-2.6	0.77	0.79	102
47	16	7.0	21	19	12	10	11	12	7.0-21	14	4.8	35
49	3.3	0.07	0.79	0.59	0.09	1.1	1.2	1.5	0.07-3.3	1.1	1.0	95
66	5.9	0.12	0.31	0.44	0.57	1.1	0.40	0.60	0.12-5.9	1.2	1.9	163
85	3.1	1.8	1.2	3.1	1.6	1.5	0.40	1.4	0.40-3.1	1.8	0.92	52
99	28	13	49	24	32	23	27	19	13-49	27	11	40
100	7.4	2.3	1.9	7.5	2.2	3.6	0.44	2.4	0.44-7.5	3.5	2.6	75
153	13	0.50	7.8	5.2	1.2	2.7	1.1	2.4	0.50-13	4.2	4.3	101
154	6.4	0.35	4.1	3.0	0.66	2.5	0.91	2.2	0.35-6.4	2.5	2.0	80
ΣPBDEs[b]	88	26	87	64	51	47	43	42	26-88	56	22	40
H1L/2: Home 1, Area 2 of Living Room												
17	<0.03	<0.03	0.44	0.05	0.05	0.27	<0.03	0.07	<0.03-0.44	0.12	0.16	135
28	0.29	<0.03	2.1	0.76	0.22	0.46	0.16	0.43	<0.03-2.1	0.55	0.66	120
47	14	7.6	35	13	20	12	10	7.1	7.1-35	15	9.1	61
49	0.11	0.16	0.95	3.1	0.15	1.1	0.18	0.47	0.11-3.1	0.78	1.0	130
66	0.31	0.26	0.62	0.44	0.51	1.2	1.0	0.35	0.26-1.2	0.59	0.34	58
85	1.2	0.66	4.6	3.3	0.50	0.97	0.47	0.77	0.47-4.6	1.6	1.5	98
99	21	12	146	32	44	28	20	22	12-146	41	44	107
100	3.6	1.0	24	6.3	2.1	1.3	0.30	1.2	0.30-24	5.0	7.9	159
153	6.3	2.0	2.0	2.6	1.4	1.9	1.5	2.9	1.4-6.3	2.6	1.6	62
154	3.4	1.4	1.2	0.39	0.87	1.9	1.3	2.6	0.39-3.4	1.6	1.0	60
ΣPBDEs[b]	50	25	217	62	70	49	35	38	25-217	68	62	91

[a] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

Table 5.2 PBDE concentrations (ng g^{-1}) in dust samples from UK homes (continued)

Congener #	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Range	Average[a]	SD[a]	RSD[a]
H1B1/1: Home 1, Bedroom 1												
17	<0.03	<0.03	0.24	0.14	0.13	<0.03	0.10	0.06	<0.03-0.24	0.09	0.08	89
28	<0.03	0.10	0.66	0.18	0.58	0.21	0.29	0.18	<0.03-0.66	0.28	0.23	82
47	8.3	6.7	21	7.9	8.7	4.1	5.6	6.4	4.1-21	8.6	5.2	61
49	0.16	0.10	0.24	0.75	0.68	0.65	0.17	1.2	0.10-1.2	0.49	0.39	79
66	0.26	0.25	0.18	0.95	0.73	0.15	0.33	0.50	0.15-0.95	0.42	0.29	69
85	1.4	1.5	0.76	2.0	0.81	0.96	0.99	0.84	0.76-2.0	1.2	0.44	38
99	16	16	55	25	6.8	13	16	11	6.8-55	20	15	76
100	1.4	3.9	0.81	2.1	0.89	1.7	1.6	0.95	0.81-3.9	1.7	1.0	60
153	2.3	2.9	2.2	5.0	4.6	0.35	1.3	1.3	0.35-5.0	2.5	1.6	65
154	1.2	2.1	2.0	2.5	2.4	0.34	0.68	0.77	0.34-2.5	1.5	0.85	57
ΣPBDEs[b]	31	34	83	47	26	21	27	23	21-83	37	20	56
H1B2/1: Home 1, Area 1 of Bedroom 2												
17	<0.03	<0.03	0.25	0.82	0.04	0.06	0.14	<0.03	<0.03-0.82	0.17	0.28	163
28	<0.03	<0.03	0.51	1.2	0.25	0.23	0.79	0.24	<0.03-1.2	0.41	0.41	101
47	9.1	8.6	23	22	18	14	9.0	8.0	8.0-23	14	6.3	45
49	0.17	0.23	1.4	1.6	0.34	<0.03	0.79	0.69	<0.03-1.6	0.65	0.58	89
66	1.2	0.15	1.3	2.8	0.77	0.65	0.28	0.30	0.15-2.8	0.93	0.87	93
85	1.7	1.4	1.8	2.8	0.91	0.63	0.42	0.34	0.34-2.8	1.3	0.84	67
99	14	14	54	31	15	11	11	9.1	9.1-54	20	15	77
100	2.2	2.9	4.0	4.4	2.0	1.5	1.0	1.0	1.0-4.4	2.4	1.3	55
153	3.1	24	3.5	6.6	22	3.1	1.8	1.5	1.5-24	8.2	9.3	113
154	1.4	7.9	2.7	1.1	14	1.5	1.1	1.3	1.1-14	3.9	4.7	121
ΣPBDEs[b]	33	59	92	74	73	33	26	22	22-92	52	26	51

[a] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

Table 5.2 PBDE concentrations (ng g^{-1}) in dust samples from UK homes (continued)

Congener #	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Range	Average[a]	SD[a]	RSD[a]
H1B2/2: Home 1, Area 2 of Bedroom 2												
17	0.17	0.24	0.25	0.79	<0.03	<0.03	0.03	0.05	<0.03-0.79	0.20	0.26	133
28	0.22	0.82	0.69	1.8	0.20	0.18	0.14	0.11	0.11-1.8	0.52	0.58	112
47	11	11	16	7.1	7.8	10	9.2	8.7	7.1-16	10	2.8	27
49	0.46	0.22	0.49	0.30	0.74	0.18	0.14	0.76	0.14-0.76	0.41	0.24	59
66	1.3	0.48	0.11	1.4	0.55	0.89	0.10	0.37	0.10-1.4	0.65	0.50	77
85	0.77	2.0	0.18	2.3	1.0	0.79	1.2	0.19	0.18-2.3	1.1	0.77	73
99	15	23	32	15	15	13	12	16	12-32	18	6.7	38
100	3.1	2.0	0.23	2.9	1.1	3.6	3.9	2.3	0.23-3.9	2.4	1.3	52
153	2.6	1.3	1.5	5.9	1.7	2.5	2.1	2.4	1.3-5.9	2.5	1.5	58
154	0.53	1.3	1.2	4.8	2.0	0.69	0.39	0.12	0.12-4.8	1.4	1.5	109
ΣPBDEs[b]	35	42	53	42	30	32	29	31	29-53	37	8.2	22
H1B2/3: Home 1, Area 3 of Bedroom 2												
17	<0.03	0.10	0.76	0.12	<0.03	0.14	0.40	0.13	<0.03-0.76	0.21	0.25	120
28	0.38	0.32	1.4	0.17	0.54	0.24	0.19	0.28	0.17-1.4	0.44	0.41	92
47	7.1	6.7	16	11	11	8.8	9.9	12	6.7-16	10	3.0	29
49	0.25	0.72	3.3	0.22	0.59	0.24	0.95	1.5	0.22-3.3	0.97	1.0	107
66	0.32	0.15	1.3	0.37	0.12	0.24	0.22	0.81	0.12-1.3	0.44	0.41	93
85	0.68	0.83	0.70	1.2	1.5	1.1	0.53	1.7	0.53-1.7	1.0	0.42	41
99	12	15	42	17	14	18	15	62	12-62	24	18	74
100	1.7	4.3	1.8	2.4	3.2	2.0	0.85	2.7	0.85-4.3	2.4	1.1	44
153	1.6	3.8	1.1	1.7	1.6	1.3	1.5	4.6	1.1-4.6	2.2	1.3	60
154	1.4	3.4	0.61	1.1	1.5	0.84	0.89	3.5	0.61-3.5	1.7	1.1	69
ΣPBDEs[b]	25	35	69	35	34	33	30	89	25-89	44	23	51

[a] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

Table 5.2 PBDE concentrations (ng g^{-1}) in dust samples from UK homes (continued)

Congener #	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Range	Average[a]	SD[a]	RSD[a]
H1B3/1: Home 1, Area 1 of Bedroom 3												
17	<0.03	0.27	0.09	0.09	0.10	<0.03	0.16	0.64	<0.03-0.64	0.17	0.21	119
28	0.33	0.66	0.40	0.19	0.79	0.25	0.34	1.1	0.19-1.1	0.51	0.31	62
47	29	9.5	12	13	8.9	11	19	16	8.9-29	15	6.6	45
49	1.3	0.29	1.1	0.22	0.16	0.41	0.09	2.8	0.09-2.8	0.80	0.93	116
66	0.42	0.32	0.41	0.27	0.09	0.11	0.21	1.3	0.09-1.3	0.39	0.39	99
85	1.5	0.91	0.95	3.9	2.2	0.96	2.3	0.54	0.54-3.9	1.7	1.1	67
99	53	18	35	34	17	29	58	22	17-58	33	15	46
100	7.6	4.6	2.1	4.8	5.8	1.2	4.4	2.4	1.2-7.6	4.1	2.1	51
153	7.3	2.7	3.2	4.2	1.5	0.60	1.1	3.9	0.60-7.3	3.1	2.2	70
154	2.0	2.5	1.3	4.0	0.67	0.51	0.86	2.2	0.51-4.0	1.8	1.2	67
ΣPBDEs[b]	102	40	57	65	37	44	86	53	37-102	61	23	38
H1B3/2: Home 1, Area 2 of Bedroom 3												
17	<0.03	0.06	<0.03	0.13	0.06	<0.03	<0.03	0.09	<0.03-0.13	0.05	0.04	87
28	<0.03	0.23	0.05	0.76	0.25	0.03	0.21	0.53	<0.03-0.76	0.26	0.26	101
47	29	7.4	17	16	15	8.7	14	11	7.4-29	15	6.7	45
49	1.8	0.26	0.31	1.0	0.66	0.10	0.10	0.46	0.10-1.8	0.59	0.58	98
66	1.6	0.39	0.19	0.32	0.20	0.29	0.15	0.53	0.15-1.6	0.46	0.48	104
85	<0.03	1.6	0.25	0.74	0.36	0.41	1.5	0.78	<0.03-1.6	0.71	0.58	82
99	182	13	24	46	16	18	32	38	13-182	46	56	122
100	9.2	4.6	0.28	1.2	1.1	1.8	4.5	2.6	0.28-9.2	3.2	2.9	92
153	36	2.8	2.6	2.8	0.91	0.48	1.7	1.2	0.48-36	6.1	12	200
154	16	2.3	1.4	1.5	1.1	0.45	0.23	0.15	0.15-16	2.9	5.3	185
ΣPBDEs[b]	276	33	46	70	36	30	54	55	30-276	75	82	109

[a] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

Table 5.2 PBDE concentrations (ng g^{-1}) in dust samples from UK homes (continued)

Congener #	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Range	Average[a]	SD[a]	RSD[a]
H1B3/3: Home 1, Area 3 of Bedroom 3												
17	<0.03	0.12	0.48	0.05	0.14	<0.03	0.05	<0.03	<0.03-0.48	0.11	0.16	142
28	0.69	0.18	2.5	0.54	1.3	0.07	0.48	0.18	0.07-2.5	0.74	0.81	109
47	32	8.4	30	21	16	12	15	13	8.4-32	18	8.6	46
49	0.58	0.20	3.0	0.20	1.9	0.26	1.4	3.1	0.20-3.1	1.3	1.2	92
66	1.0	0.36	1.9	0.24	1.4	0.10	0.37	0.91	0.10-1.9	0.79	0.63	81
85	2.3	1.1	2.5	2.0	1.3	0.62	2.1	1.7	0.62-2.5	1.7	0.65	38
99	99	32	23	49	29	30	55	52	23-99	46	25	53
100	12	2.3	8.0	9.4	2.3	0.88	5.3	3.4	0.88-12	5.4	4.0	73
153	10	3.8	2.6	3.9	1.4	1.7	2.3	1.8	1.4-10	3.4	2.8	82
154	7.1	2.8	2.6	2.8	0.49	1.6	1.1	1.8	0.49-7.1	2.5	2.0	80
ΣPBDEs[b]	165	51	77	89	55	47	83	78	47-165	81	37	46
H1B3/4: Home 1, Area 4 of Bedroom 3												
17	0.54	0.19	0.05	0.16	0.19	0.19	0.21	0.29	0.05-0.54	0.23	0.14	63
28	0.75	0.91	0.25	0.89	0.23	1.2	0.45	0.36	0.23-1.2	0.63	0.36	57
47	18	4.0	12	29	11	32	45	37	4.0-45	24	14	61
49	0.65	0.50	1.1	0.10	1.2	2.30	2.5	1.3	0.10-2.5	1.2	0.84	70
66	0.63	1.1	1.2	0.65	0.42	0.53	2.0	0.83	0.42-2.0	0.92	0.51	56
85	1.7	0.57	2.7	7.4	0.81	8.6	2.7	2.7	0.57-8.6	3.4	3.0	88
99	25	14	31	133	24	72	102	102	14-133	63	45	72
100	4.2	0.77	2.9	22	2.8	10	13	4.1	0.77-22	7.5	7.1	96
153	3.0	3.8	0.72	2.7	1.1	2.6	3.7	3.2	0.72-3.8	2.6	1.1	43
154	2.6	1.1	0.37	2.7	0.42	2.0	2.4	2.6	0.37-2.7	1.8	0.99	56
ΣPBDEs[b]	57	27	52	199	42	131	174	154	27-199	105	67	64

[a] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

Table 5.2 PBDE concentrations (ng g^{-1}) in dust samples from UK homes (continued)

Congener #	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Range	Average[a]	SD[a]	RSD[a]
H2B1/1: Home 2, Area 1 of Bedroom 1												
17	<0.03	<0.03	<0.03	0.88	<0.03	<0.03	<0.03	<0.03	<0.03-0.88	0.12	0.31	248
28	2.3	1.6	2.1	3.3	3.0	2.7	3.0	3.2	1.6-3.3	2.7	0.60	23
47	138	205	79	114	110	85	90	120	79-205	118	40	34
49	7.2	2.2	4.7	5.3	5.6	4.5	<0.03	6.4	<0.03-7.2	4.5	2.3	52
66	8.2	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-8.2	1.0	2.9	279
85	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-<0.03	0.015	0	0
99	391	563	206	242	215	192	155	260	155-563	278	135	49
100	88	137	48	46	53	39	41	70	39-137	65	33	51
153	51	49	32	21	22	19	11	17	11-51	28	15	54
154	72	83	37	32	31	28	22	43	22-83	44	22	51
ΣPBDEs[b]	758	1041	409	465	440	370	322	520	322-1041	540	241	45
H2B1/2: Home 2, Area 2 of Bedroom 1												
17	<0.03	<0.03	<0.03	<0.03	<0.03	0.44	<0.03	<0.03	<0.03-0.44	0.07	0.15	221
28	2.9	2.5	1.8	2.5	1.3	3.4	3.7	2.3	1.3-3.7	2.6	0.79	31
47	140	110	81	110	121	133	111	102	81-140	114	18	16
49	6.3	5.3	4.1	4.0	6.2	6.9	6.4	<0.03	<0.03-6.9	4.9	2.2	46
66	5.0	<0.03	<0.03	<0.03	<0.03	4.7	3.5	<0.03	<0.03-5.0	1.7	2.3	139
85	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-<0.03	0.015	0	0
99	339	222	164	230	266	264	211	208	164-339	238	52	22
100	74	54	35	45	62	61	52	51	35-74	54	12	22
153	33	18	14	23	24	30	14	4.4	4.4-33	20	9.4	47
154	53	29	27	28	41	45	33	17	17-53	34	12	34
ΣPBDEs[b]	653	441	327	443	522	548	435	385	327-653	469	102	22

[a] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

Table 5.2 PBDE concentrations (ng g^{-1}) in dust samples from UK homes (continued)

Congener #	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Range	Average[a]	SD[a]	RSD[a]
H2B1/3: Home 2, Area 3 of Bedroom 1												
17	<0.03	<0.03	0.68	0.13	<0.03	<0.03	<0.03	<0.03	<0.03-0.68	0.11	0.23	207
28	1.9	1.6	2.4	2.7	2.5	2.7	2.6	1.4	1.4-2.7	2.2	0.52	23
47	82	66	64	86	82	78	91	55	55-91	76	12	16
49	3.8	3.5	3.6	3.9	2.8	1.3	4.9	<0.03	<0.03-4.9	3.0	1.6	53
66	3.7	<0.03	2.8	<0.03	2.6	1.1	2.8	<0.03	<0.03-3.7	1.6	1.5	93
85	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-<0.03	0.015	0	0
99	178	150	136	135	134	126	176	106	106-178	143	25	17
100	40	36	28	29	35	26	38	27	26-40	32	5.5	17
153	18	15	15	6.5	5.9	4.3	13	12	4.3-18	11	5.0	45
154	25	22	23	12	17	14	19	21	12-25	19	4.5	24
ΣPBDEs[b]	352	294	275	275	282	253	347	222	222-352	288	44	15
H2B2/1: Home 2, Bedroom 2												
17	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-<0.03	0.015	0	0
28	<0.03	<0.03	0.35	1.2	<0.03	0.95	<0.03	<0.03	<0.03-1.2	0.32	0.48	150
47	7.1	15	8.7	26	17	19	14	6.4	6.4-26	14	6.7	47
49	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-<0.03	0.015	0	0
66	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-<0.03	0.015	0	0
85	<0.03	<0.03	1.1	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03-1.1	0.15	0.38	255
99	11	49	17	39	29	41	44	21	11-49	31	14	44
100	1.7	8.3	1.8	11	4.9	8.0	8.9	5.9	1.7-11	6.3	3.4	53
153	<0.03	700	0.48	<0.03	<0.03	5.0	2.6	<0.03	<0.03-700	89	247	279
154	<0.03	246	2.5	1.6	<0.03	4.0	3.9	<0.03	<0.03-246	32	86	268
ΣPBDEs[b]	20	1018	32	79	51	78	73	33	20-1018	173	342	198

[a] For purposes of calculating descriptive statistics, values <dl assumed to equal 0.5 x dl (for PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154 dl = 0.03 ng g^{-1}).

[b] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

5.3.2 Within-room spatial variation in concentrations of PBDEs in dust

The average concentrations of PBDEs in dust from individual areas within the four rooms investigated for within-room spatial variation are listed in Table 5.2. The contents of the rooms studied are given in Table 5.1. It has been suggested that the possibility of substantial variation in exposure depending on the area within the room should be considered, and it is possible that a more "biologically relevant" exposure estimate may be acquired via vacuuming only in the most-frequented areas of the room. As emphasised in a previous study by Harrad *et al*. (2008b), appreciable within-room spatial variations in PBDE levels are very pertinent where a more contaminated area coincides with for instance a toddler's playpen or a baby's playmat.

It is interesting to inspect the spatial variations in PBDE levels within H2/B1, in the context of the proximity of each sampling area to potential emission sources. As stated in Table 5.1, H2/B1 contained a TV, computer, sofa and foam chair identified as potential sources of PBDEs. It is thus expected that sample H2B1/1 sampled closest to the part of the room containing these PBDE emitters contained the highest concentration of Σ_{10}PBDEs (Figure 5.2). The other two sampling areas were located further away from these potential sources, with areas H2B1/2 and H2B1/3 one metre and two metres away respectively. This phenomenon explained why sample H2B1/1 contained approximately 1.2 and 1.9 times more Σ_{10}PBDEs than sample H2B1/2 and H2B1/3 respectively (Figure 5.2). Also, this finding could explain the statistically significant differences in Σ_{10}PBDE concentrations between sample H2B1/1 and H2B1/3, shown later (Table 5.3).

Kolmogorov-Smirnov (KS) statistical analysis revealed the levels of Σ_{10}PBDEs in 6 (H1L/2, H1B1/1, H1B2/3, H1B3/2, H1B3/3 and H2B2/1) out of the 14 individual areas sampled to deviate significantly from a normal distribution. Further visual inspection revealed these data to display a log-normal distribution. Hence, a one-way analysis of variance (ANOVA) (in rooms H1/B2 and H1/B3) and t-test (in room H1/L) of log-transformed concentrations as well as an ANOVA (in room H2/B1) of untransformed concentrations was used to assess any differences in Σ_{10}PBDE levels in the samples taken from different areas in the same room. Table 5.3 and Figure 5.2 present variations in Σ_{10}PBDE dust levels between areas within the same rooms. In the majority of cases, concentrations of Σ_{10}PBDEs did not differ significantly between different areas in the same room ($p > 0.05$). This may be because all areas within the same rooms were on the same carpeted floor. The only exceptions were areas 1 and 3 within H2/B1. Here Σ_{10}PBDE concentrations in area 1 (sample H2B1/1) nearest to the PBDE emission sources (e.g. TV, laptop, foam chair and sofa) exceeded significantly those in area 3 (sample H2B1/3) farthest from the sources and close to a room door ($p = 0.009$). Moreover, the greatest concentrations of Σ_{10}PBDEs ($p = 0.01$), BDE-47 ($p = 0.008$), BDE-99 ($p = 0.001$), BDE-100 ($p = 0.014$), BDE-153 ($p = 0.018$) and BDE-154 ($p = 0.011$) were detected in area 1 (H2B1/1), located closest to potential PBDE emitters.

Figure 5.2 Σ_{10}PBDE concentrations in dust from different areas within the same rooms (y-error bars are standard deviations)

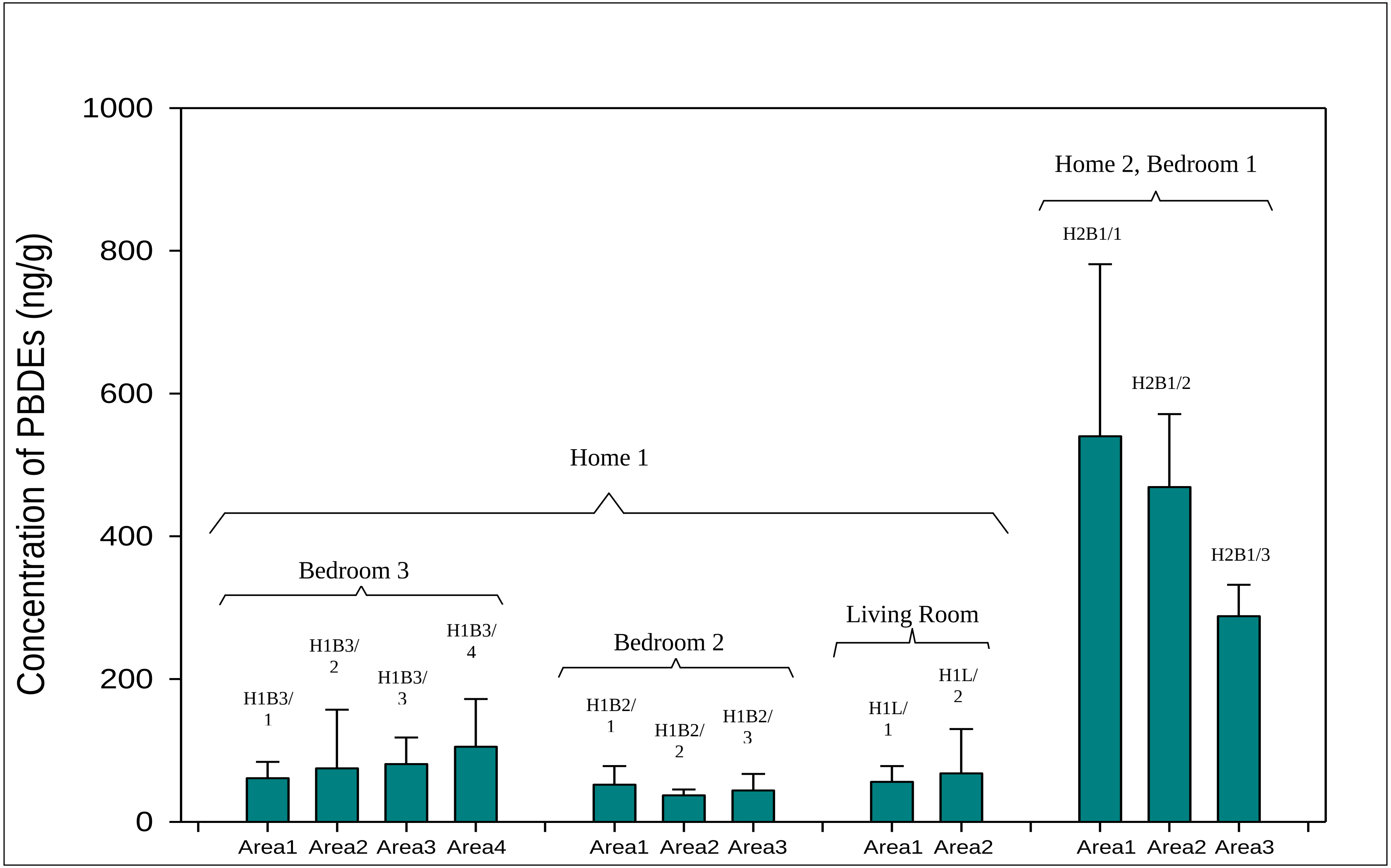


Table 5.3 Variations in Σ_{10}PBDE dust concentrations (ng g^{-1}) between areas within the same rooms

Home 1, Bedroom 3	Area 1 (H1B3/1)	Area 2 (H1B3/2)	Area 1 (H1B3/1)	Area 3 (H1B3/3)	Area 1 (H1B3/1)	Area 4 (H1B3/4)	Area 2 (H1B3/2)	Area 3 (H1B3/3)	Area 2 (H1B3/2)	Area 4 (H1B3/4)	Area 3 (H1B3/3)	Area 4 (H1B3/4)
One-way ANOVA-test *p*-value	1.000		0.746		0.564		0.687		0.503		0.990	
Home 1, Bedroom 2	Area 1 (H1B2/1)	Area 2 (H1B2/2)	Area 1 (H1B2/1)	Area 3 (H1B2/3)	Area 2 (H1B2/2)	Area 3 (H1B2/3)						
One-way ANOVA-test *p*-value	0.405		0.635		0.919							
Home 1, Living room	Area 1 (H1L/1)	Area 2 (H1L/2)										
T-test *p*-value	0.699											
Home 2, Bedroom 1	Area 1 (H2B1/1)	Area 2 (H2B1/2)	Area 1 (H2B1/1)	Area 3 (H2B1/3)	Area 2 (H2B1/2)	Area 3 (H2B1/3)						
One-way ANOVA-test *p*-value	0.628		0.009		0.068							

5.3.3 Within-house spatial and temporal variation in PBDE dust concentrations

Within-house spatial and temporal variation in concentrations of all target PBDEs was studied in two homes. In homes 1 and 2, the maximum Σ_{10}PBDE concentration (ng g^{-1}) in an individual sample exceeded the minimum by a factor of 13 (276:21) and 52 (1,041:20) respectively (Table 5.2). This supports earlier findings (Harrad *et al*., 2008b, 2009) that appreciable uncertainty may be associated with an exposure assessment based on a sample collected from one area in one room at one point in time. Furthermore, for homes 1 and 2, where substantial within-house spatial variation in Σ_{10}PBDE concentrations (the ratio of maximum:minimum average concentrations of Σ_{10}PBDEs in homes 1 and 2 are 2.2 and 2.5 respectively) occurs (Table 5.4), one could conclude that all rooms in a given house must be sampled to accomplish a representative sample. The considerable spatial variation observed between rooms in homes 1 and 2 also highlights the difficulty in obtaining a “biologically-relevant” sample for the purposes of accurate exposure assessment.

Interestingly, areas H1/B3 and H2/B1 containing the highest average concentrations in home 1 and home 2 respectively (Figure 5.3), were both carpeted and top floor rooms and adjoined a road. Similarly, in home 2, samples taken from the carpeted floor room H2/B1 contained on average about 2.5 times Σ_{10}PBDEs than samples collected in room H2/B2 with a bare wooden floor (Figure 5.3). This result could explain the significant differences in levels of Σ_{10}PBDEs between samples from H2/B1 and H2/B2, presented later (Table 5.5 and Figure 5.3). The findings reported here indicate that floor covering type and room contents with respect to potential PBDE sources may influence concentrations of PBDEs in dust. This may be related to the use of PBDEs as a flame retardant in carpet underlay material.

Since Kolmogorov-Smirnov (KS) analysis revealed that concentrations of Σ_{10}PBDEs in 4 (H1/L, H1/B1, H2/B1 and H2/B2) out of 6 individual rooms were log-normally distributed, a one-way analysis of variance (ANOVA) and t-test analysis of log-transformed concentrations was applied to compare Σ_{10}PBDE concentrations between rooms within the same house for homes 1 and home 2 respectively. These analyses were conducted using average concentrations for a given room at each date (e.g. comparing average concentrations for all 3 areas sampled in H1/B2 at each sampling date with the average concentrations for the 4 areas sampled in H1/B3, the 2 areas sampled in H1/L, and in the single area of H1/B1 sampled). The results of this statistical analysis for Σ_{10}PBDE concentrations and individual congeners are given in Table 5.5-5.15, while the variations in Σ_{10}PBDE dust concentrations in different rooms within the same house are illustrated in Figure 5.3.

It is evident in Table 5.5-5.15 that concentrations of Σ_{10}PBDEs in different rooms within the same house were not statistically significantly different ($p > 0.05$) in 61 out of 77 cases. The exceptions (n=16) were bedrooms 1 and 3, living room and bedroom 1 and bedroom 2 and bedroom 3 in home 1 as well as bedrooms 1 and 2 in home 2. One-way ANOVA showed significant differences in concentrations of Σ_{10}PBDEs ($p = 0.007$), BDE-47 ($p = 0.002$), BDE-99 ($p = 0.013$) and BDE-100 ($p = 0.010$) between bedroom 1 (sample H1/B1) and bedroom 3 in home 1 (sample H1/B3). A possible explanation for these apparent differences is the large difference in sample numbers between bedroom 1 (sample H1/B1) (n=8) and bedroom 3 (sample H1/B3) (n=32) although both rooms were carpeted. For home 2, a t-test indicated statistically significant differences in levels of Σ_{10}PBDEs ($p = 0.001$), BDE-28 ($p = 0.001$), BDE-47 ($p < 0.001$), BDE-49 ($p < 0.001$), BDE-66 ($p = 0.013$), BDE-99 ($p < 0.001$), BDE-100 ($p < 0.001$), BDE-153 ($p = 0.025$) and BDE-154 ($p = 0.018$) between bedroom 1 (sample H2/B1) and bedroom 2 (sample H2/B2). Despite the fact that both bedroom 1 and 2 faced the same road, bedroom 2 contained a new bare wooden floor, whereas bedroom 1 contained an old carpeted floor. There is no obvious explanation for significant differences in levels of BDE-47 ($p = 0.05$) and BDE-99 ($p = 0.041$) between living room (H1/L) and bedroom 1 (H1/B1) as well as Bedroom 2 (H1/B2) and Bedroom 3 (H1/B3) in home 1 respectively.

Table 5.4 Between-room variation in average concentrations (ng g^{-1}) of PBDEs in dust sampled monthly over 8 months in 2 different houses

Congener/ Sample	BDE 17	BDE 28	BDE 47	BDE 49	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	Σ_{10}PBDEs[a]
Home 1 (4 rooms)											
H1/L[b]	0.24	0.66	15	0.94	0.90	1.7	34	4.3	3.4	2.1	62
H1/B1[b]	0.09	0.28	8.6	0.49	0.42	1.2	20	1.7	2.5	1.5	37
H1/B2[b]	0.19	0.46	11	0.68	0.67	1.1	21	2.4	4.3	2.3	44
H1/B3[b]	0.14	0.54	18	0.97	0.64	1.9	47	5.1	3.8	2.3	81
Min	0.09	0.28	8.6	0.49	0.42	1.1	20	1.7	2.5	1.5	37
Max	0.24	0.66	18	0.97	0.90	1.9	47	5.1	4.3	2.3	81
Home 2 (2 rooms)											
H2/B1[b]	0.10	2.5	103	4.1	1.4	<0.03	220	50	20	32	432
H2/B2[b]	<0.03	0.32	14	<0.03	<0.03	0.15	31	6.3	89	32	173
Min	<0.03	0.32	14	<0.03	<0.03	<0.03	31	6.3	20	32	173
Max	0.10	2.5	103	4.1	1.4	0.15	220	50	89	32	432

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

[b] Average concentrations based on all samples taken within the specified room.

Table 5.5 Variations in Σ_{10}PBDE dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.126		0.811		0.589		0.512		0.007		0.160	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.001											

Table 5.6 Variations in BDE-17 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.629		0.996		0.979		0.491		0.395		0.998	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.082											

Table 5.7 Variations in BDE-28 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.074		0.899		0.999		0.270		0.058		0.850	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.001											

Table 5.8 Variations in BDE-47 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.051		0.842		0.597		0.254		0.002		0.184	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.000											

Table 5.9 Variations in BDE-49 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.354		0.771		0.997		0.891		0.262		0.656	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.000											

Table 5.10 Variations in BDE-66 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.290		0.983		0.996		0.483		0.398		0.999	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.013											

Table 5.11 Variations in BDE-85 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.706		0.581		0.812		0.997		0.226		0.157	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.351											

Table 5.12 Variations in BDE-99 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.230		0.484		0.527		0.956		0.013		0.041	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.000											

Table 5.13 Variations in BDE-100 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.269		0.971		0.415		0.500		0.010		0.210	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.000											

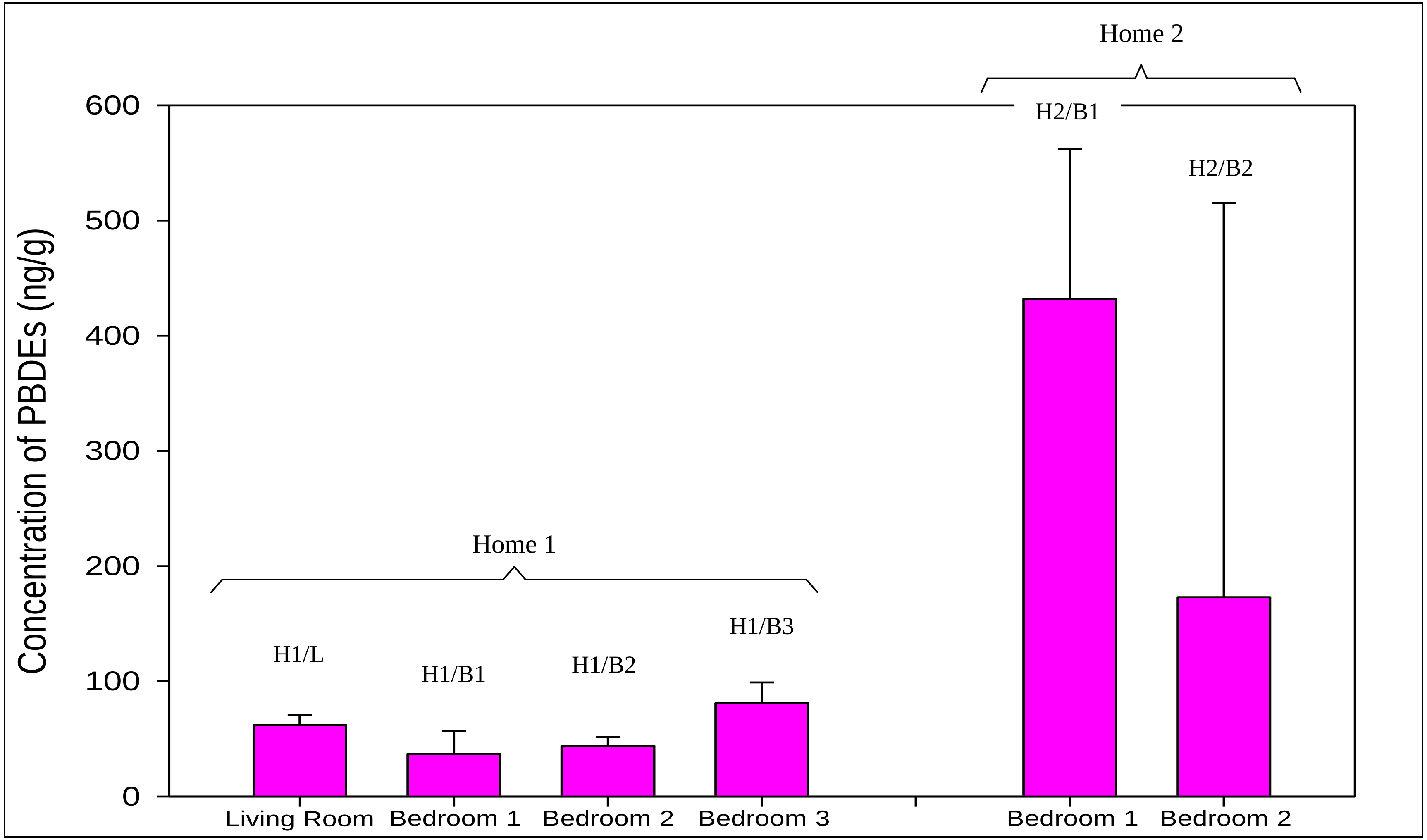
Table 5.14 Variations in BDE-153 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.843		0.878		1.000		0.413		0.790		0.918	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.025											

Table 5.15 Variations in BDE-154 dust concentrations (ng g^{-1}) between rooms within the same homes

Home 1	Living room (H1/L)	Bedroom 1 (H1/B1)	Living room (H1/L)	Bedroom 2 (H1/B2)	Living room (H1/L)	Bedroom 3 (H1/B3)	Bedroom 1 (H1/B1)	Bedroom 2 (H1/B2)	Bedroom 1 (H1/B1)	Bedroom 3 (H1/B3)	Bedroom 2 (H1/B2)	Bedroom 3 (H1/B3)
One-way ANOVA-test *p*-value	0.882		0.991		0.996		0.735		0.778		1.000	
Home 2	Bedroom 1 (H2/B1)	Bedroom 2 (H2/B2)										
T-test *p*-value	0.018											

Figure 5.3 Average concentrations of Σ_{10}PBDEs in dust from different rooms within the same homes (y-error bars are ± one standard deviation)



5.3.4 Within-room temporal variation in PBDE dust concentrations

Within-room temporal variation of tri- to hexa-BDEs (Σ_{10}PBDEs) was studied in fourteen individual areas within six rooms in two different homes. Table 5.2 presents concentrations of the ten individual congeners and of Σ_{10}PBDEs, along with the RSDs of these parameters in each area sampled. The RSDs of concentrations of Σ_{10}PBDEs in these samples (15-198%) exceeded substantially that obtained from replicate analysis of SRM 2585 house dust reference material (2.6%) (Table 5.16). In particular, the ratio of maximum:minimum concentrations of Σ_{10}PBDEs in areas H1L/2, H1B3/2, H1B3/4 and H2B2/1 were 8.7, 9.2, 7.4, and 51 respectively. Such findings are consistent with an earlier study of within-room temporal variation in PBDE concentrations that reported appreciable variation, depending on when a given area is vacuumed (Harrad *et al*., 2008b). A study of within-room temporal variability in three UK rooms by Harrad *et al*. (2008b) reported RSDs of concentrations of Σtri-hexa-BDEs (PBDEs 28, 47, 49, 66, 99, 100 153 and 154) ranging between 52-156%. In addition to the implications for exposure assessment; within-room temporal variability could if linked with changes in room contents – as reported previously for PBDE concentrations in air from one office – offer insights into potential emission sources (Hazrati and Harrad, 2006). Hence, temporal variations in concentrations of ΣPBDEs in dust samples in the fourteen areas monitored were inspected relative to any changes in room content during this study. The contents of the rooms investigated are summarized in Table 5.1.

Figures 5.4-5.5 and Figures E-1 to E-6 (Appendix E) illustrate the intra-room temporal variations in PBDE dust concentrations during the 8 month monitoring campaign in houses 1 and 2. The temporal variations detected in this study are attributable to differences in PBDE source strengths, room usage pattern and ventilation, heating and cooling characteristics and house contents.

Table 5.16 Sample preparation and analytical variability (RSD) of SRM 2585 indoor dust reference material (n=10)

PBDE congener	Sample preparation & analytical variability (RSD)
BDE 17	6.8%
BDE 28	3.4%
BDE 47	0.96%
BDE 49	0.80%
BDE 66	6.7%
BDE 85	2.9%
BDE 99	0.87%
BDE 100	0.05%
BDE 153	1.8%
BDE 154	13%
ΣPBDEs[a]	2.6%

[a] Sum of PBDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154.

The clearest features of the temporal trend in H1L (a living room), relates to the fact that it contained a TV that is a potential emission source of PBDEs. The 28 inch TV was placed in the room in the middle of October 2007, but was not used at all during its stay in the room. Concentrations of Σ_{10}PBDEs, BDE-47 and BDE-99 in the next samples (taken on 7/11/07) from H1L/1 and H1L/2 increased by a factor of 3.0-3.8 and 4.6-12.2 respectively from those in the previous samples (Figure 5.4 and Figures E-1 to E-2). Consistent with the hypothesis that the TV was the source of PBDEs, the increases in concentrations of Σ_{10}PBDEs and all congeners studied except for BDE-153 and BDE-154 were greater in the area closest to the TV (sample H1L/2) (Table 5.2). Concentrations decrease in the next samples taken at the end of November 2007, coinciding with the removal from the room of the TV. After this point, concentrations appear to attain a steady state at concentrations within a range similar to that existing before the introduction of the TV, and there is little subsequent temporal variation in concentrations of Σ_{10}PBDEs, BDE-47 and BDE-99. This finding is consistent with the results of Harrad *et al.* (2009), who reported that higher concentrations of ΣHBCDs and a higher relative abundance of γ-HBCD were seen in the presence in a room of a TV and that concentrations and the relative abundance of γ-HBCD increased with proximity to the TV.

The obvious feature in H1B1 (a bedroom) is the increase in concentrations of Σ_{10}PBDEs, BDE-47 and BDE-99 in the sample taken on 7 November, 2007 (Figure 5.4 and Figures E-1 to E-2). There is no obvious source-related explanation for this. Instead, this feature may possibly reflect cross-contamination of these H1B1 samples which were sampled after vacuuming samples H1L/1 and H1L/2 on 7/11/07. However, the vacuum cleaner was cleaned between sample collections to avoid cross contamination, and there is no definitive evidence that the cross-contamination is the cause of the rise in concentration of PBDEs.

In H1B2 (a bedroom), a noticeable increase in concentration of Σ_{10}PBDEs, BDE-47 and BDE-99 occurs on 7 November, 2007 (Figure 5.4 and Figures E-1 to E-2). This may be due to the fact that two old mattresses were used by the room occupants between the middle of October and the middle of November 2007.

There are three obvious features in H1B3 (a loft bedroom). The first of these involves the replacement of the bed present in the room when the first sample was taken. The new bed placed in the room on September 11th 2007 (i.e. after the 1st sample was taken), is unlikely to contain PBDEs as the production and use of penta- and octa-BDE have been banned in the EU since 2004. In the first sample after the new bed was introduced, the concentrations of Σ_{10}PBDEs, BDE-47 and BDE-99 in sample H1B3/1, H1B3/2, H1B3/3 and H1B3/4 fell by a factor of 2.6-3.1, 3.9-14, 3.1-3.8 and 1.8-4.5 respectively (Figure 5.4 and Figures E-1 to E-2). The second and third feature is the high levels of Σ_{10}PBDEs, BDE-47 and BDE-99 in the samples taken on November 28th 2007 and June 9th 2008 respectively, possibly because of heavy PC use in November 2007 and during the first two weeks of June 2008. These findings are consistent with a previous study that reported an appreciable rise in BDE-209 levels due to the introduction of a new mattress and curtains as well as the fitting of a new fabric padded bed cover and polyester fabric window blinds (Harrad *et al*., 2008b).

A fall in concentrations of Σ_{10}PBDEs, BDE-47 and BDE-99 in H2B1 (a bedroom) between the sample taken on August 6th 2008 and that taken on September 16th 2008 is apparent in sample series H2B1/1 (Figure 5.5 and Figures E-3 to E-4). The lower concentration may be associated with the permanent removal of a radio and desk lamp from the room. After this point, there is little temporal variation in Σ_{10}PBDE concentrations.

In H2B2 (a bedroom), a marked rise from the previous sample in concentrations of Σ_{10}PBDEs (Figure 5.5), BDE-153 (Figure E-5) and BDE-154 (Figure E-6) occurs in the sample H2B2/1 taken on 8 August, 2008. This is most likely due to the use of two laptops in the room over this sampling period. Little temporal variability in Σ_{10}PBDE concentrations was observed subsequently.

As described above and as presented in Figures 5.4-5.5 and Figures E-1 to E-6; despite the fact that the increases in levels of Σ_{10}PBDEs, BDE-47 and BDE-99 observed in H1L (a living room), H1B1 (a bedroom) and H1B2 (a bedroom) arise principally as a consequence of room content changes during the 8 month monitoring period, these may also be ascribed to building-specific factors (especially changes in household characteristics). However, based on a survey of house-specific factors, an apparent house-related (as opposed to room-related) cause of the rise in PBDE concentrations seen in the rooms is not identify.

Figure 5.4 Temporal variations in Σ_{10}PBDE dust concentrations in different four rooms, home 1

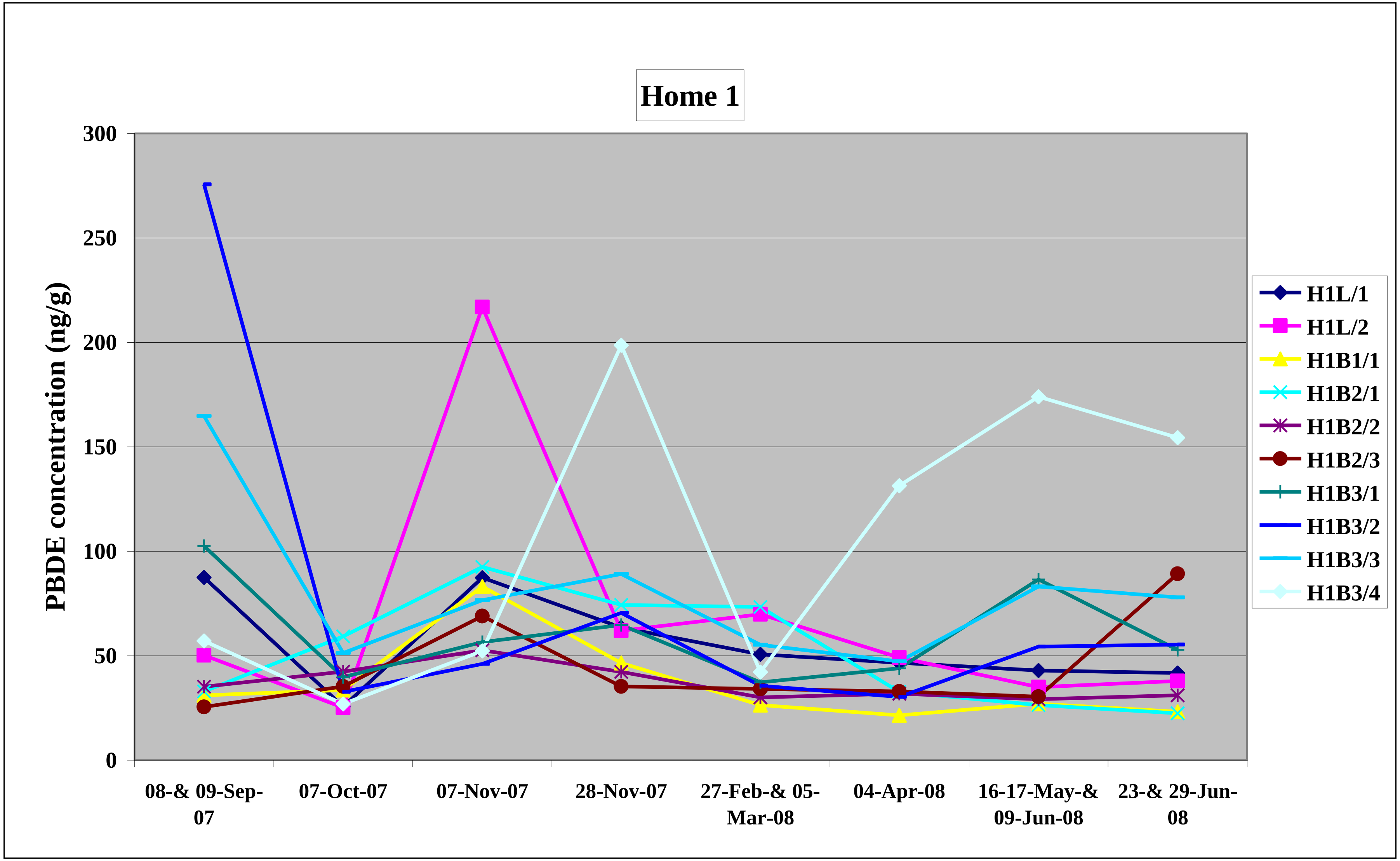
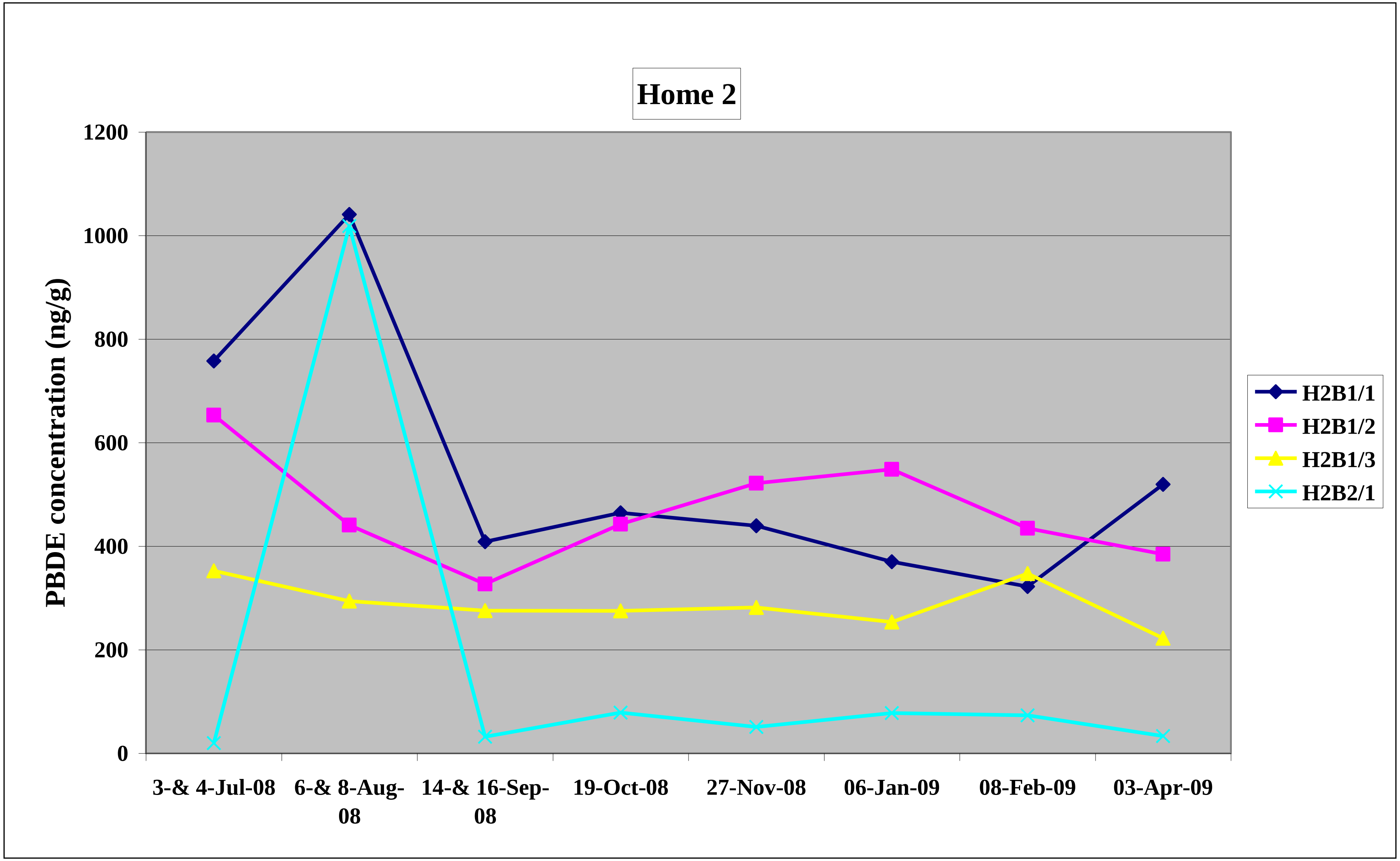


Figure 5.5 Temporal variations in Σ_{10}PBDE dust concentrations in different two rooms, home 2



In this study, t-tests were used to assess the differences in concentrations of Σ_{10}PBDEs, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 between warmer months (i.e. spring and summer from 21st of March to 20th of September) and colder months (i.e. autumn and winter from 21st of September to 20th of March). The results for these analyses are summarized in Table 5.17.

As is evident from Table 5.17, seasonal differences in concentrations of Σ_{10}PBDEs and all selected PBDE congeners in almost all of the fourteen areas studied were not statistically significant (p>0.05). Furthermore, in some rooms, concentrations in colder months exceeded those in warmer months. Nonetheless, PBDE concentrations in summer (June to August) and autumn (September to November) in a number of rooms exceed those observed in winter (December to February) and spring (March to May), with the highest Σ_{10}PBDE levels in dust from all rooms in home 1 and home 2 seen in autumn (November) and summer (August) respectively. This is consistent with the findings of Hazrati and Harrad (2006), who reported that while airborne levels of Σtri- through hexa-BDEs in warmer months were generally higher than those in colder months, seasonal variability in outdoor air levels was more significant than in indoor air. Such higher levels in summer (but not significantly so) are consistent with the hypothesis of Hazrati and Harrad (2006) that temperature-related increases in indoor contamination in warmer months are mitigated by: (a) a lower annual temperature range indoors; and (b) concomitant increases in room ventilation in warmer periods.

Table 5.17 Seasonal variations in PBDE dust concentrations (ng g^{-1}) in UK homes

Location/Congener		BDE 28		BDE 47		BDE 99		BDE 100		BDE 153		BDE 154		Σ_{10}PBDEs	
		W^a	C^b	W	C	W	C	W	C	W	C	W	C	W	C
H1L/1	Average	0.94	0.60	12	15	24	30	3.5	3.5	4.8	3.7	3.0	2.0	55	57
	S.D.	1.1	0.31	2.6	6.4	4.1	15	2.9	2.7	5.5	3.4	2.4	1.8	22	25
	T-test *p*-value	0.588		0.513		0.529		0.994		0.741		0.538		0.909	
HL1/2	Average	0.34	0.77	11	19	23	59	1.6	8.4	3.2	2.0	2.3	0.97	43	94
	S.D.	0.14	0.94	2.9	12	3.6	60	1.4	11	2.2	0.49	0.91	0.44	7.6	85
	T-test *p*-value	0.396		0.232		0.318		0.257		0.343		0.038		0.280	
H1B1/1	Average	0.17	0.38	6.1	11	14	26	1.4	1.9	1.3	3.7	0.75	2.3	26	48
	S.D.	0.12	0.28	1.7	6.7	2.4	21	0.33	1.4	0.80	1.3	0.35	0.24	4.4	25
	T-test *p*-value	0.241		0.199		0.309		0.515		0.023		0.000		0.136	
H1B2/1	Average	0.32	0.49	10	18	11	29	1.4	3.3	2.4	14	1.3	6.4	29	75
	S.D.	0.34	0.52	2.7	6.6	2.0	19	0.57	1.1	0.85	10	0.17	5.8	5.4	14
	T-test *p*-value	0.591		0.068		0.162		0.021		0.112		0.178		0.001	
H1B2/2	Average	0.16	0.88	9.7	10	14	21	3.2	1.6	2.4	2.6	0.43	2.3	32	42
	S.D.	0.05	0.67	1.0	4.1	1.8	8.1	0.70	1.2	0.22	2.2	0.24	1.7	2.5	9.4
	T-test *p*-value	0.077		0.732		0.171		0.048		0.868		0.068		0.085	
H1B2/3	Average	0.27	0.61	9.5	11	27	22	1.8	2.9	2.3	2.1	1.7	1.7	44	43
	S.D.	0.08	0.55	2.1	3.8	24	13	0.77	1.1	1.6	1.2	1.3	1.2	30	17
	T-test *p*-value	0.273		0.455		0.738		0.144		0.846		0.996		0.956	
H1B3/1	Average	0.51	0.51	19	11	41	26	3.9	4.3	3.2	2.9	1.4	2.1	71	50
	S.D.	0.40	0.27	7.6	2.0	18	9.8	2.8	1.6	3.1	1.1	0.83	1.5	27	13
	T-test *p*-value	0.984		0.090		0.215		0.800		0.849		0.423		0.225	
H1B3/2	Average	0.19	0.32	16	14	68	25	4.5	1.8	9.8	2.3	4.2	1.6	104	46
	S.D.	0.24	0.31	9.1	4.4	77	15	3.3	1.9	17	0.92	7.9	0.51	115	17
	T-test *p*-value	0.530		0.731		0.316		0.204		0.450		0.551		0.394	
H1B3/3	Average	0.36	1.1	18	19	59	33	5.4	5.5	4.0	2.9	2.9	2.2	93	68
	S.D.	0.28	1.0	9.4	9.1	29	11	4.8	3.7	4.0	1.2	2.8	1.1	50	18
	T-test *p*-value	0.195		0.901		0.147		0.973		0.644		0.648		0.382	

Table 5.17 Seasonal variations in PBDE dust concentrations (ng g^{-1}) in UK homes (continued)

Location/Congener		BDE 28		BDE 47		BDE 99		BDE 100		BDE 153		BDE 154		Σ_{10}PBDEs	
		W[a]	C[b]	W	C	W	C	W	C	W	C	W	C	W	C
H1B3/4	Average	0.69	0.57	33	14	75	51	7.8	7.1	3.1	2.1	2.4	1.1	129	80
	S.D.	0.38	0.38	11	11	36	55	4.4	10	0.46	1.4	0.28	1.1	51	80
	T-test *p*-value	0.671		0.050		0.484		0.901		0.244		0.067		0.342	
H2B1/1	Average	2.3	3.0	136	100	355	201	86	45	37	18	59	28	682	399
	S.D.	0.67	0.24	53	14	159	37	38	6.2	16	5.0	22	4.5	280	65
	T-test *p*-value	0.097		0.237		0.147		0.077		0.093		0.069		0.135	
H2B1/2	Average	2.4	2.7	108	119	233	243	54	55	17	23	32	37	452	487
	S.D.	0.46	1.1	24	11	75	27	16	8.0	12	6.6	15	7.7	142	57
	T-test *p*-value	0.572		0.461		0.819		0.873		0.457		0.561		0.659	
H2B1/3	Average	1.8	2.6	67	84	143	143	33	32	15	7.4	23	16	286	289
	S.D.	0.43	0.10	11	5.6	30	23	6.3	5.5	2.4	3.8	1.7	3.1	54	40
	T-test *p*-value	0.011		0.032		0.990		0.863		0.016		0.006		0.920	
H2B2/1	Average	0.09	0.54	9.3	19	25	38	4.4	8.2	175	1.9	62	2.4	276	70
	S.D.	0.18	0.63	3.9	5.1	17	6.5	3.2	2.5	350	2.4	123	1.9	495	13
	T-test *p*-value	0.250		0.024		0.179		0.116		0.395		0.402		0.467	

[a] Warmer months (spring and summer from 21st of March to 20th of September).
[b] Colder months (autumn and winter from 21st of September to 20th of March).

5.3.5 Relationship between concentrations of PBDEs in dust and dust loadings

It has been suggested that the practice of basing estimates of PBDE exposure on a default dust ingestion rate, regardless of the dust loading of the room, may not always be appropriate (Harrad *et al*., 2008b). As stated by Harrad *et al*. (2008b), "by way of illustration, consider two identically-ventilated and dimensioned rooms, containing identical PBDE emission strengths, but different dust loadings. In which room will human exposure be higher? One may hypothesise there to be a lower mass-based level of PBDEs because of dilution in a dustier room, but will the diminished exposure arising from the lower mass-based PBDE levels be lessened to some extent by a higher dust ingestion rate in such a microenvironment?" As mentioned in an earlier study by Harrad *et al*. (2008b), a plot of log (ΣPBDE levels) versus log (dust loading) should be linear with a negative slope of 1 and a y-intercept that is related to the PBDE burden of the room at steady state, provided: (a) PBDE emissions in the room are relatively constant during the investigated period, and (b) the sources of PBDEs and of dust are independent (e.g. the PBDEs present in dust are present as a result of sorption from the vapour phase rather than in particles or fibres abraded from flame-retarded items). There have been two studies evaluating the hypothesis that higher dust loadings dilute BFR levels in dust. The two studies reported significant negative correlation seen in one room between dust loading (g dust m^{-2} of area sampled) and concentrations of BFRs in dust, suggesting that "dilution" occurs at greater dust loadings (Harrad *et al*., 2008b, 2009).

In this study, to examine for a negative slope, log [dust loadings (g dust m^{-2} floor)] was regressed against log [concentrations of Σ_{10}PBDEs, BDE-47 and BDE-99] from the fourteen individual areas investigated over the 8 month period. Based on the evaluation of the Σ_{10}PBDE dataset, significant negative association was found (R^2=0.54; p<0.05) in sample series area H1B3/2. For sample series area H1L/1 (Table 5.2), no significant correlation is observed (p>0.05). Nevertheless, inclusion of sample H1L/1 taken on October 7th 2007 (Month 2) violates condition (a) as it was taken when a substantial fall in concentration of Σ_{10}PBDEs occurred. If this sample is excluded, then there is a significant negative relationship (R^2=0.93; p<0.001) (Figure 5.6). In addition, for sample series area H1B2/2 (Table 5.2), if sample H1B2/2 taken on 7/11/07 (Month 3) is excluded (on the basis that during this period there is a marked rise in levels of Σ_{10}PBDEs coinciding with the introduction of the two old mattresses), then the significance of the negative correlation rises (R^2=0.65; p<0.05).

A significant negative relationship between log BDE-47 concentrations and log dust loadings was identified (R^2=0.51; p<0.05) in sample series area H1B3/2. Furthermore, for sample series area H1L/1 and H2B1/3 (Table 5.2), a significant negative association (R^2=0.66; p<0.05, R^2=0.62; p<0.05) is observed if samples H1L/1 and H2B1/3 taken on 7/10/07 (Month 2) and 3/04/09 (Month 8) respectively, are excluded because they were sampled when unusually low concentrations of BDE-47 were seen.

Examination of the BDE-99 data revealed a significant negative correlation (R^2=0.68; p<0.05) in sample series area H1B2/2. The significant negative relationship is observed if sample H1B2/2 taken on 7/11/07 (Month 3) is excluded as it was collected when an appreciable increase in BDE-99 concentrations due to the introduction of the two old beds was seen. These observations in areas (H1L/1, H1B2/2, H1B3/2 and H2B1/3) are consistent with the hypothesis that higher dust loadings reduce or dilute concentrations of Σ_{10}PBDEs, BDE-47 or BDE-99 and also indicated that the sources of Σ_{10}PBDEs, BDE-47 or BDE-99 in these areas are independent of the sources of the dust.

For a positive association, a significant relationship ($R^2=0.67$; $p<0.05$) between log levels of BDE-47 and log dust loadings was found in sample series area H2B2/1 (Figure 5.7). Moreover, for sample series area H1B3/4 (Table 5.2), if the sample taken on June 9th 2008 (Month 7) is excluded (on the basis that during this period there is a substantial increase in BDE-47 concentrations coinciding with heavy PC use), then a significant positive relationship is observed ($R^2=0.67$; $p<0.05$). This positive correlation found in areas H1B3/4 and H2B2/1 implies that as dust loadings increase, so do the BDE-47 levels in the dust collected from these areas. It is difficult to explain these observations and they may well be artefacts; however, one can speculate that in these areas, that while both dust loadings and PBDE emissions increase in tandem, the increase in the latter is greater (i.e. the sources of the dust and of the PBDEs are independent – e.g. a substantial proportion of the PBDEs entering the dust in these rooms may arise from abraded fibres or particles of PBDE-treated materials).

Figure 5.6 Negative relationship between log (dust loading) and log (concentrations of Σ_{10}PBDEs) in house dust from H1L/1

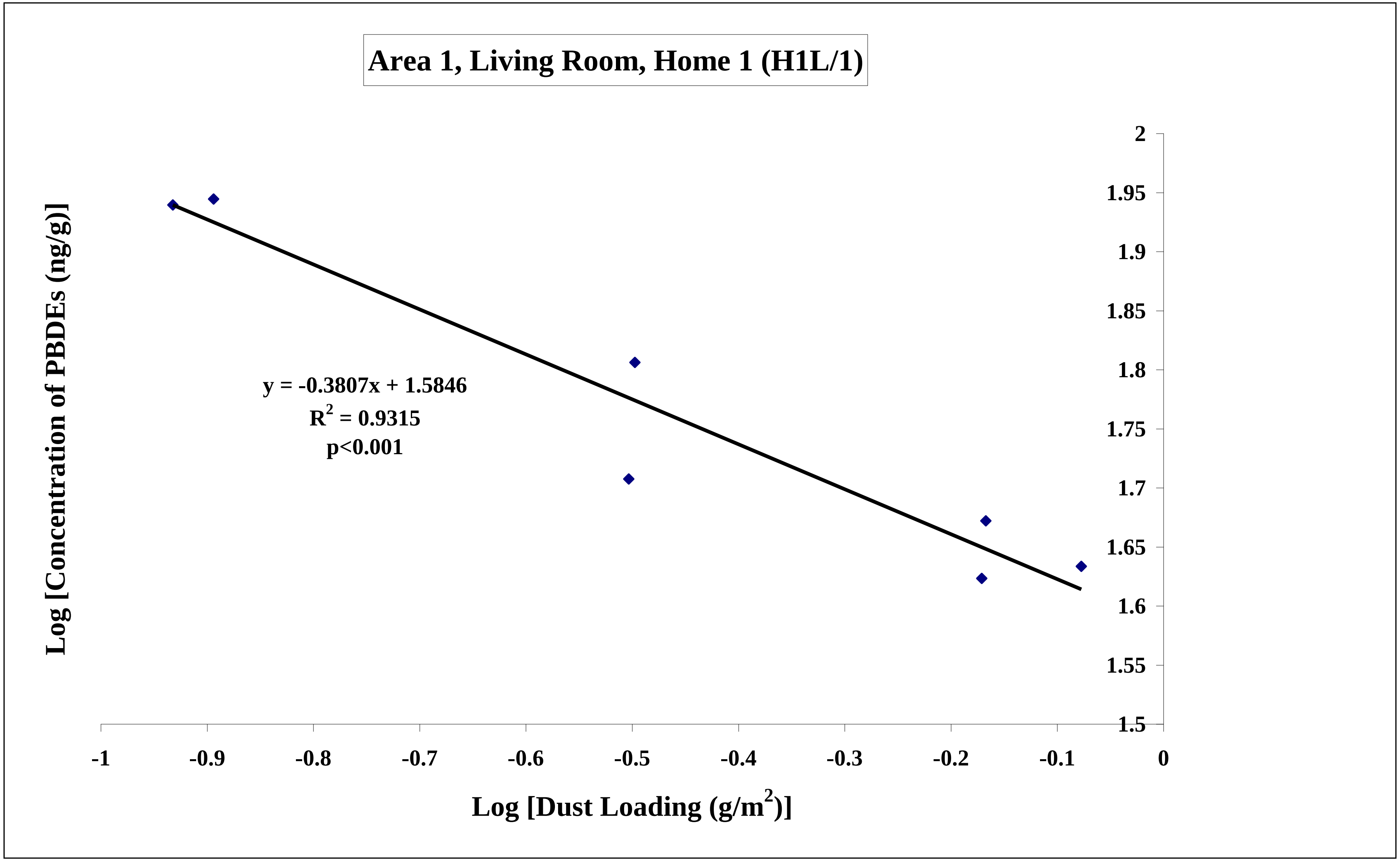
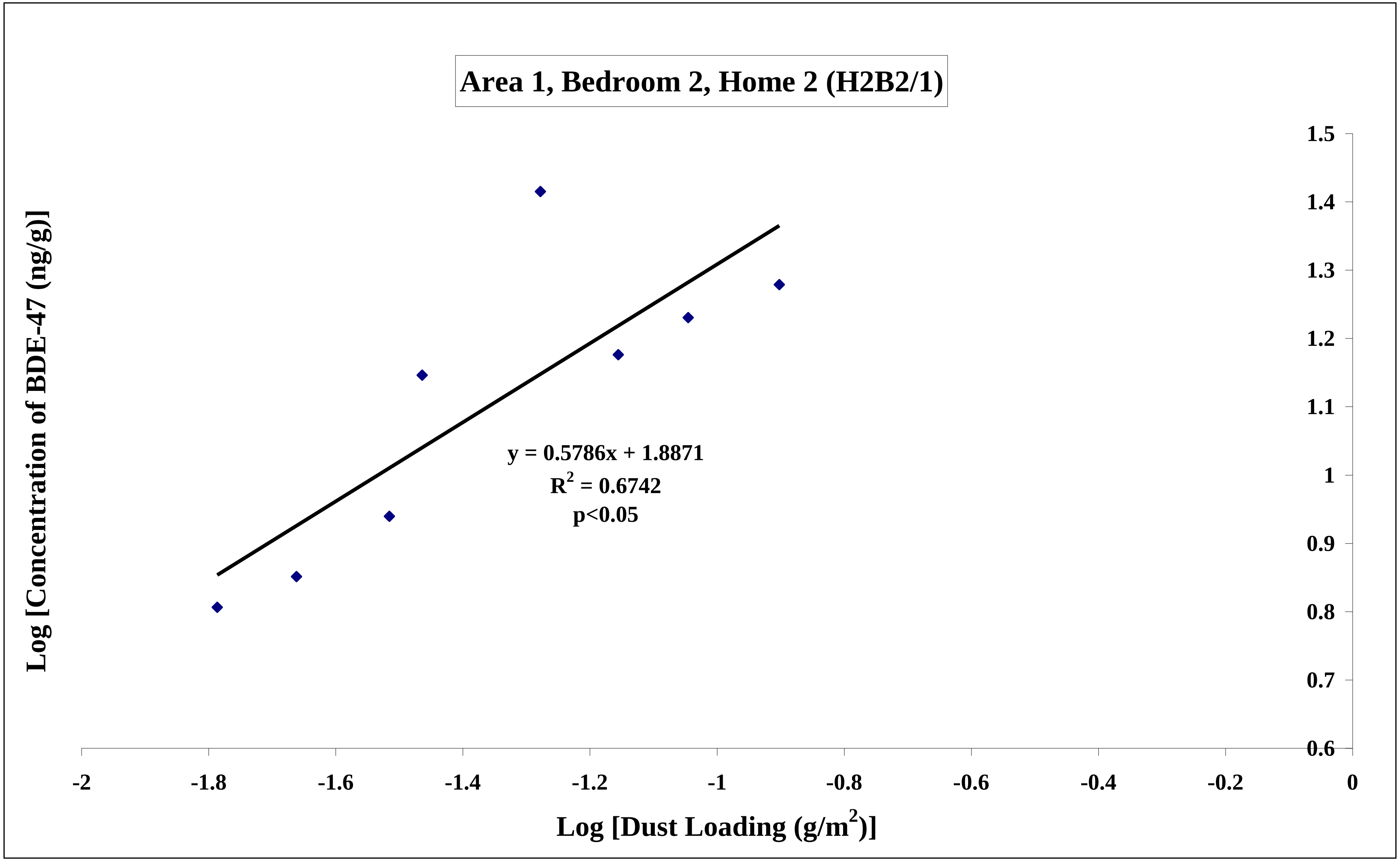


Figure 5.7 Positive relationship between log (dust loading) and log (concentrations of BDE-47) in house dust from H2B2/1



5.4 Conclusion and recommendation

This chapter reports within-room temporal variations as well as within-room and within-house spatial variations in concentrations of tri- to hexa-BDEs (Σ_{10}PBDEs) observed in dust sampled from two UK homes. To the author's knowledge, this is easily the most detailed study to date of within-room and within-home spatial variability in concentrations of PBDEs (and indeed BFRs) in floor dust. Levels of tri-hexa-PBDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154) are comparable to those reported in previous UK studies. BDE 99 and 47 were the dominant congeners measured in all samples.

The within-room spatial variability observed in this study indicates that the entire area of a room must be vacuumed in order to obtain a dust sample that is representative of that present in the room as a whole. It also suggests that in some instances, the most-frequented areas (the most biologically-relevant areas) should be sampled to attain a more relevant exposure estimate. However, for most of the areas monitored within the same rooms, PBDE concentrations were not statistically significantly different. Interestingly, in one room, significantly elevated levels of PBDEs were detected in an area located close to potential PBDE sources.

The results of the within-house spatial variability study suggested that this variability could be appreciable, and highlighted the need to sample either all rooms or the most biologically-relevant room to achieve a more accurate exposure assessment. For the majority of rooms within the same houses, concentrations of PBDEs were not statistically significantly different between rooms. Nonetheless, a room containing an old carpeted floor displayed higher PBDE concentrations than a room in the same house containing a new bare wooden floor.

Within-room temporal variations in Σ_{10}PBDE concentrations seen in dust were higher than that attributable to sample homogenisation, sieving, and analytical measurement; revealing that considerable variation in exposure estimates is possible, depending on when a given area is sampled. The temporal variations monitored in this study result from variations in room contents, room usage pattern and room ventilation. In general, PBDE concentrations in summer (June to August) and autumn (September to November) exceed those observed in winter (December to February) and spring (March to May), although the differences for Σ_{10}PBDEs, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 in almost all of the studied areas were not statistically significant. The reasons for the temporal variations in this study arise mainly from room-specific factors (particularly changes in room characteristics over time) rather than house-specific factors, seasonal variation and environmental conditions of the rooms investigated like temperature, humidity, air flow and ventilation rates.

Dilution of PBDE levels in dust at high dust loadings has been identified for Σ_{10}PBDEs, BDE-47 and BDE-99 in three, three and one out of the fourteen areas in which within-room temporal variation was investigated. This indicated that Σ_{10}PBDE, BDE-47 and BDE-99 levels in dust can be reduced as dust loadings increase, provided that the sources of the dust and of Σ_{10}PBDEs, BDE-47 and BDE-99 are independent of each other.

Interestingly, significant positive correlation between log (dust loading) and log (BDE-47 levels) was observed in two areas for the first time. It is suggested that in such instances, while both dust loadings and PBDE emissions increase in tandem, the increase in the latter is greater, indicating that PBDEs are emitted to dust as a result of abrasion of fibres or particles of PBDE-treated materials.

While this study has added substantially to knowledge in this area; future investigations are still required due to the absence of clear and consistent correlations between PBDE concentrations in indoor environments and month-to-month or seasonal variations, building-specific factors and specific environmental conditions of the rooms studied.

CHAPTER 6

Summary

6.1 Summary

Polybrominated diphenyl ethers (PBDEs) are collectively one of the most extensively used classes of brominated flame retardants (BFRs) added to various polymers used in a broad array of industrial and consumer products such as electrical and electronic equipments, plastics and furniture to prevent the spread of fires (WHO/IPCS, 1994, 1997). The three most widely produced and commercially used PBDE formulations are decabromodiphenylether [deca-BDE]; octabromodiphenylether [octa-BDE]; and pentabromodiphenylether [penta-BDE] (La Guardia *et al*., 2006; de Boer and Cofino, 2002).

PBDEs are global contaminants of concern since they are toxic, persistent and subject to long-range atmospheric transport (LRAT) as well as possessing the capacity to bioaccumulate and biomagnify. The physicochemical properties of PBDEs have led to their accumulation and magnification in humans, wildlife and ecosystems. At present, owing to a growing number of both human health and environmental concerns relating to PBDEs, the penta- and octa-BDE formulations have already been banned in the European Union (EU) and in some states within the United States from 2004; while deca-BDE was severely restricted within the EU in July 2008 (Directorate-General Environment, 2005; U.S. EPA, 2006; Vonderheide *et al*., 2008; Kemmlein *et al*., 2009; Kierkegaard *et al*., 2009). Furthermore, the penta- and octa-BDE products were listed under the Stockholm Convention on POPs in May 2009 (Stockholm Convention on POPs, 2009b).

Given the above, the principal objectives of this thesis were to examine levels of PBDEs in a large number of residential and workplace outdoor/indoor environments in Thailand and the U.K. as well as to investigate the temporal and spatial variability in PBDE concentrations in domestic dust collected from Birmingham, U.K.

The major findings of this research project can be summarised as follows:

- BDE-47 and 99 were the main PBDEs detected in air samples taken at five e-waste storage facilities in Thailand. Levels of PBDEs in outdoor (n=10; 8-150 pg m^{-3}) and indoor air (n=5; 46-350 pg m^{-3}) in this study were appreciably lower than those seen in e-waste processing facilities in other countries. While this is most likely mainly due to the fact that e-waste was only *stored* in the facilities studied here, the lower levels recorded may also be a reflection of the far lower use of the Penta-BDE product in Asia compared to North America (BSEF, 2001) and of the fact that the PUF disk samplers used underestimated particle-phase PBDE concentrations. The indoor concentrations were generally higher than those outdoors, although the difference is not dramatic for these facilities. This is likely attributable to high volatilization resulting from high ambient temperatures during the sampling period, good air ventilation and considerable outdoor-indoor air exchange in the plants; the latter two reasons resulting from the open design of the storage facilities. The downwind atmospheric levels of PBDEs at two out of 5 individual facilities exceeded those recorded at upwind locations, suggesting that these plants represent a PBDE source to the outdoor environment. In contrast, the PBDE concentrations at the other 3 facilities were lower at the downwind sites than the upwind sites which is likely a result of the fact that the upwind sampling locations for these plants were sited adjacent to e-waste point sources.
- The major BFRs in dust from four Thai e-waste storage facilities were BDE-209, BDE-183, BDE-206, BDE-207, BDE-99, BDE-197, BDE-47, BDE-208 and DBDPE. Concentrations of Σ_{21}PBDEs, DBDPE and BB-209 in dust (n=25) were respectively, 320-290,000 ng g^{-1}, 43-8,700 ng g^{-1} and <20-2,300 ng g^{-1}. With the exception of BDE-209 in US and UK dust, the dust PBDE levels presented in this study were higher than those detected in UK, Canadian and New Zealand homes, UK offices and Chinese e-waste recycling workshop (Ma *et al.*, 2009), but were lower than levels measured in U.S. houses (Harrad *et al.*, 2008a,b). For DBDPE, concentrations (43-8,700 ng g^{-1}) exceeded those recorded in a Japanese hotel (Takigami *et al.*, 2009b) and Swedish homes (Karlsson *et al.*, 2007), and were more in line with those reported for UK homes, offices and cars (Harrad *et al.*, 2008b) and the U.S. residences (Stapleton *et al.*, 2008b). Debromination of BDE-209 to BDE-208 was observed in dust samples and there were no apparent trends in the correlations between the type of e-waste stored and the BFR levels and pattern of dust contamination. Interestingly, there was a significant and positive relationship (r^2 = 0.554,

p <0.001) between levels of BDE-209 and DBDPE in dust, implying that BDE-209 and DBDPE have similar emission sources, and is consistent with the use of DBDPE as a Deca-BDE “replacement”.

- The PBDE congener profile in indoor air samples collected from Thai houses was dominated by BDE-47 and 99. The residential indoor air levels of PBDEs in this study (n=3; 23-72 pg m^{-3}) were higher than those found in Kuwait and Japan (Gevao *et al*., 2006b; Takigami *et al*., 2009a), but were lower than those seen in Germany, Sweden, Canada, Australia and the U.S. (Fromme *et al*., 2009; Karlsson *et al*., 2007; Wilford *et al*., 2004; Toms *et al*., 2009a,b; Batterman *et al*., 2009). The BDE-47:99 ratios in the air samples (average of 2.3, median of 3.7) exceeded those observed in UK homes, UK indoor microenvironments overall, German, Australian and Kuwaiti homes (Hazrati and Harrad, 2006; Fromme *et al*., 2009; Toms *et al*., 2009a; Gevao *et al*., 2006b), but were lower than those reported for household indoor air in Ottawa, and similar to those determined in Japanese houses (Wilford *et al*., 2004; Takigami *et al*., 2009a). The different ratios may possibly be ascribed to the use of different PBDE formulations in Thailand compared to the UK, Germany, Australia, Kuwait and Canada.
- BDE-99 and 47 were present principally in house dust from Thailand. Levels of all BDE congeners in domestic dust in this study (n=53, 0.59-260 ng g^{-1}) were lower than measurements made in various countries around the world. However, the values of BDE-28, 47, 99, 100 and 154 exceeded those detected in homes in Japan (Takigami *et al*., 2009a). The low concentrations in dust may possibly be attributed to greater application of BFRs like TBBP-A in Thailand, as well as non-carpeted rooms and the small number of potentially PBDE-treated products in rural Thai residences.
- BDEs 99 and 47 were found to be the dominating PBDE congeners recovered in Thai car dust samples. PBDE contents in vehicle dust reported in this study (n=30; 0.68-38 ng g^{-1}) were much lower than those measured in the UK, the US and Portugal (Harrad *et al*., 2008b; Lagalante *et al*., 2009; Cunha *et al*., 2010). The ratios of BDE 47:99 in the dust (average of 0.62, median of 0.55) were in line with results from the UK, the US and Portugal, revealing that Thai, UK, American and Portuguese automobiles are treated with similar commercial PBDE mixtures. A one-way ANOVA test resulted in no difference between Σ_{10}PBDE values in Thai car dust samples from different car manufacturers (p = 0.521).

- The most predominant PBDE congeners in residential dust samples (n=112) taken from two UK homes were BDE-99 and 47. PBDE levels in dust samples (n=80) from UK home 1 varied from 21-280 ng g^{-1}, with the greatest levels observed in an area of a bedroom, which was located on the top/carpeted floor and adjoined a road. PBDE concentrations in dust samples (n=32) from UK home 2 ranged from 20-1,000 ng g^{-1}, with the highest levels found in an area adjacent to TV, laptop, sofa and foam chair in a bedroom located on the top/carpeted floor and a road frontage. In general, the average concentrations of BDE-153 and BDE-154 measured in samples taken from each area of UK home 1 were lower than the average levels reported for homes in Birmingham, the UK (Harrad *et al*., 2008a,b). On the other hand, average levels of BDE-154 in dust sampled from each area of UK home 2 were higher than those reported for Birmingham homes (Harrad *et al*., 2008a,b).
- Levels of tri- to hexa-BDEs (Σ_{10}PBDEs) in Thai house dust were significantly higher than those in Thai vehicle dust (p = 0.001), and levels of all congeners studied, except for BDE-28, were significantly greater in Thai house dust than in Thai car dust (p = <0.001-0.004), indicating more extensive use of the Penta-formulation in Thai houses. Principal Component Analysis (PCA) showed no differences in PBDE congener patterns between Thai domestic and vehicle dust, suggesting that the tri- to hexa-BDEs determined in Thai house and automobile dust derive from similar sources. For Thai and UK house dust, the PCA implied that, while BDEs 49, 66, 99, 153 and 154 are the key influences on Thai samples, the UK samples are primarily governed by BDE 99. This supports the idea that the PBDE sources in Thailand differ from those in European countries such as the UK.
- Under high-end exposure scenarios, workers in Thai e-waste storage facilities were occupationally exposed to BDE-99 via dust ingestion (0.56-1.69 ng/kg bw/day) above a recently-published Health Based Limit Value for this congener (0.23–0.30 ng/kg bw/day). Conversely, all estimated exposures of the workers to BDE-209 via dust ingestion (0.06-47 ng/kg bw/day) were below the U.S. EPA's reference dose (RfD) of daily oral exposure to this congener (7 μg/kg bw/day).
- Estimated non-occupational exposures of Thai adults to BDE-99 via air inhalation (0.001-0.005 ng/kg bw/day) and dust ingestion (0.0001-0.01 ng/kg bw/day) were well within a health-based limit value proposed by Netherlands researchers (0.23–0.30 ng/kg bw/day). For both young male and female Thai children aged 2 years old, low-end (0.0017-0.0019 ng/kg bw/day) and "typical" BDE-99 exposure estimates (0.015-0.017 ng/kg bw/day)

involving dust ingestion did not exceed the proposed HBLV (0.23–0.30 ng/kg bw/day). In contrast, under a high-end exposure scenario, the exposure to BDE-99 of such Thai children via dust ingestion (0.22-0.25 ng/kg bw/day) is either very close to or in exceedance of the HBLV.

- Within-room spatial variation of PBDEs in UK house dust was investigated in individual areas within the four rooms. A one-way analysis of variance (ANOVA) and t-test demonstrated that Σ_{10}PBDE levels in the majority of studied areas did not differ significantly between different areas in the same room ($p > 0.05$). This may be because all areas within the same rooms were on the same carpeted floor. On the other hand, a one-way ANOVA test in bedroom 1 in home 2 indicated that Σ_{10}PBDE concentrations in area nearest to the PBDE emitters (i.e. a TV, computer, sofa and foam chair) exceeded significantly those in area farthest from the sources and close by a room door ($p = 0.009$). Additionally, the highest levels of Σ_{10}PBDEs ($p = 0.010$), BDE-47 ($p = 0.008$), BDE-99 ($p = 0.001$), BDE-100 ($p = 0.014$), BDE-153 ($p = 0.018$) and BDE-154 ($p = 0.011$) were observed in area located closest to the potential emission sources.
- Within-house spatial and temporal variability of PBDEs was studied in two UK homes. In homes 1 and 2, the maximum Σ_{10}PBDE level (ng g^{-1}) in an individual sample exceeded the minimum by a factor of 13 and 52 respectively, indicating that substantial uncertainty may be related to an exposure assessment based on a sample collected from one area in one room at one point in time. In addition, the ratio of maximum:minimum average levels of Σ_{10}PBDEs in homes 1 and 2 was 2.2 and 2.5 respectively, suggesting that appreciable within-house spatial variation in Σ_{10}PBDE levels occurs. Moreover, for home 2, a t-test showed statistically significant differences in levels of Σ_{10}PBDEs ($p = 0.001$), BDE-28 ($p = 0.001$), BDE-47 ($p < 0.001$), BDE-49 ($p < 0.001$), BDE-66 ($p = 0.013$), BDE-99 ($p < 0.001$), BDE-100 ($p < 0.001$), BDE-153 ($p = 0.025$) and BDE-154 ($p = 0.018$) between bedroom 1 and bedroom 2. In spite of the fact that both bedroom 1 and 2 faced the same road, bedroom 1 contained an old carpeted floor, whilst bedroom 2 contained a new bare wooden floor. Combined, these observations could indicate that all rooms in a house must be sampled to obtain a sample representative of what the occupants are exposed to. However, ANOVA and t-test analysis suggested that levels of Σ_{10}PBDEs in different rooms within the same house were not statistically significantly different ($p > 0.05$) in 61 out of 77 cases.

- Within-room temporal variation of PBDEs was studied in fourteen individual areas within six rooms in two different homes. The ratio of maximum:minimum concentrations of Σ_{10}PBDEs in four individual areas in two houses were 8.7, 9.2, 7.4, and 51 respectively, demonstrating appreciable variation, depending on when a given area is sampled. In home 1, a noticeable rise in levels of Σ_{10}PBDEs, BDE-47 and BDE-99 were seen in a living room, a bedroom 2 and a bedroom 3 owing to the presence of a TV, the introduction of two old mattresses and the heavy use of a PC respectively. Also in a bedroom 2 in home 2, a marked increase in concentrations of Σ_{10}PBDEs, BDE-153 and BDE-154 were observed because of the use of two laptops in the room. Moreover, a fall in levels of Σ_{10}PBDEs, BDE-47 and BDE-99 was found in a living room in home 1, bedroom 3 in home 1 and a bedroom 1 in home 2 due to the removal from the room of a TV, the introduction of a new bed and the permanent removal of a radio and desk lamp from the room, respectively. A t-test analysis revealed that the seasonal differences in concentrations of Σ_{10}PBDEs, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 in almost all of the fourteen areas studied were not statistically significant ($p>0.05$). Nonetheless, PBDE levels in summer (June to August) and autumn (September to November) generally exceeded those seen in winter (December to February) and spring (March to May). The temporal variations in this study arise chiefly from changes in room content over time.
- A relationship between concentrations of PBDEs in dust and dust loadings was examined by regressing log [dust loadings (g dust m^{-2} floor)] against log [concentrations of Σ_{10}PBDEs, BDE-47 and BDE-99] from the fourteen individual areas investigated over the 8 month period. A significant negative association has been identified for Σ_{10}PBDEs, BDE-47 and BDE-99 in three ($R^2=0.54$; $p<0.05$, $R^2=0.93$; $p<0.001$ and $R^2=0.65$; $p<0.05$), three ($R^2=0.51$; $p<0.05$, $R^2=0.66$; $p<0.05$ and $R^2=0.62$; $p<0.05$) and one ($R^2=0.68$; $p<0.05$) out of the fourteen areas respectively. This is consistent with the hypothesis that Σ_{10}PBDE, BDE-47 and BDE-99 levels in dust can be reduced or diluted as dust loadings increase, provided that the sources of the dust and of Σ_{10}PBDEs, BDE-47 and BDE-99 are independent of each other. Interestingly, a significant positive correlation has been identified for BDE-47 in two areas ($R^2=0.67$; $p<0.05$ and $R^2=0.67$; $p<0.05$) for the first time. While such observations may be artefacts, it is possible that they could arise in situations where both dust loadings and PBDE emissions increase in tandem, but where the increase in the latter is greater, consistent with a situation where a substantial source of

PBDEs to dust in that room arise as a result of abrasion of fibres or particles of PBDE-treated materials.

6.2 Recommendations for future studies

There is an expanding database relevant to the environmental presence, fate and behaviour of PBDEs as well as human exposure to these compounds. Nonetheless, salient research gaps still exist and further studies are required to:

- Monitor levels of other emerging BFRs like BTBPE in a large range of home and workplace outdoor/indoor environments, especially e-waste dismantling plants.
- Investigate a broader array of automobiles with respect to types of vehicle (i.e. saloon, van, mini-truck, truck or bus), year and country of manufacture, manufacturer and model.
- Elucidate the exact mechanism of and factors influencing debromination of BDE-209 in and between various environmental matrices (i.e. dust, indoor and ambient air). This may be accomplished via scientific experiments (e.g. controlled chamber experiments) or multimedia mathematical modeling.
- Characterize mechanisms of BFR releases (i.e. volatilization or particle abrasion) from different types of e-waste (e.g. P.C., TV, printer, fridge and washing machine) into the surrounding environmental compartments. This also highlights the need to elucidate the relationships between the different types of e-waste and the BFR concentrations and pattern of contamination.
- Improve understanding of the causes of intra-room and intra-home spatial, intra-room and intra-home temporal and seasonal variability in concentrations of BFRs. This may be achieved by conducting empirical studies which include information regarding brand, age and usage time of potential PBDE-treated goods (i.e. a TV and PC) as well as information about environmental conditions and characteristics of the monitored rooms/houses such as temperature, humidity, air flow, ventilation rates, floor types (i.e. carpeted and bare wooden, cement, marble, ceramic tile and rubber tile floor) and ventilation systems (i.e. natural, air conditioned, floor/table/ceiling fan).
- Perform wider and more powerful studies to facilitate better understanding of the critical factors affecting BFR contamination of workplace environments. The factors studied may include meteorological (e.g. ambient temperature and prevailing wind direction) and

physical workplace conditions (e.g. air ventilation, outdoor-indoor air exchange and location of processes involving use of BFRs).

- Explore effective alternatives to non-invasive bioindicators such as scalp hair, fingernails, saliva, sweat, urine and faeces for assessing human exposure to BFRs, particularly for infants, toddlers and young children.
- Develop more accurate estimates of intake of BFRs by various age groups via dust ingestion and indoor air inhalation as well as consolidating and improving the database on deleterious effects of individual PBDE congeners and other BFRs on human and environmental health for establishing safe levels for humans (i.e. reference dose; RfD) and ecosystems (i.e. no-observed-adverse-effects-level; NOAEL).
- Provide more information on non-dietary (i.e. dust ingestion, air inhalation and incidental soil and dust dermal contact) and dietary exposure to BFRs especially BDE-209, DBDPE, BB-209, BTBPE and TBBP-A.

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APPENDICES

APPENDIX A
Questionnaires

Questionnaire A-1: Outdoor Air Samples

Sample ID:

Address from which place is taken:

Date Sample taken:

Approximate distance of the sampler from ground level (cm):

Specifications of sampling location (i.e., wind direction, ambient temperature, etc.):

Questionnaire A-2: Indoor Air Samples

Sample ID:

Address from which place is taken:

Type of indoor microenvironment: ☐ **Office** ☐ **Home** ☐ **Other**

Sample taken in: ☐ **Living Room** ☐ **Bedroom** ☐ **Other**

Date Sample taken:

Approximate distance of the sampler from floor (cm):

Room specifications:
(Details of the room sampled)

1. Room ventilation: ☐ **Natural** ☐ **Air conditioned**

2. Is the room carpeted?

3. Number of sponge containing chairs: **How old?**

4. Number of sofas: **How old?**

5. Number of beds: **How old?**

6. Number of computers: **How old?**

7. Number of fridges/freezers: **How old?**

8. Number of TVs: **How old?**

**9. Number of other electronics (i.e., printers, stereos, microwaves, video players, etc.)
List them and add how old they are:**

Questionnaire A-3: Indoor & House Dust Samples

Sample ID:

Address from which place is taken:

Type of indoor microenvironment: ☐ Office ☐ Home ☐ Other

Sample taken in: ☐ Living Room ☐ Bedroom ☐ Other

Date Sample taken:

Approximate time since last vacuumed:
(if smooth floor please leave at least 2 days since last vacuuming)

Room specifications:
(Details of the room sampled)

1. Room ventilation: ☐ Natural ☐ Air conditioned

2. Is the room carpeted?

3. Number of sponge containing chairs:	**How old?**
4. Number of sofas:	**How old?**
5. Number of beds:	**How old?**
6. Number of computers:	**How old?**
7. Number of fridges/freezers:	**How old?**
8. Number of TVs:	**How old?**

**9. Number of other electronics (i.e., printers, stereos, microwaves, video players, etc.)
List them and add how old they are:**

Questionnaire A-4: Car Dust Samples

Sample ID (for researcher's use only):

Date:

Car manufacturer and model:

Year of manufacture:

No. of seats:

Car ventilation: ☐ **Natural** ☐ **Air conditioned**

Type of seat cover: ☐ **Fabric** ☐ **Leather**

Electronics inside the car (please tick box if appropriate):

Stereo ☐

Speakers ☐ **No.:**

GPRS ☐ **No.:**

DVD Player (Built-in) ☐ **No.:**

Other electronic devices either built-in or used regularly (i.e., portable DVD player) (please specify):

Approximate time since vehicle last vacuumed:

Manufacturer, model number and date of manufacture (if known) of child seat (s).
(If more than one, please give details of each):

Approximate time (hours per week) spent in the car by:

(a) family adults

(b) children

APPENDIX B
Details of air and dust samples from Thai e-waste storage facilities

Table B-1 Details of air samples from Thai e-waste storage facilities

Sample ID	Type	Sampling Location	Duration
Blank 1	Field blank	Field blank	-
Blank 2	Field blank	Field blank	-
TH Air 1	Indoor	Wongpanich storage plant, Bang Pa Inn Branch, Ayuthaya Province, Central Thailand (Facility 1)	8 Dec.07-26 Jan.08 (50 days)
TH Air 2	Outdoor (Upwind)	Wongpanich storage plant, Bang Pa Inn Branch, Ayuthaya Province, Central Thailand (Facility 1)	8 Dec.07-26 Jan.08 (50 days)
TH Air 3	Outdoor (Downwind)	Wongpanich storage plant, Bang Pa Inn Branch, Ayuthaya Province, Central Thailand (Facility 1)	8 Dec.07-26 Jan.08 (50 days)
TH Air 4	Indoor	Wongpanich storage plant, Rod Ja Na Branch, Ayuthaya Province, Central Thailand (Facility 2)	8 Dec.07-26 Jan.08 (50 days)
TH Air 5	Outdoor (Upwind)	Wongpanich storage plant, Rod Ja Na Branch, Ayuthaya Province, Central Thailand (Facility 2)	8 Dec.07-26 Jan.08 (50 days)
TH Air 6	Outdoor (Downwind)	Wongpanich storage plant, Rod Ja Na Branch, Ayuthaya Province, Central Thailand (Facility 2)	8 Dec.07-26 Jan.08 (50 days)
TH Air 7	Indoor	Wongpanich storage plant, Hi-tech Industrial Estate Branch, Ayuthaya Province, Central Thailand (Facility 3)	8 Dec.07-26 Jan.08 (50 days)
TH Air 8	Outdoor (Upwind)	Wongpanich storage plant, Hi-tech Industrial Estate Branch, Ayuthaya Province, Central Thailand (Facility 3)	8 Dec.07-26 Jan.08 (50 days)
TH Air 9	Outdoor (Downwind)	Wongpanich storage plant, Hi-tech Industrial Estate Branch, Ayuthaya Province, Central Thailand (Facility 3)	8 Dec.07-26 Jan.08 (50 days)
TH Air 10	Indoor	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	9 Dec.07-26 Jan.08 (49 days)
TH Air 11	Outdoor (Upwind)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	9 Dec.07-26 Jan.08 (49 days)
TH Air 12	Outdoor (Downwind)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	9 Dec.07-26 Jan.08 (49 days)
TH Air 13	Indoor	Jaroenchai storage plant, Bangkok, Capital of Thailand (Facility 5)	7 Dec.07-2 Feb.08 (58 days)
TH Air 14	Outdoor (Upwind)	Jaroenchai storage plant, Bangkok, Capital of Thailand (Facility 5)	15 Dec.07-2 Feb.08 (50 days)
TH Air 15	Outdoor (Downwind)	Jaroenchai storage plant, Bangkok, Capital of Thailand (Facility 5)	15 Dec.07-2 Feb.08 (50 days)
	Total	15 samples	

Table B-2 Details of dust samples from Thai e-waste storage facilities

Sample ID	Sampling Location	Area	Sampling Date
TH Dust 1* (*The sample contains sand and soil)	Wongpanich storage plant, Bang Pa Inn Branch, Ayuthaya Province, Central Thailand (Facility 1)	Area 1 (The right side of the PC & printer waste storage cabinet)	8 Dec.07
TH Dust 2* (*The sample contains sand and soil)	Wongpanich storage plant, Bang Pa Inn Branch, Ayuthaya Province, Central Thailand (Facility 1)	Area 2 (The left side of the PC & printer waste storage cabinet)	8 Dec.07
TH Dust 3* (*The sample contains sand and soil)	Wongpanich storage plant, Bang Pa Inn Branch, Ayuthaya Province, Central Thailand (Facility 1)	Area 1 (The right side of the PC & printer waste storage cabinet)	26 Jan.08
TH Dust 4* (*The sample contains sand and soil)	Wongpanich storage plant, Bang Pa Inn Branch, Ayuthaya Province, Central Thailand (Facility 1)	Area 2 (The left side of the PC & printer waste storage cabinet)	26 Jan.08
TH Dust 5* (*The sample contains sand and soil)	Wongpanich storage plant, Rod Ja Na Branch, Ayuthaya Province, Central Thailand (Facility 2)	The portable TV waste storage room	8 Dec.07
TH Dust 6* (*The sample contains sand and soil)	Wongpanich storage plant, Rod Ja Na Branch, Ayuthaya Province, Central Thailand (Facility 2)	The portable TV waste storage room	26 Jan.08
TH Dust 7* (*The sample contains sand and soil)	Wongpanich storage plant, Hi-tech Industrial Estate Branch, Ayuthaya Province, Central Thailand (Facility 3)	The vicinity of the PC & TV waste storage area	8 Dec.07
TH Dust 8	Wongpanich storage plant, Hi-tech Industrial Estate Branch, Ayuthaya Province, Central Thailand (Facility 3)	The PC & TV waste storage room	26 Jan.08
TH Dust 9* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 1 (PC & printer waste storage room)	9 Dec.07
TH Dust 10* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 2 (PC & printer waste storage room)	9 Dec.07

Table B-2 Details of dust samples from Thai e-waste storage facilities (continued)

Sample ID	Sampling Location	Area	Sampling Date
TH Dust 11* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 3 (PC & printer waste storage room)	9 Dec.07
TH Dust 12* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 4 (PC & printer waste storage room)	9 Dec.07
TH Dust 13* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 5 (PC & printer waste storage room)	9 Dec.07
TH Dust 14* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 6 (PC & printer waste storage room)	9 Dec.07
TH Dust 15* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 7 (PC & printer waste storage room)	9 Dec.07
TH Dust 16* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 8 (PC & printer waste storage room)	9 Dec.07
TH Dust 17* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 9 (PC & printer waste storage room)	26 Jan.08
TH Dust 18* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 10 (PC & printer waste storage room)	26 Jan.08
TH Dust 19* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 11 (Fridge & washing machine waste storage room)	26 Jan.08

Table B-2 Details of dust samples from Thai e-waste storage facilities (continued)

Sample ID	Sampling Location	Area	Sampling Date
TH Dust 20* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 12 (TV & VDO player storage area in electrical equipment waste storage room)	26 Jan.08
TH Dust 21* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 13 (TV & fan storage area in electrical equipment waste storage room)	26 Jan.08
TH Dust 22* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 14 (TV, microwave & fan storage area in electrical equipment waste storage room)	26 Jan.08
TH Dust 23* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 15 (TV, stereo & radio storage area in electrical equipment waste storage room)	26 Jan.08
TH Dust 24* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 16 (Rice cooker, photocopier, kettle, air conditioner, & drinking water cooler storage area in electrical equipment waste storage room)	26 Jan.08
TH Dust 25* (*The sample contains soil)	A donation center, Suan Kaew Foundation, Wat Suan Kaew, Nonthaburi Province, Central Thailand (Facility 4)	Area 17 (Typewriter, VDO, till & domestic telephone storage area in electrical equipment waste storage room)	26 Jan.08
Total	25 samples		

APPENDIX C
Details of indoor air, house and car dust samples from Thailand

Table C-1 Details of indoor air samples from Thai homes

Sample ID	**Sampling Location**	**Duration**	**Room ventilation**	**Total no. of TVs & computers**
THH In. Air 1	House no. 28 in Phuket Province, Southern Thailand	5 Dec.07-20 Jan.08 (47 days)	Air conditioned & fan	2
THH In. Air 2	House no. 15 in Yala Province, Southern Thailand	6 Dec.07-25 Jan.08 (51 days)	Ceiling & table fan	1
THH In. Air 3	House no. 44 in Surin Province, Northeastern Thailand	5 Dec.07-20 Jan.08 (47 days)	Fan & air conditioned	1
Total	3 samples			

Table C-2 Details of house dust samples from Thai homes

Sample ID	Sampling Location	Area	Sampling Date	Room ventilation	Total no. of TVs & computers
TH-HD 1 & 2	B. M. Apartment, Bangkok, Capital of Thailand	Room no. 401	6 Dec.07 & 25 Jan.08	Ceiling fan	3
TH-HD 3	House no. 37/2 in Chonburi Province, Eastern Thailand	Living room	13 Dec.07	Floor fan	2
TH-HD 4	House no. 37/2 in Chonburi Province, Eastern Thailand	Bedroom	13 Dec.07	Air conditioned	2
TH-HD 5	House no. 36/21 in Chonburi Province, Eastern Thailand	Computer & game room	14 Dec.07	Floor fan	2
TH-HD 6	House no. 36/1 in Chonburi Province, Eastern Thailand	Living room	14 Dec.07	Floor fan	1
TH-HD 7	B. M. Apartment, Bangkok, Capital of Thailand	Room no. 202	15 Dec.07	Ceiling fan	1
TH-HD 8	B. M. Apartment, Bangkok, Capital of Thailand	Room no. 206	16 Dec.07	Air conditioned & ceiling fan	2
TH-HD 9 & 10	House no. 73 in Bangkok, Capital of Thailand	Living room	18 Dec.07 & 2 Jan.08	Floor fan	2
TH-HD 11*	House no. 295 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	29 Dec.07	Ceiling fan	1
TH-HD 12* & 16*	House no.295 in Nakhonsrithammarat Province, Southern Thailand	The right side of TV in living room	29 Dec.07 & 24 Jan.08	Ceiling fan	2
TH-HD 13*	House no.295 in Nakhonsrithammarat Province, Southern Thailand	The left side of TV in living room	29 Dec.07	Ceiling fan	2
TH-HD 14	House no.295 in Nakhonsrithammarat Province, Southern Thailand	The left side of unused three TVs and unused stereo	29 Dec.07	Floor fan	2
TH-HD 15 & 17	House no.295 in Nakhonsrithammarat Province, Southern Thailand	The right side of unused three TVs and unused stereo	29 Dec.07 & 24 Jan.08	Floor fan	2

* The samples contain sand and soil.

Table C-2 Details of house dust samples from Thai homes (continued)

Sample ID	Sampling Location	Area	Sampling Date	Room ventilation	Total no. of TVs & computers
TH-HD 18	House no.31/1 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Natural	1
TH-HD 19	House no.31/1 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	3 Jan.08	Floor fan	0
TH-HD 20	House no.347/1 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Table fan	1
TH-HD 21	House no.347/1 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	3 Jan.08	Table fan	1
TH-HD 22	House no.347 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Natural	1
TH-HD 23	House no.347 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	3 Jan.08	Natural	0
TH-HD 24	House no.44/2 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Table fan	0
TH-HD 25*	House no.44 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Natural	1
TH-HD 26	House no.31 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Table fan	1
TH-HD 27	House no.46 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Table fan	2
TH-HD 28	House no.115 in Nakhonsrithammarat Province, Southern Thailand	Living room	3 Jan.08	Floor & table fans	1

Table C-2 Details of house dust samples from Thai homes (continued)

Sample ID	Sampling Location	Area	Sampling Date	Room ventilation	Total no. of TVs & computers
TH-HD 29	House no.395 in Nakhonsrithammarat Province, Southern Thailand	Living room	15 Jan.08	Ceiling fan	1
TH-HD 30 & 31	House no.26/3 in Nakhonsrithammarat Province, Southern Thailand	2 areas in living room	19 Jan.08	Ceiling & floor fans	1
TH-HD 32	House no.26/3 in Nakhonsrithammarat Province, Southern Thailand	Bedroom1	19 Jan.08	Table fan	0
TH-HD 33	House no.26/3 in Nakhonsrithammarat Province, Southern Thailand	Bedroom2	19 Jan.08	Table fan	0
TH-HD 34, 35 & 36	House no.492 in Nakhonsrithammarat Province, Southern Thailand	3 areas in living room	19 Jan.08	Floor fans	1
TH-HD 37	House no.492 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	19 Jan.08	Ceiling fan	1
TH-HD 38*	House no.17 in Nakhonsrithammarat Province, Southern Thailand	Living room	19 Jan.08	Floor fan	1
TH-HD 39	House no.321 in Nakhonsrithammarat Province, Southern Thailand	Living room	19 Jan.08	Ceiling fan	1
TH-HD 40	House no.121 in Nakhonsrithammarat Province, Southern Thailand	Living room	19 Jan.08	Floor fan	1
TH-HD 41	House no.62 in Nakhonsrithammarat Province, Southern Thailand	Living room	20 Jan.08	Natural	0
TH-HD 42	House no.62 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	20 Jan.08	Air conditioned	1

Table C-2 Details of house dust samples from Thai homes (continued)

Sample ID	Sampling Location	Area	Sampling Date	Room ventilation	Total no. of TVs & computers
TH-HD 43	House no.23 in Nakhonsrithammarat Province, Southern Thailand	Living room	20 Jan.08	Floor fan	1
TH-HD 44	House no.23 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	20 Jan.08	Floor fan	0
TH-HD 45*	House no.400 in Nakhonsrithammarat Province, Southern Thailand	Living room	20 Jan.08	Table fan	1
TH-HD 46	House no.400 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	20 Jan.08	Table fan	0
TH-HD 47	House no.44/1 in Nakhonsrithammarat Province, Southern Thailand	a barber's shop	20 Jan.08	Table fans	1
TH-HD 48	House no. 44/1 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	20 Jan.08	Table fan	1
TH-HD 49	House no.62 in Nakhonsrithammarat Province, Southern Thailand	Living room	20 Jan.08	Floor & table fans	1
TH-HD 50	House no.250 in Nakhonsrithammarat Province, Southern Thailand	Bedroom	20 Jan.08	Table fans	1
TH-HD 51	House no.007 in Nakhonsrithammarat Province, Southern Thailand	Living room	20 Jan.08	Ceiling fan	2
TH-HD 52	House no.338 in Nakhonsrithammarat Province, Southern Thailand	Living room	20 Jan.08	Table fan	1
TH-HD 53	House no.382 in Nakhonsrithammarat Province, Southern Thailand	Living room	20 Jan.08	Ceiling fans	1
Total	53 samples				

Table C-3 Details of car dust samples from a Thai car care centre

Sample ID	Car manufacturer & model	Sampling Date
TH Car 1	NISSAN BIG M BDI(Mini-truck)	9 March 09
TH Car 2	ISUZU D-MAX HI-LANDER (Mini-truck)	9 March 09
TH Car 3	ISUZU D-MAX SL-X (Mini-truck)	9 March 09
TH Car 4	TOYOTA HILUX D4D (Mini-truck)	10 March 09
TH Car 5	ISUZU D-MAX SL-X (Mini-truck)	10 March 09
TH Car 6	MITZUBISHI TRITON (Mini-truck)	10 March 09
TH Car 7	ISUZU D-MAX SL-X (Mini-truck)	11 March 09
TH Car 8	ISUZU D-MAX SL-X (Mini-truck)	11 March 09
TH Car 9	ISUZU SPARK EX (Mini-truck)	12 March 09
TH Car 10	ISUZU D-MAX HI-LANDER 2.5 Ddi i-TEQ (Mini-truck)	12 March 09
TH Car 11	FORD RANGER HI-RIDER XLT 4 WHEEL ABS (Mini-truck)	12 March 09
TH Car 12	TOYOTA HILUX TIGER D4D 16 VALVE TURBO (Mini-truck)	12 March 09
TH Car 13	ISUZU D-MAX HI-LANDER 3.0 Ddi i-TEQ (Mini-truck)	13 March 09
TH Car 14	TOYOTA HILUX VIGO D4D SMART CAB(Mini-truck)	13 March 09
TH Car 15	TOYOTA HILUX TIGER D4D (Mini-truck)	13 March 09
TH Car 16	TOYOTA HILUX TIGER (Mini-truck)	14 March 09
TH Car 17	TOYOTA COLOLLA ALTIS (Saloon)	14 March 09
TH Car 18	HONDA CIVIC 2.0 i-VTEC (Saloon)	14 March 09
TH Car 19	TOYOTA HILUX TIGER (Mini-truck)	16 March 09
TH Car 20	ISUZU SX D-MAX 2.5 Di-TURBO (Mini-truck)	16 March 09
TH Car 21	ISUZU D-MAX SL-X (Mini-truck)	17 March 09
TH Car 22	TOYOTA HILUX VIGO D4D (Mini-truck)	18 March 09
TH Car 23	ISUZU 4WD 2.8 TURBO (Mini-truck)	18 March 09
TH Car 24	TOYOTA HILUX TIGER D4D (Mini-truck)	19 March 09
TH Car 25	ISUZU SX D-MAX 2.5 Di-TURBO (Mini-truck)	19 March 09
TH Car 26	TOYOTA SOLUNA VIOS 1.5 S WT-i (Saloon)	19 March 09
TH Car 27	ISUZU KB 2500 Di (Mini-truck)	19 March 09
TH Car 28	ISUZU SLX D-MAX 2.5 Ddi i-TEQ (Mini-truck)	20 March 09
TH Car 29	MITZUBISHI LANCER GLX (Saloon)	20 March 09
TH Car 30	NISSAN SUNNY(Saloon)	21 March 09
Total	30 samples	

APPENDIX D
Details of house dust samples from UK

Table D-1 Details of dust samples taken in UK homes

Sample ID	Sampling Location (Room, Home number)	Area	Sampling Dates
UK Dust 1, 11, 21, 31, 41, 51, 61 & 71	Living Room, Home 1 (a carpeted & 1st floor room)	Area 1 (the right side of fire place, near the door)	9 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 27 Feb.08 4 April 08 16 May 08 23 June 08
UK Dust 2, 12, 22, 32, 42, 52, 62 & 72	Living Room, Home 1	Area 2 (the left side of fire place, near the kitchen)	9 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 27 Feb.08 4 April 08 16 May 08 23 June 08
UK Dust 3, 13, 23, 33, 43[a], 53, 63 & 73	Bedroom 1, Home 1 (a carpeted & 2nd floor room)	Area 1 (the vicinity of bed, wooden table, TV & wooden wardrobe)	8 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 27 Feb.08 4 April 08 16 May 08 23 June 08
UK Dust 4, 14, 24, 34, 44, 54, 64 & 74	Bedroom 2, Home 1 (a carpeted & 2nd floor room)	Area 1 (the vicinity of bed & heater)	9 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 27 Feb.08 4 April 08 17 May 08 23 June 08
UK Dust 5, 15, 25, 35, 45, 55, 65 & 75	Bedroom 2, Home 1	Area 2 (the vicinity of bed, studying desk & stereo)	9 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 27 Feb.08 4 April 08 17 May 08 23 June 08

Table D-1 Details of dust samples taken in UK homes (continued)

Sample ID	Sampling Location (Room, Home number)	Area	Sampling Dates
UK Dust 6, 16, 26, 36, 46, 56, 66 & 76	Bedroom 2, Home 1	Area 3 (the vicinity of room door)	9 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 27 Feb.08 4 April 08 17 May 08 23 June 08
UK Dust 7, 17, 27[b], 37, 47, 57, 67 & 77	Bedroom 3, Home 1 (a carpeted & top floor room)	Area 1 (the vicinity of bed & heater)	8 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 5 March 08 4 April 08 9 June 08 29 June 08
UK Dust 8, 18, 28, 38, 48, 58, 68 & 78	Bedroom 3, Home 1	Area 2 (the vicinity of bed & wooden table)	8 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 5 March 08 4 April 08 9 June 08 29 June 08
UK Dust 9, 19, 29, 39, 49, 59, 69 & 79	Bedroom 3, Home 1	Area 3 (the vicinity of stereo & studying desk)	8 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 5 March 08 4 April 08 9 June 08 29 June 08
UK Dust 10, 20, 30, 40, 50, 60, 70 & 80	Bedroom 3, Home 1	Area 4 (the vicinity of room door, banister & wooden wardrobe)	8 Sept.07 7 Oct.07 7 Nov.07 28 Nov.07 5 March 08 4 April 08 9 June 08 29 June 08

Table D-1 Details of dust samples taken in UK homes (continued)

Sample ID	Sampling Location (Room, Home number)	Area	Sampling Dates
UK Dust 81, 85, 89, 93, 97, 101, 105 & 109	Bedroom 1, Home 2 (a carpeted & top floor room)	Area 1 (the vicinity of TV, sofa & studying desk)	3 July 08 6 Aug.08 16 Sept.08 19 Oct.08 27 Nov.08 6 Jan.09 8 Feb.09 3 April 09
UK Dust 82, 86, 90, 94, 98, 102, 106 & 110	Bedroom 1, Home 2	Area 2 (the vicinity of heater & wooden wardrobe)	3 July 08 6 Aug.08 16 Sept.08 19 Oct.08 27 Nov.08 6 Jan.09 8 Feb.09 3 April 09
UK Dust 83, 87, 91, 95, 99, 103, 107 & 111	Bedroom 1, Home 2	Area 3 (the vicinity of bed & room door)	3 July 08 6 Aug.08 16 Sept.08 19 Oct.08 27 Nov.08 6 Jan.09 8 Feb.09 3 April 09
UK Dust 84, 88, 92, 96, 100, 104, 108 & 112	Bedroom 2, Home 2 (a non-carpeted & 1st floor room)	The entire area of bedroom	4 July 08 8 Aug.08 14 Sept.08 19 Oct.08 27 Nov.08 6 Jan.09 8 Feb.09 3 April 09
Total	112 samples		

[a] The sample contains a small amount of brick dust.
[b] The sample contains a lot of cigarette ash.

APPENDIX E
Temporal variations in BDE-47 and BDE-99 dust concentrations

Figure E-1 Temporal variations in BDE-47 dust concentrations in different four rooms, home 1

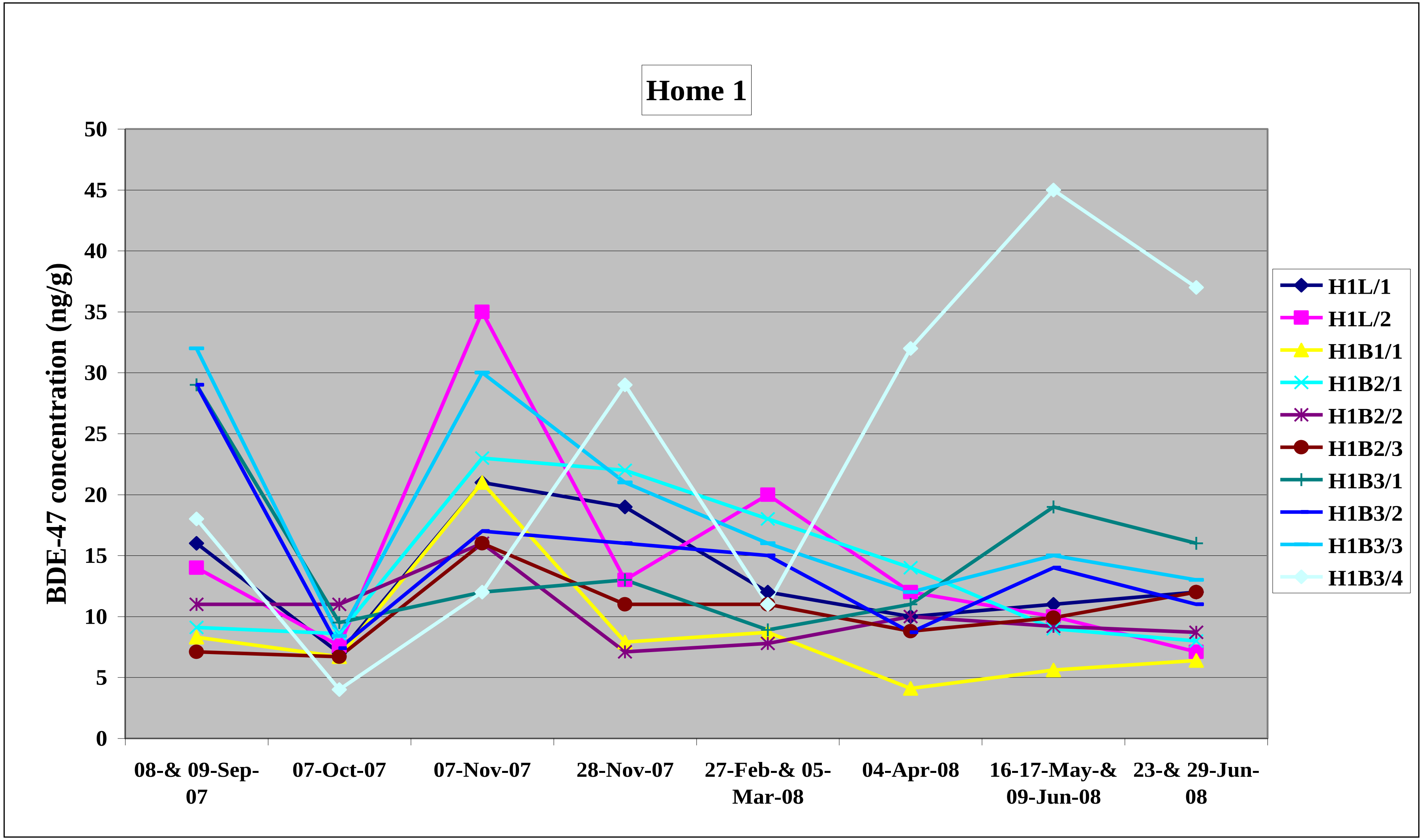

Figure E-2 Temporal variations in BDE-99 dust concentrations in different four rooms, home 1

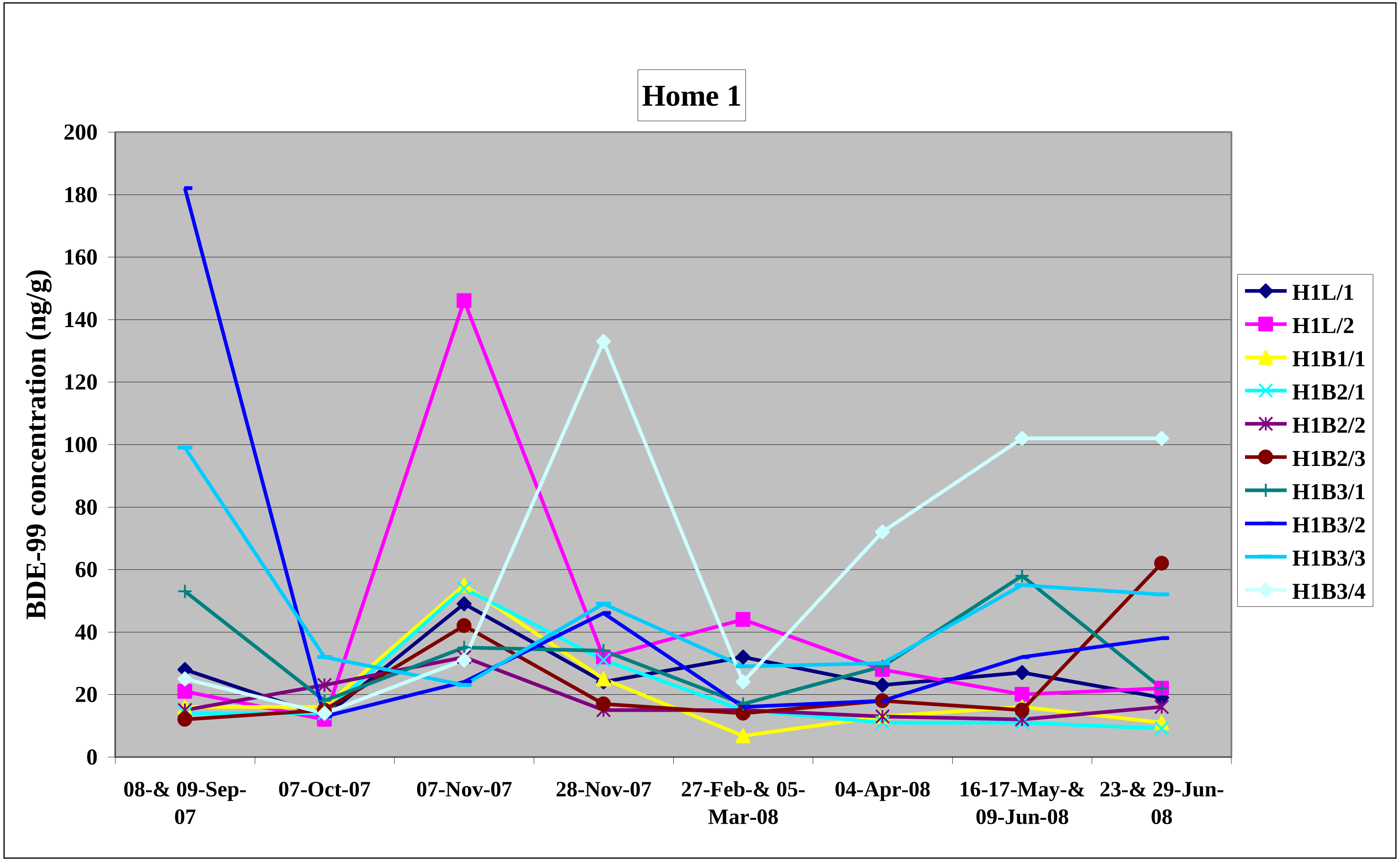

Figure E-3 Temporal variations in BDE-47 dust concentrations in different two rooms, home 2

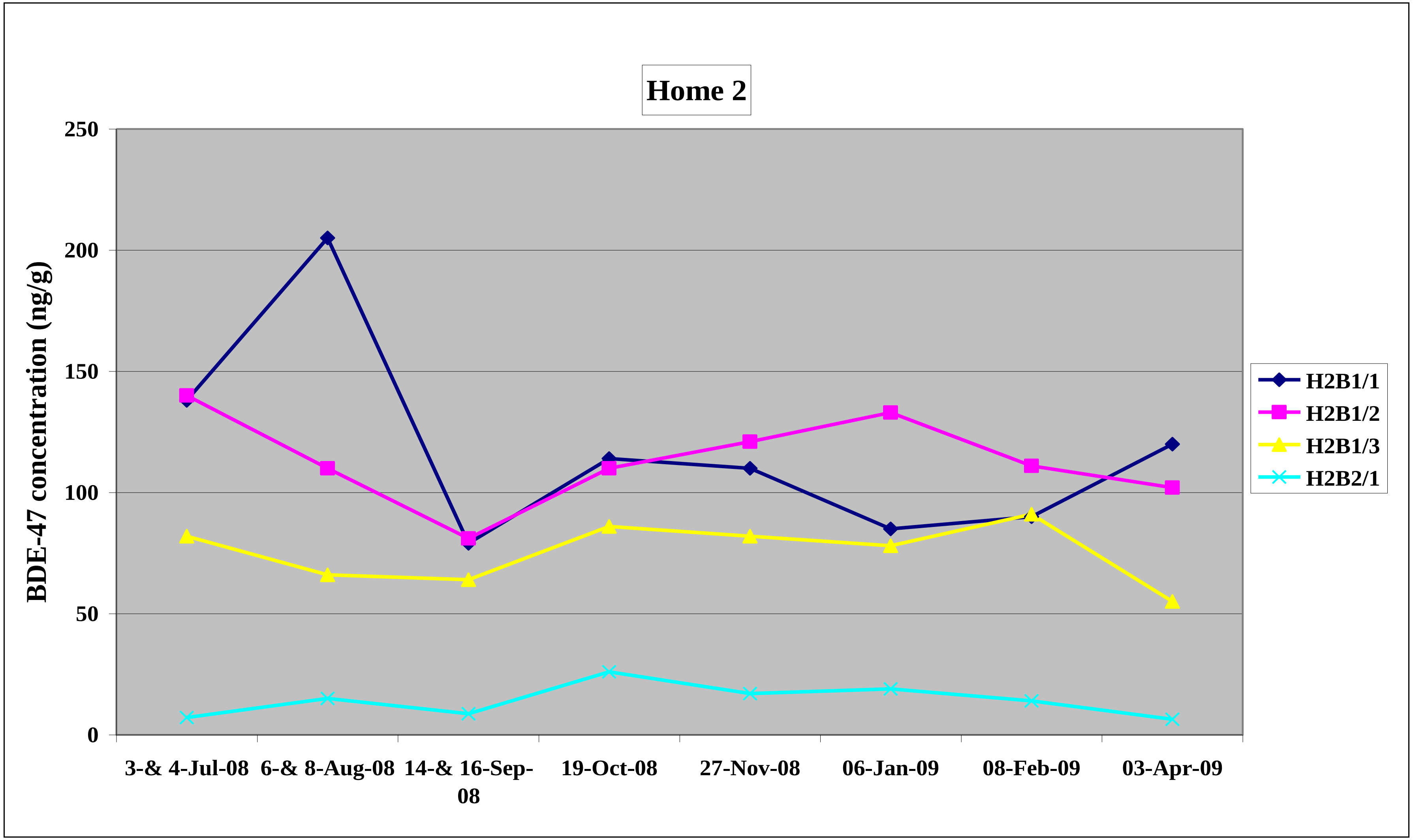

Figure E-4 Temporal variations in BDE-99 dust concentrations in different two rooms, home 2

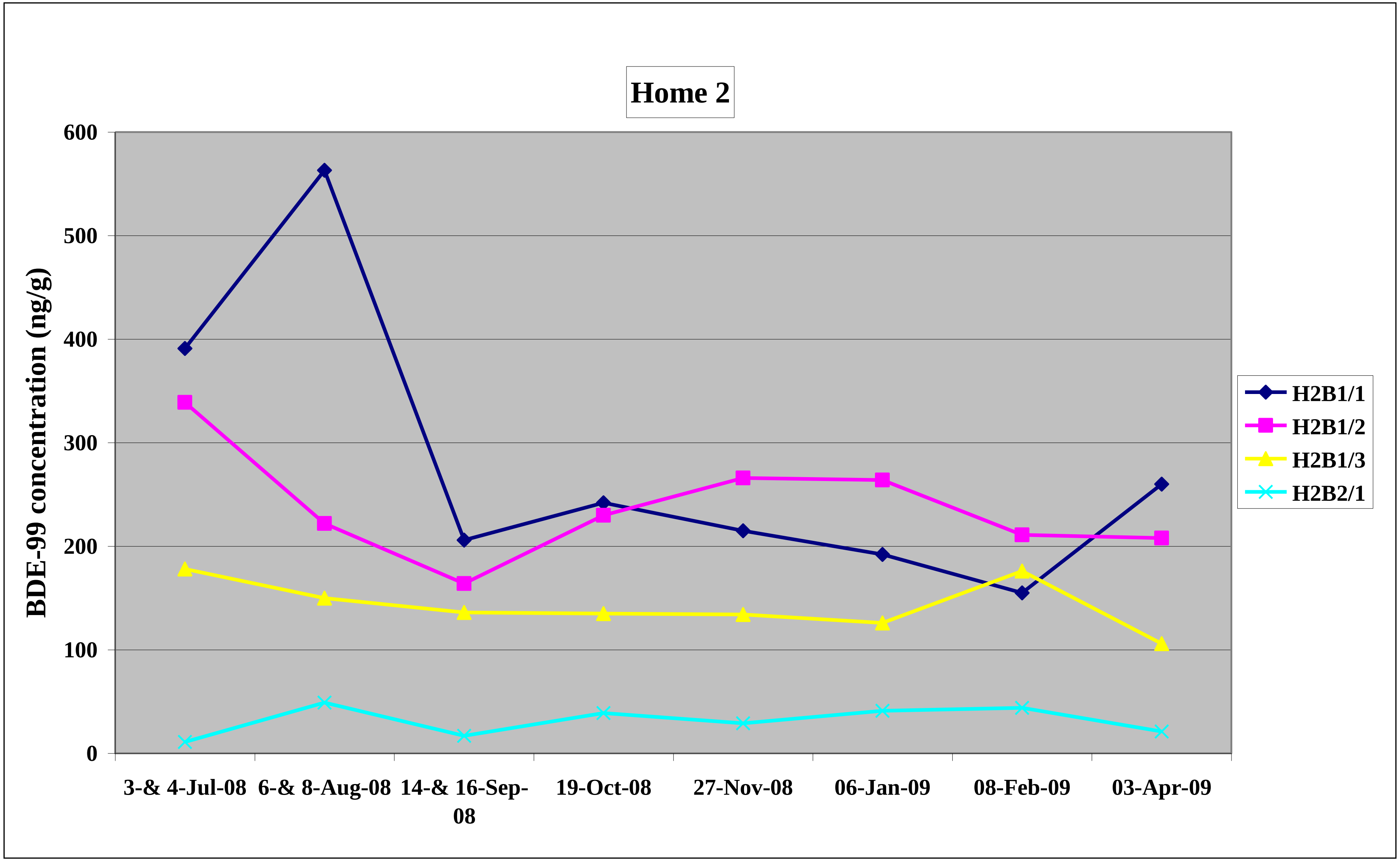

Figure E-5 Temporal variations in BDE-153 dust concentrations in different two rooms, home 2

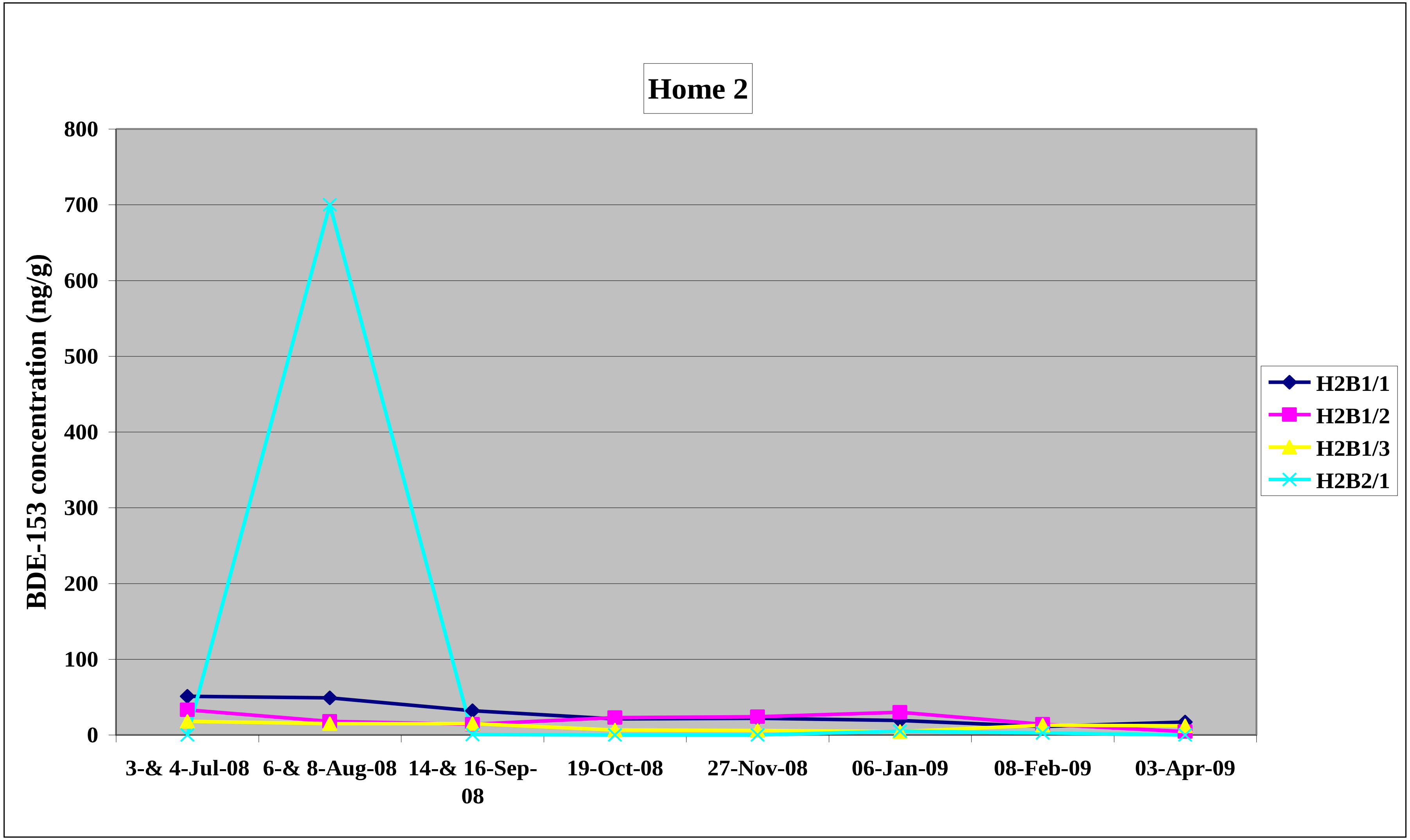

Figure E-6 Temporal variations in BDE-154 dust concentrations in different two rooms, home 2