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BROMINATED MICROPOLLUTANTS WITHIN THE INTEGRATED STEEL-MAKING PROCESS AND THEIR FATE IN THE ENVIRONMENT

by

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Abstract

Polybrominated diphenyl ethers (PBDEs) were found to be present in substantial quantities in the raw sinter mix (RSM) used in iron ore sintering during the steel making process. Measurement of corresponding output samples (electrostatic precipitator (ESP) dust, sinter product and stack emissions) permitted a mass balance calculation. This revealed that there is a net reduction of PBDEs as a result of the sintering process. Polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) were also detected in stack emission samples. PBDEs and PBDD/Fs were also investigated using a sinter pot (SP) – a laboratory scale version of the sintering process – under various conditions. Whilst evidence was found to suggest that *de novo* synthesis of PBDD/Fs occurs within the sintering process, there was also evidence suggesting that this was not due to the PBDE contamination in the RSM. Furthermore, the results from the SP suggested that PBDEs are not formed within the sintering process.

Temporal and spatial trends of PBDEs were investigated in air and soil from the UK. Whilst there is strong evidence to suggest that PBDEs have decreased since the implementation of legislative use restrictions, their persistence was highlighted by their continued detection. Furthermore ∑PBDE concentrations in both air and soil decreased with increasing distance from the centre of Birmingham, highlighting the higher density of PBDE sources in urban areas.

Soils from Australia were considerably less contaminated with PBDEs than those taken at a similar time in the UK. However, similar spatial patterns were found in both countries, with industrial and urban locations showing an increased likelihood of elevated ∑PBDE concentrations, with an increased contribution from Penta-BDE based congeners compared to remote sites. Agricultural sites in Australia were the only samples found to show an influence of Octa-BDE based congeners.

Sediment core samples from Port Jackson, New South Wales, Australia demonstrated that PBDEs were still rising at the end of the 20th Century with the highest levels in the uppermost layers. Industrial processes were highlighted as sources to the harbour as three cores from the more industrialised western side of the harbour contained higher ∑PBDE concentrations than the core measured in the north-east of Port Jackson, which is classified as urban rather than industrial.

Table of Contents

List of Tables

Chapter I: Introduction

Chapter II: Sampling and Analytical Methodology

Chapter III: PBDEs and PBDD/Fs in the Sintering Process

Chapter IV: An investigation in PBDE and PBDD/F formation within the sintering process

Chapter V: Concentrations of PBDEs in air and soil across an urban rural transect and in soil from various UK locations in 2004-05

Chapter VI: Concentrations of PBDEs in Australian Soils and Sediments

List of Figures

Chapter I: Introduction

Chapter II: Sampling & Analytical Methodology

Chapter III: PBDEs and PBDD/Fs in the Sintering Process

Chapter IV: An investigation into PBDE and PBDD/F formation within the sintering process

Chapter V: Concentrations of PBDEs in air and soil across an urban rural transect and in soil from various UK locations in 2004-05

Chapter VI: Concentrations of PBDEs in Australian Soils and Sediments

Abbreviations

ANOVA	analysis of variance
APCI	atmospheric pressure chemical ionisation
APPI	atmospheric pressure photoionisation
ASE	accelerated solvent extraction
BFR	Brominated Flame Retardant
BSEF	Bromine science and environmental forum
DCM	dichloromethane
EAF	electric arc furnace
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
ESP	electrostatic precipitator
GC	gas chromatography
GFF	glass fibre filter
HRGC	high resolution gas chromatography
HRMS	high resolution mass spectrometry
IG	ignitable content
IS	Internal Standard
$\mathbf{K_{oc}}$	octanol-carbon partition coefficient
$\mathbf{K_{ow}}$	octanol-water partition coefficient
LC	Liquid Chromatography
LOD	limit of detection
LOQ	limit of quantification
m/z	mass to charge ratio
Max.	maximum
Min.	minimum
MRM	multiple reaction monitoring
MS	mass spectrometry
NAEL	no adverse effect level
OC	organic carbon
PAS	passive air sampler
PBDD	polybrominated dibenzo-p-dioxin
PBDE	polybrominated diphenyl ether
PBDF	polybrominated dibenzo furan
PCA	principal component analysis
PCB	polychlorinated biphenyls
PCDD/Fs	polychlorinated dibenzo-p-dioxins/furans
PLE	pressurised liquid extraction
POP	persistent organic pollutant
PTSP	Port Talbot sinter plant
PUF	polyurethane foam
QA/QC	quality assurance/quality control
RDS	Recovery Determination Standard
RfD	reference dose
RRF	relative response factor
RSD	relative standard deviation

RSM	raw sinter mix
RT	retention time
SD	standard deviation
SES	Sampling Evaluation Standard
SP	sinter pot
SSP	Scunthorpe sinter plant
TBBP-A	tetrabromo bisphenol A.
TDI	tolerable daily intake
TEF	toxic equivalency factor
TEQ	toxic equivalent
U.S. EPA	United States Environmental Protection Agency
UNEP	United Nations Environment Programme
WHO	World Health Organisation

Chapter I

Introduction

1.1 Background of PBDEs and PBDD/Fs

PBDEs

Polybrominated diphenyl ethers (PBDEs) are hydrophobic chemicals consisting of two brominated aromatic rings linked by an oxygen atom (Figure 1.1). They are structurally similar to polychlorinated biphenyls (PCBs) and share many of their physicochemical properties, such as the aforementioned hydrophobicity and resistance to physical, chemical and biological degradation (Borghesi et al., 2009). They are used to reduce the flammability of both commercial and household products by being mixed additively with synthetic polymers such as polystyrene foams, polyurethane foams and epoxy resins (Birnbaum and Staskal, 2004, Toms et al., 2009b), computers, electrical and electronic equipment, textiles, foam furniture and building materials (Birnbaum and Staskal, 2004). There are three principal commercial formulations of PBDEs with a wide range of uses discussed further in Section 1.3; PentaBDE (e.g. foam mattresses and cushioning); OctaBDE (e.g. plastics for computer cases and monitors); DecaBDE (e.g. high impact polystyrene and other materials for electronic and electrical appliances, vehicles, construction, building applications and textiles) (Harrad et al., 2004).However, recent research suggests they are toxic to the environment as well as to animals and humans (Ren et al., 2009). The most recent data available (2001) states that a global demand of 67000 tonnes (t) of PBDEs per annum exists (Bromine Science and Environmental Forum (BSEF), 2003)

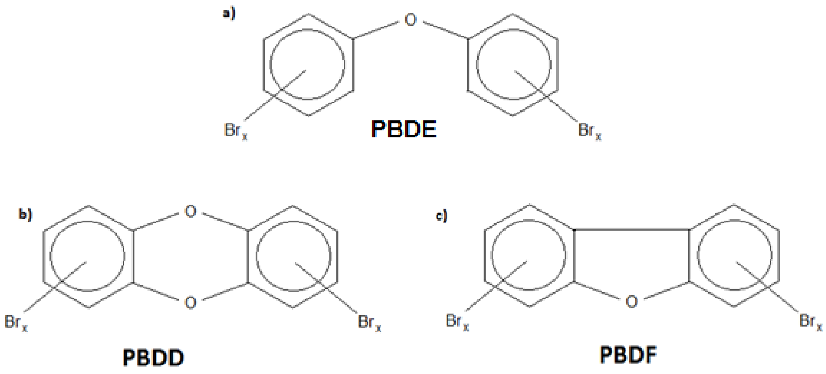


Figure 1.1 The chemical structure of a) PBDEs; b) PBDDs; and c) PBDFs

PBDD/Fs

Polybrominated dibenzo-*p*-dioxins and polybrominated dibenzo-*p*-furans (PBDD/Fs) are also toxic environmental contaminants with comparable physicochemical properties to their chlorinated analogues – PCDD/Fs (Ren et al., 2009). The main form of release of PBDD/Fs is believed to be as by-products associated with the use, manufacture and recycling of brominated flame retardant (BFR) containing products. They are thought to be formed via by thermolysis of PBDE containing BFRs, for example when combusting plastics (Hayakawa et al., 2004) as well as other combustion processes, such as incineration of BFR-containing waste (e.g. circuit boards and electronics goods (Li et al., 2007, Söderström and Marklund, 2002) metallurgical processes such as those in the steel industry, which are discussed further in Section 1.6 (e.g. sintering and electronic arc furnaces (Wang et al., 2010b)).

1.1.1 Environmental Levels and Exposure

Both PBDEs and PBDD/Fs are persistent in the environment upon their release. Figure 1.2 highlights the principal transfer processes in the environment for persistent compounds like PBDEs and PBDD/Fs. Due to their physicochemical properties (as outlined in Section 1.2) they preferentially reside in substances high in fat or organic carbon giving them the ability to accumulate in some environmental compartments, including soil and biota.

It is therefore unsurprising, based on the processes in Figure 1.2 that they have also been detected in various biota: birds and bird eggs – Crosse et al. (2012) found ∑PBDE concentrations of 382-54972 ng/g lipid weight in UK sparrowhawk eggs, whilst Chinese Kingfishers contained 2030-26400 ng/g lipid weight (Mo et al., 2012); animals (marine – Klosterhaus et al. (2012) measured median ∑PBDE concentrations in white croaker, shiner surfperch and adult harbour seal blubber of 1670, 1860 and 770 ng/g lipid weight respectively in San Francisco Bay, USA; and terrestrial – Belgian and Dutch hedgehogs contained muscle ∑PBDE concentrations of 7-24212 ng/g lipid weight (D'Have et al., 2005)); and food (cow’s milk from the UK was found to contain up to 960 ng ∑PBDEs / kg lipid weight (Lake et al., 2013), whilst Fernandes et al. (2009) detected both PBDEs and PBDD/Fs in all of eggs, chicken, beef fat, beef liver, pigs, sheep and other poultry).

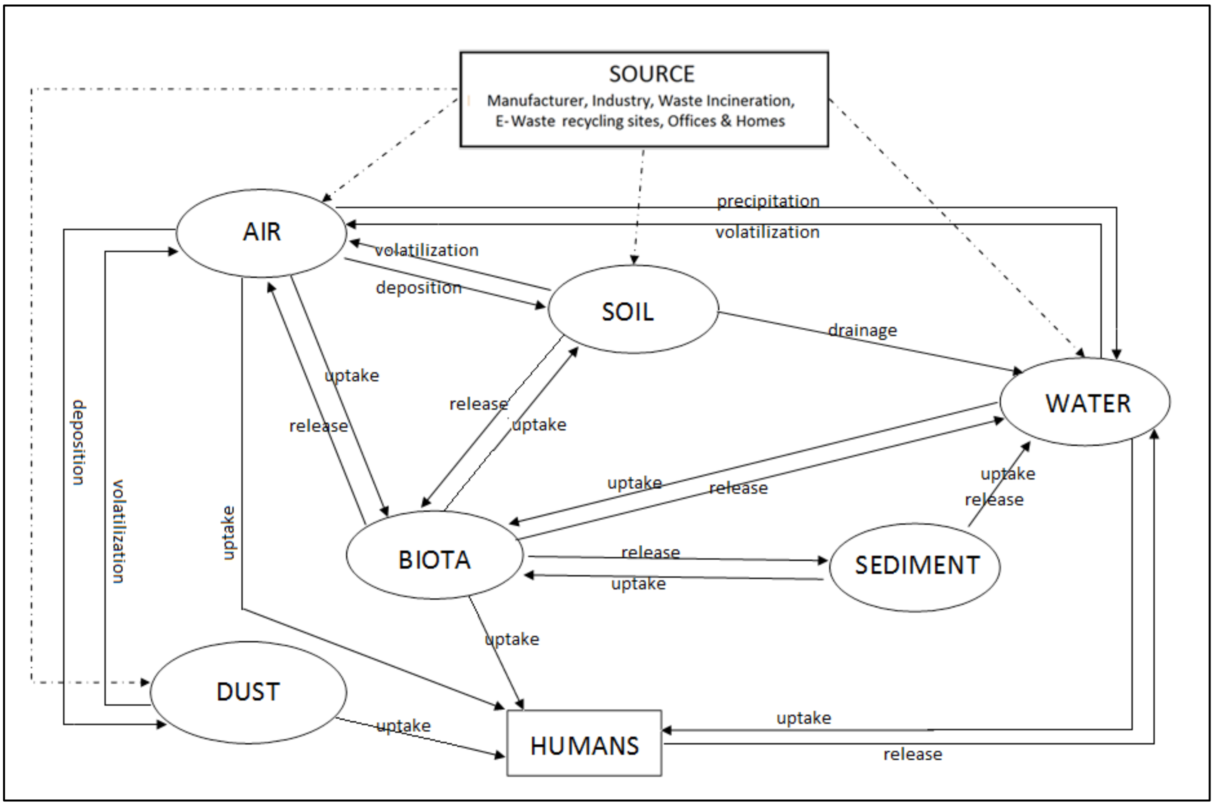


Figure 1.2 A schematic diagram showing the movement/transfer of PBDEs (and other POPs) to various environmental compartments along with human exposure – modified from UNEP (1999)

With PBDEs and PBDD/Fs being found in biota, along with air, soil and dust, there are also human exposure concerns (Costa, 2008). Figure 1.3 highlights the principal pathways of exposure to humans, and a summary of both internal and external exposure is given below.

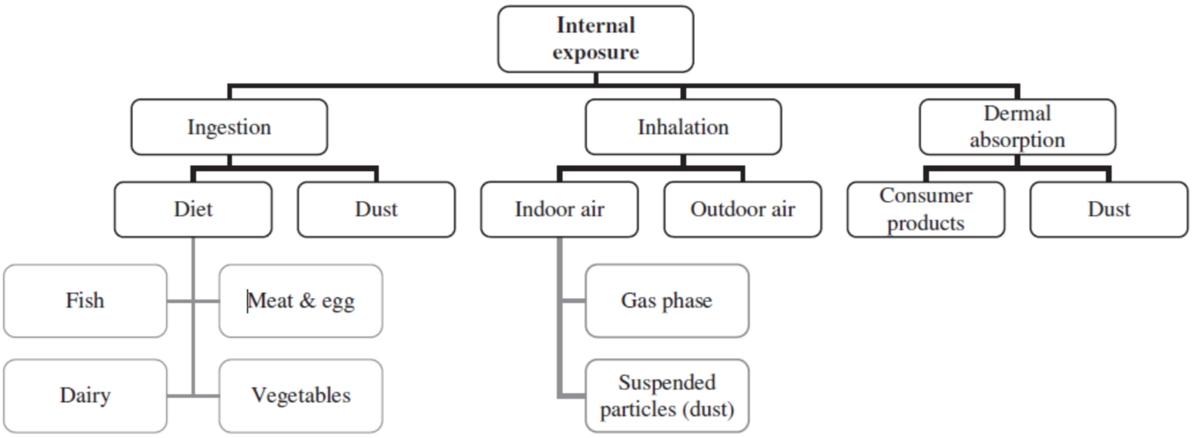


Figure 1.3 Principal pathways of exposure for humans to PBDEs and other POPs (Frederiksen et al., 2009)

The indoor environment has been highlighted as a source of exposure for PBDEs and, to a lesser extent, PBDD/Fs in both home and occupational settings (Suzuki et al., 2006) as well as cars (Frederiksen et al., 2009, Mandalakis et al., 2008). It was originally believed that diet and inhalation were the principal pathways of exposure to PBDEs with diet contributing more than 90% to human PBDE exposure (Harrad et al., 2004). However, Jones-Otazo et al. (2005) carried out extensive research on PBDE exposure and found that in humans older than 6 months dust ingestion was a key contributor to overall exposure, whilst for babies under 6 months, although dust ingestion remained at least as high, consumption of breast milk was the most significant pathway of exposure. Jones-Otazo et al. (2005) also stated that for toddlers, up to 90% of their total PBDE exposure is likely to come from dust ingestion. However, they state thatfor children, teenagers and adults, whilst dust ingestion is still the major pathway of exposure; diet (especially dairy, meat and eggs) also makes a significant contribution. Further studies have continued to show how important a role dust plays with regards to exposure with estimated exposures for children of 120-6000 ng/day based on a 50 mg/day dust ingestion rate for children (Stapleton et al., 2005). Harrad et al. (2006) re-evaluated pathways of exposure for the UK population and calculated that dust ingestion can contribute up to 37% and 69% of daily PBDE intake for adults and toddlers respectively in the UK. The same research group (Harrad et al., 2008a) later reported that, when also measuring BDE-209, PBDE concentrations in indoor dust are increased by a factor of 1000 (260000 ng/g in Harrad et al. (2008a) where tri-hepta PBDEs and BDE-209 were measured; 215 ng/g in Harrad et al. (2006) where only tri-hexa PBDEs were measured).

PBDEs are found in dust at high levels worldwide, with that from North America and the UK containing the highest concentrations: Stapleton et al. (2005) found median ∑PBDE concentrations of 4250 ng/g (n=16, range = 780-30100 ng/g), whilst median USA concentrations were found to be 1910 ng/g (n=11, range = 590-34400 ng/g) (Wu et al., 2007). Levels in the UK were found to be higher still by Greenpeace (2003) at 7290 ng/g (n=10, range = 3850-25000 ng/g) with BDE-209 making up 97% of the 80 BDE congeners measured. Harrad et al. (2008b) also found an overwhelming contribution of BDE-209 in UK dust making up 99.5% of the average concentration of 45000 ng/g (range: 360-520000 ng/g) in Birmingham. European and Australian PBDE levels in dust appear to be much lower than those in the UK and North America with median German concentrations at 70 ng/g (n=10, range not given, (Sjodin, 2004)); Spanish at 356 ng/g (n=6, range = 316-1855 (Regueiro et al., 2007)) and dust from Australia containing median concentrations of 571 ng/g (n=30, range = 60-84000 ng/g (Stasinska et al., 2013)). The UK's increased levels in comparison with the rest of Europe, are attributed to a greater usage of the commercial DecaBDE formulations to meet more stringent flame retardancy legislation in furniture (Thomas et al., 2006). Suzuki et al. (2006) measured both PBDEs and PBDD/Fs in home and office dust in Japan with mean PBDE concentrations of 1000 and 3300 ng/g respectively and PBDD/F concentrations of 2.1 and 3.8 ng/g – although TEQ concentrations were not provided, this still represents a high exposure to both PBDEs and PBDD/Fs through dust ingestion.

The debate about the relative contributions of dust and diet to overall exposure has continued and it appears to vary based on a number of factors, such as location, occupation, diet and habits. For example, Norwegian fish and seafood consumers are exposed to high levels of PBDEs with cod liver and halibut containing approximately 9.5 and 6.5 ng/g wet weight respectively and a daily intake of around 1.5 ng/kg body weight/day (kg/bw/day) based on a 70 kg adult (Knutsen et al., 2008). This is higher than the intake of an average Belgian, which was estimated to be 0.54 ng/kg bw/day (Voorspoels et al., 2007) and German – 1.2 ng/kg bw/day (Fromme et al., 2009) based on the same bodyweight, with fish and seafood containing the highest concentrations of all food groups at 0.46 ng/g wet weight (Voorspoels et al., 2007). It would appear in many other cases that fish and seafood contain the highest PBDE levels with concentrations of 0.56 ng/g wet weight in Catalonia, Spain (Domingo et al., 2008), although this study did not measure BDE-209. Schecter et al. (2006) found average fish concentrations to be 1.1 ng/g wet weight with herring, salmon and sardines to particularly contaminated (2.8, 1.7-3.1 and 3.7 ng/g wet weight respectively), with meat concentrations being lower at 0.38 ng/g wet weight. The same study calculated that the average U.S adult male and female are exposed to 1.3 and 0.9 ng/kg bw/day (Schecter et al., 2006), whilst Webster et al. (2005) estimated that adults are exposed to 0.6 ng/kg bw/day for just BDE-47. An interesting study by Ni et al. (2012) suggested that adults in Shenzhen, China, are exposed to PBDEs mainly by food, soil and dust (2, 0.21, 0.093 ng/kg bw/day respectively. However, Dirtu and Covaci (2010) estimated that a 70 kg Romanian adult is exposed to 0.57 ng/kg bw/day from diet and 0.43-1.2 ng/kg bw/day from dust (based on the rate of dust ingestion used). Sjodin et al. (2008) highlighted that simply location can alter the principal pathway to exposure by measuring PBDE levels in dust from Germany, Australia, UK and USA, which had substantially different median concentrations of 74, 1200, 10000 and 4200 ng/g respectively. These studies show that the principal pathways of human exposure to PBDEs can vary based on multiple factors, but diet and dust ingestion (especially the latter when BDE-209 is measured) appear to be the most significant.

Whilst dust ingestion and diet are now considered the principal pathways of exposure to PBDEs, inhalation of both indoor and outdoor air must not be ignored. As with indoor dust, PBDEs are found in measurable concentrations worldwide in the home (Sweden - 192 pg/m^3 (Karlsson et al., 2007); UK – 24 pg/m^3 (only tri-hexa BDE congeners measured (Harrad et al., 2006)); Canada – 100 pg/m^3 (only tri-hexa BDE congeners measured (Wilford et al., 2004)).

With such a wide range of concentrations within different media, it is clear that individuals can suffer a variety of different exposure levels with respect to PBDEs depending on the microenvironments they spend time in. Harrad and Abdallah (2011) found median dust levels in UK and American cars to be in excess of 100000 and 50000 ng/g respectively) whilst outdoor air and soil close to e-waste sites, has been found to contain significantly elevated levels as shown in Tables 1.5 and 1.6. The following inhalation exposure equation taken from Harrad et al. (2004) shows that it is clear that a number of factors can increase human exposure to PBDEs, PBDD/Fs and related pollutants.

$$\sum exposure = ((C_w F_w) + (C_h F_h) + (C_o F_o))R_R$$

Where $\sum exposure$ is daily exposure via inhalation (ng PBDE/day), $C_{w/h/o}$ is the concentration of PBDEs (or other pollutants) in work, home or outdoor air; $F_{w/h/o}$ is the time spent at work, home or outdoors; R_R is the respiration rate. The same equation can be applied to dust by using ingestion rate instead of R_R, and the two can be summed together, along with daily intake via diet to show total exposure. This therefore demonstrates that an individual's exposure can be influenced by many factors including their occupation, lifestyle and diet.

As discussed in Section 1.5 there is a wide range of PBDE concentrations in outdoor air both within and between countries worldwide. In even particularly remote locations, some PBDE congeners have still been detected and measured. For example, congeners from the commercial PentaBDE formulation have been found at concentrations of 2.2 pg/m^3 (∑BDEs-47; 99; 100; 153; 154) near Galway on the west coast of Ireland (Lee et al., 2003), whilst Birgul et al. (2012) found outdoor air in Manchester to contain concentrations as high as 47 pg/m^3 for the same congeners in 2003. PBDEs have also been detected in a variety of concentrations in other outdoor compartments such as soil, sediment and sludge. A summary of these concentrations in a global context is discussed in more detail in Section 1.5, highlighting urban and industrial areas as sources of PBDEs to the environment.

1.1.2 Levels of PBDEs and PBDD/Fs in Humans

With so many sources of external exposure, it is unsurprising that both PBDEs and, to a lesser extent, PBDD/Fs have been found in human samples. A wide range of adult human body burdens of PBDEs have been found in various parts of the world. Choi et al. (2003b) measured PBDEs ($BDE_{28:183}$) and PBDD/Fs in adipose tissue from Japanese adults in 1970 and 2000. Median concentrations for 1970 (n=10) were 29 and 5.1 pg/g lipid weight for PBDEs and PBDD/Fs respectively, whilst in 2000 (n=10) they were 1300 and 4 pg/g lipid weight showing that samples from 2000 contained significantly more PBDEs than those from 1970 with BDE-47 always the dominant PBDE congener (although BDE-209 was not measured). 2,3,7,8-TBDF was detected in all samples, whilst 2,3,7,8-TBDD was found in most 1970 samples but only 2 from 2000. Other studies for comparison of PBDD/F body burdens are scarce. From within Asia, breast milk from the Phillippines was found to contain significantly higher PBDE concentrations from adults living close to a waste disposal site (3.9 ng/g lipid weight) than those living in the control site (2.2 ng/g lipid weight), with the highest concentration of 11 ng/g lipid weight found in a mother residing in the vicinity of the waste disposal site (Malarvannan et al., 2013). Other studies have shown similar levels for both milk and blood serum with mean concentrations of 3.93 ng/g lipid weight in Taiwanese milk (Chao et al., 2007) whilst a South Chinese population contained 3.9, 4.4 and 3.5 ng/g lipid weight for fetal serum, maternal serum and maternal milk respectively (Bi et al., 2006). The highest concentrations appear to be consistently found in North America, particularly USA, where several studies have shown body burdens to exceed those elsewhere. Daniels et al. (2010) reported mean $BDE_{28:183}$ concentrations of 89 ng/g lipid weight (range: 1-2010 ng/g lipid weight) amongst women from North Carolina, with BDE-47 the most dominant congener found. They also noted that PBDEs were higher in women aged 25-29 than those over 34. In Canada, breast milk concentrations were found to be lower for $BDE_{47:153}$ in Ontario (22 ng/g lipid weight) and Quebec (23 ng/g lipid weight). However, BDE-209 was also present at relatively high concentrations at 17 and 13 ng/g lipid weight for Ontario and Quebec respectively, which is somewhat surprising given the general consensus about the low bioavailability of BDE-209. Other than this, BDE-47 was the dominant congener in Canadian breast milk (Siddique et al., 2012). Similar levels have also been found in other regions of North America, such as maternal and foetal blood from volunteers in Indiana which contained median levels of 37 and 39 ng/g lipid weight respectively for $BDE_{47:183}$ (Mazdai et al., 2003) and mothers' milk from Texas which measured 34 ng/g lipid weight for $BDE_{47:209}$ with BDE-209 found in 6 out of 47 samples (Schecter et al., 2003). In both cases, BDE-47 was the principal congener. Furthermore, Hites (2004) demonstrated that the increased usage from the 1980s to 2001 has caused a substantial rise in blood serum concentrations from 1.47 ng/g lipid weight in 1988 (Sjödin et al., 2001) to 41.1 ng/g lipid weight in 2001 (Mazdai et al., 2003) when examining the same congeners in both cases. Figure 1.4 also shows this trend in Sweden at lower concentrations which saw an exponential increase between the 1970s and 1999 in breast milk, whilst Thomsen et al. (2002) measured an increase in blood serum concentrations from 0.44 ng/g lipid weight to 3.10 ng/g lipid weight between 1977 and 1999 in Norway; and Schroter-Kermani et al. (2000) showed similar findings in Germany.

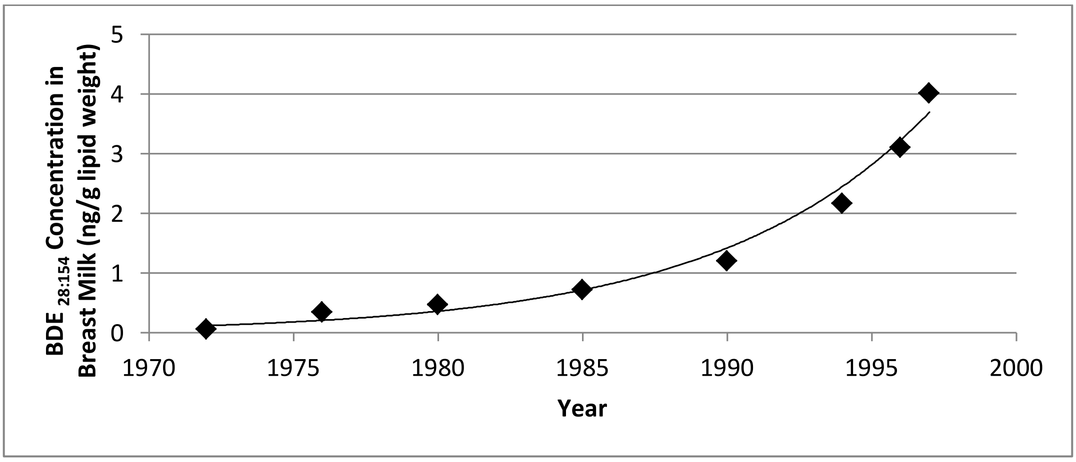


Figure 1.4 PBDE concentrations in breast milk from Swedish mothers between 1972 and 1999 (Meironyte et al., 1999)

Other studies in Scandinavia have found similar levels in both blood and breast milk such as those of Glynn et al. (2011) and Lind et al. (2003), whilst Sjodin et al. (1999) demonstrated that occupational exposure to PBDEs can lead to a much higher body burden with median $BDE_{47:209}$ concentrations of 26 ng/g lipid weight for electronics dismantlers compared with 4.1 and 3.3 ng/g lipid weight for hospital cleaners and computer clerks in Sweden.

PBDEs have also been found in human samples from the UK. Thomas et al. (2006) measured PBDEs in blood from 154 adults across 13 cities of various ages, backgrounds and occupations finding median levels of 5.6 ng/g lipid weight with the highest concentration measuring 420 ng/g lipid weight. BDE-47 was the main congener found, whilst they also found BDE-209 in 11 samples and small amounts of BDE-183, prompting the suggestion that subjects had been exposed to primarily the Penta-BDE formulation, but also to some Deca- and Octa-BDE. Similar median levels (6.6 ng/g lipid weight) were found in London and

Lancaster breast milk, which was dominated by BDE-47, although BDEs -183 and -209 were not measured in this study (Kalantzi et al., 2004).

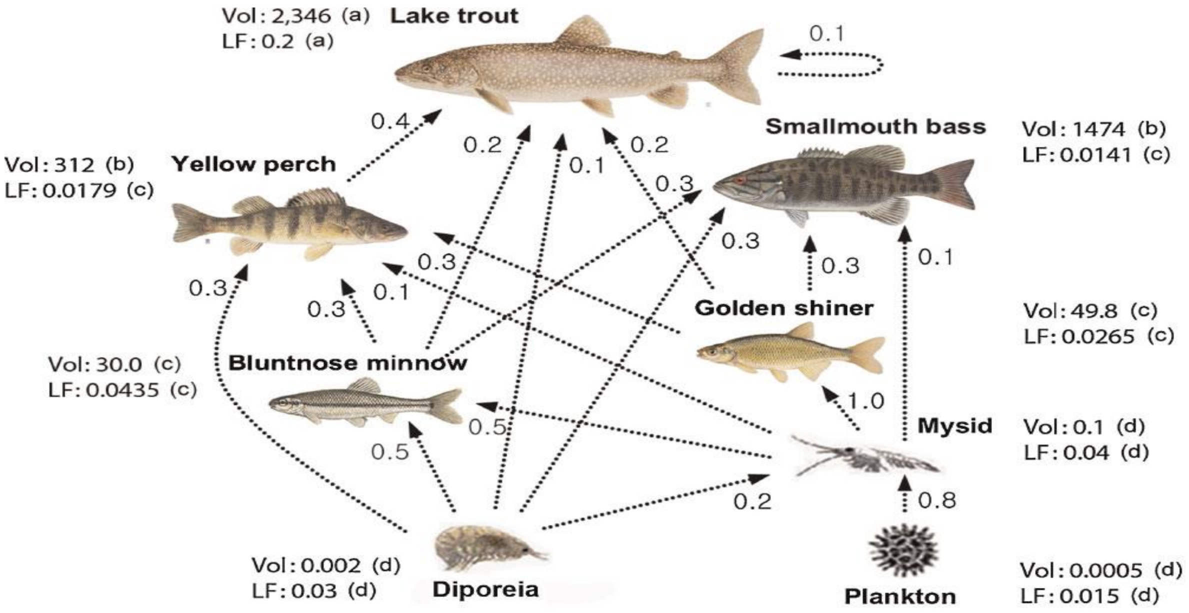
More recently, Garí and Grimalt (2013) measured PBDE concentrations in blood from 731 adults from Catalonia, Spain. BDE-209 was found with a median concentration of 3.3 ng/g lipid weight, whilst BDE-47 and -99 were 2.6 and 1.2 ng/g lipid weight respectively. Median ∑PBDE concentrations were 15.4 ng/g – one of the highest outside of Asia and North America. They also noted that the highest concentrations were found in adults aged under 30 years, a common trend seen. They attribute this to the increased usage since the 1980s, meaning that those under 30 have been exposed for a greater proportion of their lifetime. Australian human blood and milk falls within a similar range to that of the UK and Europe with median milk concentrations of 10.2 ng/g lipid weight (Toms et al., 2007) and 7.0-8.7 ng/g lipid weight in blood (Hearn et al., 2013). Interestingly, whilst BDE-209 was not measured in the milk samples (and so no comparison is available) (Toms et al., 2007), it was measured in blood, but was not detected in a single sample (Hearn et al., 2013). Surprisingly, a small study of blood in 23 New Zealanders revealed median $BDE_{47:183}$ concentrations of 6.12 ng/g lipid weight – similar to Australia and Europe and higher than Scandinavia. This is surprising due to the absence of any known PBDE production within New Zealand, and was attributed by the authors to imported consumer goods and food (Harrad and Porter, 2007).

Given the extensive use of PBDEs, the above sources of exposure and body burdens found in previous work (including both the UK and Australia), coupled with their potential to behave as pre-cursors for conversion to PBDD/Fs, it is important that further understanding is gained of the environmental sources, fate and impacts of both compound groups.

1.2 Physicochemical Properties, Biochemistry and Environmental Fate

PBDEs

There are 209 different BDE congeners, containing any number of bromine atoms from 1 (mono-BDEs) through to 10 (deca-BDE). The physicochemical properties of PBDEs vary between congeners (D'Silva et al., 2004). The octanol-water partition coefficient (K_{OW}) is used as an indicator of their environmental behaviour. Chemicals with high K_{OW} are hydrophobic and therefore are potentially bioaccumulative. PBDEs have a high K_{OW} (Table 1.1) and will accumulate in fatty tissues and oils (D'Silva et al., 2004). This combined with resistance to being metabolised can give them the ability to biomagnify up the food chain as demonstrated by Figure 1.5 which shows the bioaccumulation of PBDEs in fish from Lakes Huron and Erie, USA.



Note – Vol = Lipid Volume; LF = Lipid Fraction Dietary preference is shown by fractions at the end of arrows = e.g. 80% of Mysid diet comes from Plankton and 20% from Diporeia.

Figure 1.5 Schematic diagram of Lake Heron and Lake Erie, USA, demonstrating the biomagnification of PBDEs along the food chain in the two lake. Taken from Lim and Lastoskie (2011) and sources within.

It is generally believed that the lower brominated PBDEs, such as those from the Penta- and Octa- formulations are fairly mobile and are able to undergo long distance transport in air as they partition to at least some degree to the vapour phase, whilst the higher brominated molecules, such as BDE-209, are heavier with substantially lower vapour pressures and so have a tendency to sorb to soil and dust and are therefore far less amenable to long range atmospheric transport (Schenker et al., 2008). However, the data from the literature presented in Section 1.5, along with other studies, has shown that many PBDE congeners, including BDE-209 have been found in extremely remote locations, such as the Norwegian and Canadian Arctic, despite the absence of any local sources of PBDEs, suggesting that long range transport of all PBDEs occurs. A potential explanation for this was offered by de Wit et al. (2010) who stated that “periods of stable air conditions and high winds, such as during Arctic haze events will lead to episodes of long range transport for particulate-bound contaminants”.

The physicochemical properties of PBDEs govern the way they behave in all environmental compartments. Whilst, on the whole PBDEs are persistent and resistant to degradation, their differing properties with increased bromination mean that those with a higher molecular weight (e.g. octa- to deca- brominated) can behave differently in various environmental compartments.Studies such as that of Schenker et al. (2008) have suggested that BDE-209 and other highly brominated congeners undergo photolysis to form lower brominated congeners with an estimation that 13% of penta- and 2% of tetra-brominated PDBE congeners in the environment arise from the degradation of BDE-209. Stapleton et al. (2006) found that BDE-209 can also undergo debromination via metabolisation in rainbow trout and carp – a possible contributory factor to the highly variable human body burdens of BDE-209, despite the substantial use of DecaBDE in some regions.

The fate of PBDEs in the environment is still relatively unknown, but it has been proven that they can undergo significant degradation in the presence of anaerobic microorganisms (Gerecke et al. 2005) as well as photolytic degradation in the presence of ultraviolet light (Soderstrom et al. 2004).

Gerecke et al. 2005 were the first to show the microbial degradation of BDE-209, with a 30% loss in its content after 238 days in an anaerobic inoculation (with increases in octa- and nona- brominated congeners), whilst there was no significant loss in sterile conditions over the same time period. He et al. (2006) demonstrated that BDE-209 and some octa-brominated congeners undergo debromination in the presence of bacteria (*Sulfurospirillum mutivorans* and *Debalococcoides*). They found that BDE-209 degraded to form hepta- and octa-brominated congeners, whilst octa-brominated congeners degraded to form di- through to hepta-brominated congeners including BDEs -154 (hexa-), -99 (penta-), -49 and -47 (both toxic) which are considered to be more toxic (He et al. 2006). Microbial degradation of PBDEs has been demonstrated by several others in soil as well as sediment. The majority of evidence suggests that BDE-209 undergoes the most rapid degradation through debromination; however, Yen et al. 2009 has also shown that BDE-47 can undergo rapid degradation in the presence of anaerobic microbes with concentrations declining from 100 ng/mL of culture medium to the detection limit (not reported) after 63 days when the same concentrations of BDEs -99, -100, -153 and -154 had decreased by less than 20% over the same time period with estimated half-lives of 220-950 days. The more facile degradation of BDE-47 has been attributed to a higher bioavailability for anaerobic microbes whereby they are able to source their entire carbon requirements from BDE-47 (Vonderheide et al. 2006, Yen et al. 2009). Whilst these studies have demonstrated that microbial degradation of PBDEs is possible in laboratory conditions, it is likely that the persistence of PBDEs is underestimated, given the overwhelming evidence of their detection in deep layers of sediment, such as Marvin et al. (2007), Kohler et al. (2008) and others.

Wong et al. 2012 demonstrated that the ability of anaerobic bacteria to degrade PBDEs in soils decreases with time. The air soil partition coefficient (K_{SA}) for BDEs -17, -28, -47 and -99 (was measured as an indicator of volatility) at regular intervals from spiked urban soil under incubated laboratory conditions. It was found that the K_{SA} increased over time, meaning that the likelihood of their volatilisation from the soil decreased with the aging of the soil.

Nyholm et al. (2010) also stated that the persistence of PBDEs appears to increase in aging soil, with a high bioavailability to earthworms for the first 30 days of exposure (seen by increasing accumulation of lower brominated congeners in the earthworms). However, after 30 days, the accumulation rates slowed to that of the higher brominated congeners as the congeners became less bioavailable attributed by the authors to a stronger affinity to pores in the soils that earthworms and microbes were unable to feed on (Nyholm et al. 2010).

BDE-209 has also been found to undergo degradation to form hydroxylated and methoxylated PBDEs. Huang et al. 2010 examined BDE-209 in several plant species in order to observe its accumulation in their roots in a laboratory soil-plant system. There was a significant correlation of BDE-209 uptake and lipid content in roots, unsurprising given its high K_{ow}. The soil was also measured at different stages and was found to have developed increased concentrations in di- through to nona- brominated congeners as well as five different hydroxylated PBDEs. PBDEs were also further brominated within plants as di- through to penta- brominated congeners increased steadily. Finally a significant negative correlation was found between residual BDE-209 concentration in the soil and microbial biomass, again highlighting the ability of microbes to degrade BDE-209.

As previously mentioned, higher brominated congeners (particularly BDE-209) can undergo photolytic debromination in air (Schenker et al. 2008). Soderstrom et al. (2004) found that this was also the case in air, but also that PBDFs could be formed via the same mechanism. This has led to the postulation that erratic levels of BDE-209 in air, along with potential summer decreases are due to its photolytic degradation (Gevao et al. 2013).

Overall, there is clear evidence that PBDEs can undergo degradation via a variety of pathways and mechanisms. However, typical of first order decay, such degradation slows over time, related in part to increased binding to soil and sediment organic matter over time.

Moreover, where such degradation occurs it results primarily in the formation of lower brominated congeners, as well as hydroxylated and methoxylated PBDEs. As a result it would appear that they can display substantial persistence in soils and sediments, with one study reporting half-lives of 12.7 years for BDEs -47 and 99; and 22.8 years for BDE-209 (Andrade et al. 2010).

PBDD/Fs

PBDD/Fs are structurally identical to their chlorinated homologues (PCDD/Fs), which are well known. However, due to the heavier bromine atoms in PBDD/Fs (with C-Br being a weaker bond than C-Cl with bond dissociation energies of 330-350 and 368-393 KJ/mol respectively (Chen et al., 1989)) replacing the chlorine in PCDD/Fs, their behaviour in the environment is thought to differ slightly (Schecter, 2012).

The high K_{OW} values for PBDD/Fs (Table 1.2) means that, like PBDEs, they are likely to accumulate in fats and organic matter; this combined with their resistance to degradation and metabolism makes them bioaccumulative and persistent in the environment.

Experimentally derived data on the physicochemical properties of PBDD/Fs are scarce due to the expense and difficulty in obtaining appropriate standards. However Buser (1988) and Neupert et al. (1988) have both shown that all PBDD/Fs are unstable as they undergo photo-decomposition to form lower brominated PBDD/Fs and benzyl substitutes.

Chemical Nomenclature	**Common Name**	**Chemical Formula**	**Molecular Weight**	**Melting Point**	**V_p at 298.15 K (Pa)**	**Log K_{OW}**
2,4,4’-Tribromodiphenyl ether	BDE-28	$C_{12}H_7Br_3O$	406.9	64 °C[a]	2.19 x 10^{-3} [d]	5.94[f]
2,2’,4,4’-Tetrabromodihenyl ether	BDE-47	$C_{12}H_6Br_4O$	485.8	79-82 ºC[b]	1.86 x 10^{-4} [d]	6.81[f]
2,2’,3,4,4’-Pentabromodiphenyl ether	BDE-85	$C_{12}H_5Br_5O$	564.7	N/A	9.86 x 10^{-6} [d]	7.37[f]
2,2’,4,4’,5-Pentabromodiphenyl ether	BDE-99	$C_{12}H_5Br_5O$	564.7	93 ºC[b]	1.76 x 10^{-5} [d]	7.32[f]
2,2’,4,4’,6-Pentabromodiphenyl ether	BDE-100	$C_{12}H_5Br_5O$	564.7	97-98 ºC[b]	2.86 x 10^{-5} [d]	7.24[f]
2,2’,4,4’,5,5’-Hexabromodiphenyl ether	BDE-153	$C_{12}H_4Br_6O$	643.6	183 ºC[c]	2.09 x 10^{-6} [d]	7.90[f]
2,2’4,4’5,6’-Hexabromodiphenyl ether	BDE-154	$C_{12}H_4Br_6O$	643.6	N/A	3.80 x 10^{-6} [d]	7.82[f]
2,2’,3,4,4’,5’,6-Heptabromodiphenyl ether	BDE-183	$C_{12}H_3Br_7O$	722.5	172 °C[a]	4.68 x 10^{-7} [d]	8.27[f]
Decabromodiphenyl ether	BDE-209	$C_{12}Br_{10}O$	959.2	290-306ºC[b]	9.02 x 10^{-13} [e]	9.97[a]

NB – V_p = Vapour pressure; Melting point not available in literature for BDEs -85 and -154 [a] Wania and Dugani (2003)[b] Darnerud et al. (2001); [c] U.S.EPA (2008); [d] Tittlemier et al. (2002); [e] Fu and Suuberg (2011); [f] D'Silva et al. (2004);

Table 1.1 Physicochemical properties of selected PBDE congeners

Homologue Group	Molecular Formula	Molecular Weight	Log K_{OW}[a]	Log K_{OA}[a]	Melting Point[b]	V_p at 298.15 K (Pa)[b]	Water Solubility (log S) (mol/Litre)[b]
Mono-BDD	$C_{12}H_7Br_1O_2$	262.9	5.08	8.33	93-106 °C	3.5-4.0 x 10^{-3}	-6.12
Di-BDD	$C_{12}H_6Br_2O_2$	341.8	5.65	9.23	150-194 °C	1.5-1.7 x 10^{-3}	-6.9
Tri-BDD	$C_{12}H_5Br_3O_2$	420.7	6.16	10.2	N/A	N/A	N/A
Tetra-BDD	$C_{12}H_4Br_4O_2$	499.6	6.69	11.1	334-336 °C	6.4 x 10^{-7}	-8.72
Penta-BDD	$C_{12}H_3Br_5O_2$	578.5	7.19	12.1	N/A	N/A	-9.45
Hexa-BDD	$C_{12}H_2Br_6O_2$	657.4	7.69	13.0	N/A	N/A	N/A
Hepta-BDD	$C_{12}H_1Br_7O_2$	736.3	8.13	14	N/A	N/A	-10.89
Octa-BDD	$C_{12}Br_8O_2$	815.2	8.6	15	376	4.1 x 10^{-11}	-11.69
Mono-BDF	$C_{12}H_7Br_1O$	246.9	4.83	7.66	N/A	5.5-12 x 10^{-4}	-5.42
Di-BDF	$C_{12}H_7Br_1O$	325.8	5.35	8.58	N/A	3.5-4.5 x 10^{-5}	-6.25
Tri-BDF	$C_{12}H_7Br_1O$	404.7	5.87	9.51	144-148 °C	3.4-4.4 x 10^{-6}	-7.26
Tetra-BDF	$C_{12}H_7Br_1O$	483.6	6.38	10.5	240-302 °C	3.9-4.5 x 10^{-7}	-7.99
Penta-BDF	$C_{12}H_7Br_1O$	562.5	6.88	11.4	N/A	3.6-5.6 x 10^{-8}	-8.71
Hexa-BDF	$C_{12}H_7Br_1O$	641.4	7.36	12.4	N/A	4.6 x 10^{-8}	-9.43
Hepta-BDF	$C_{12}H_7Br_1O$	720.3	7.79	13.4	N/A	9 x 10^{-11}	N/A
Octa-BDF	$C_{12}H_7Br_1O$	799.2	8.26	14.4	N/A	N/A	N/A

NB – Due to a lack of literature some values are unavailable, whilst other values presented in this table are calculated/predicted [a] calculated by Schecter (2012) from Puzyn et al. (2008); [b] World Health Organization (WHO) (1998)

Table 1.2 – Summary of some physicochemical properties of PBDD/Fs

1.3 Applications and uses

PBDEs

PBDEs have been used to flame retard many household and commercial goods with a UK annual usage of 1500 t in upholstered furniture, 85 t in electrical goods (such as casing for plugs, wiring and televisions), and 25 t in DIY products (such as polyurethane foams (PUF) pipes and sealants) (D'Silva et al., 2004, Bromine Science Environmental Forum (BSEF), 2007).

There are 3 commercial PBDE formulations (the proportions of which are shown in Figure 1.10 in Section 1.7); however in 2004, the Penta- and Octa- formulations were banned in the EU (Birnbaum and Staskal, 2004) and Australia in 2005 (Toms et al., 2009b), whilst voluntary bans of these have occurred in the U.S. (Lagalante et al., 2009). As of July 2008, the DecaBDE formulation has been significantly restricted after the European Union restriction-of-hazardous-substances (EU ROHS) exemption ended on 1st July 2008 (Deffree, 2008). Moreover, in 2009, the Penta- and Octa- formulations were listed as 2 of 9 new persistent organic pollutants (POPs) recognised under the Stockholm Convention (Stockholm Convention, 2009). Yet in many parts of Asia, PBDEs are still used commercially without any regulations (Li et al., 2009). Although these substances are now widely restricted, such restrictions apply to their manufacture and new use, meaning that products already manufactured containing PBDEs will remain in use for the foreseeable future.

The exact proportions attributed to individual formulations are unavailable in the literature, but it is believed to be primarily DecaBDE – a demand of 150 t of PentaBDE was required for the entire usage of Europe in 2001 (Bromine Science and Environmental Forum (BSEF), 2003) PBDEs are incorporated additively into products as opposed to being chemically bound as in the case of reactive flame retardants such as tetrabromobisphenol A (TBBP-A). As a result PBDEs are more susceptible to migration from their original products into the environment (World Health Organization (WHO), 1994). The wide range of uses for the three principal commercial formulations of PBDEs are shown in Table 1.3. RPA Ltd. (2000) report that approximately 95% of PentaBDE used in the EU is in the furniture, automotive and packaging industries. Small amounts of Penta-BDE are also used in solid polyurethane applications such as housing for electronic goods. The RPA report also states PentaBDE may also have been used in specialised applications such as treatment of textiles and safety wear which is required to be fire-resistant such as industrial tyres and conveyor belts. It has also been reported that curtains and carpets have been treated with both Penta- and DecaBDE at concentrations of between 5-30% by weight (European Food Safety Authority (EFSA), 2011).

The use of each commercial formulation varies widely across the globe – for example, from the most recently available figures (for 2001), 95% of the global PentaBDE demand (7100 t) comes from the Americas, whilst Europe uses 7500 t DecaBDE compared with 24000 t for each of Asia and the Americas (Bromine Science and Environmental Forum (BSEF), 2003).

Resins and Polymers	DecaBDE	OctaBDE	PentaBDE
Acrylonitrile–butadiene–styrene		✓	
Epoxy-resins	✓		
Phenolic resins	✓		✓
Polyacrylonitrile	✓		
Polyamide	✓	✓	
Polybutadiene terephthalate	✓	✓	
Polyethylene	✓		
Polyethylene terephthalate	✓		
Polypropylene	✓		
Polystyrene (high impact)	✓	✓	
Polyvinyl chloride	✓		✓
Polurethane			✓
Polyesters	✓		✓
Rubber	✓		✓
Paints/lacquers	✓		✓
Textiles	✓		✓

Table 1.3 Applications of commercial PBDE mixtures (EBFRIP, 1990, D'Silva et al., 2004)

PBDD/Fs

PBDD/Fs have never been intentionally manufactured, and it is not known exactly how they are formed, although there is evidence to suggest that they are formed during processes involving high temperatures and brominated precursors, such as BFRs like PBDEs and TBBP-A (Schecter, 2012). Weber and Kuch (2003) state that PBDF formation from PBDEs requires “only an intra-molecular elimination of Br_2 or HBr” which normally occur during thermal degradation of the polybrominated aromatic rings at temperatures above 500 °C. Once, this thermolysis has occurred, the remainder of the PBDE molecule can then self-condense to form a PBDF. Alternatively, the molecule can undergo oxidation to form a bromophenate ion, which then undergoes self-condensation to form a PBDD molecule, although PBDD formation from PBDEs thermolysis is thought to occur to a much lesser extent than that of PBDFs (Weber and Kuch, 2003). Figure 1.6 demonstrates examples of how BDE-209 can undergo thermal degradation to form other PBDE congeners as well as PBDD/Fs.

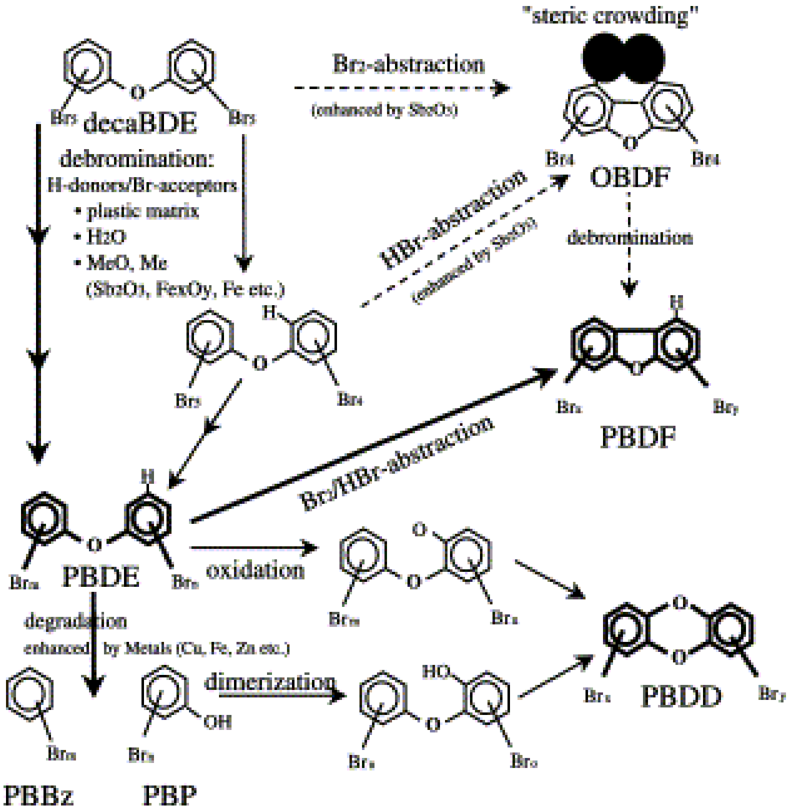


Figure 1.6 Formation pathways of PBDD/Fs during thermal degradation of BDE-209. Taken from Weber and Kuch (2003)

In addition, considering their identical structure to their chlorinated analogues, it cannot be ruled out that the mechanism of PBDD/F formation is the same – i.e. via *de novo synthesis*, formation from the basic elemental components (carbon, oxygen, hydrogen and bromine) under appropriate conditions (Bumb et al., 1980). Such conditions occur during combustion processes like waste incineration (Li et al., 2007) various industrial processes such as steel manufacture (Wang et al., 2008) and accidental fires such as 9/11 (Litten et al., 2003).

Buser (1986) also discovered that PBDEs act as precursors to PBDD/Fs at temperatures of 510-630 °C in the presence of air, as they undergo thermolysis. This was backed up by Weber and Kuch (2003), however they also state that under "controlled combustion conditions" PBDEs can be destroyed without the formation of PBDD/Fs. There is evidence that PBDEs are converted to PBDD/Fs in industrial processes, such as steel manufacture, as the presence of both compounds has been shown in emissions from steel manufacturing (Wang et al., 2010b) as well as in environments close to incineration and recycling of e-waste as mentioned above (Leung et al. 2007, Li et al. 2008). The presence of PBDEs and PBDD/Fs in the steel industry is discussed in more detail in Section 1.6.

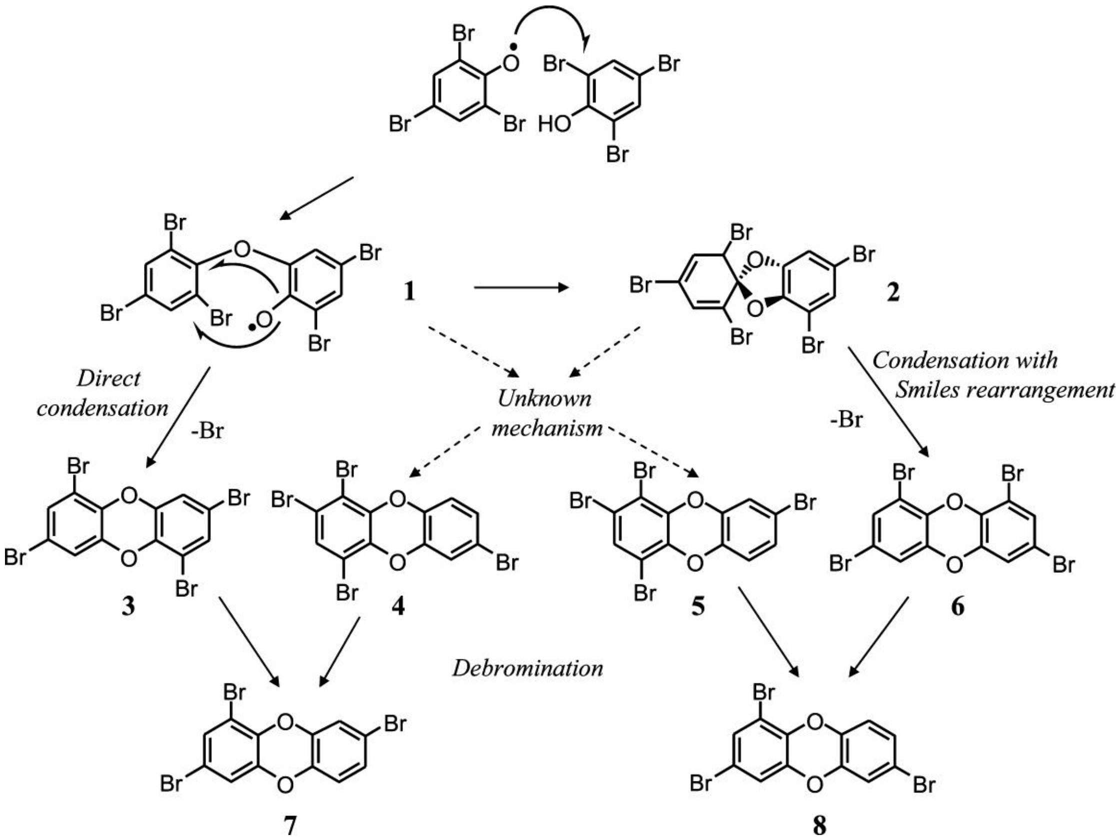


Figure 1.7 Potential mechanism for natural formation of PBDDs by cyanobacteria (Arnoldsson et al., 2012)

There is also evidence to suggest natural formation of PBDDs by marine biota. Specifically Haglund et al. (2007) detected them in Baltic marine environments where there were no known anthropogenic sources, whilst they were absent from freshwater environments in close proximity, leading the authors to postulate that they must be released into the environment naturally via excretion by algae and/or cyanobacteria. This was investigated further, where it was proposed that PBDDs are formed naturally via enzymatic coupling of bromophenols – a two stage process shown fully in Figure 1.7 – the coupling of a C-O bromophenoxy radical with another radical to form a bromophenoxyphenol; followed by ring closure to form a PBDD. However, it could not be concluded whether this was the principal formation pathway of PBDD/Fs in biota or whether there was an alternative exposure pathway (Arnoldsson et al., 2012).

1.4 Toxicology and Health Effects

PBDEs

PBDEs can be highly toxic to humans and animals. They are thought to disrupt levels of sex hormones, such as LH and FSH, in men (Meeker et al., 2009) and may be detrimental to human and animal health both through chronic and acute exposure, causing disruption to the liver, kidneys and thyroid gland; neurodevelopmental problems; various cancers; and inhibition of foetal and infant development (Costa, 2008). PBDEs are not completely resistant to metabolism and the liver has been found to oxidise congeners to form hydroxylated PBDEs (OH-PBDEs) such as the study by Erratico et al. (2012) who showed that human liver microsomes can metabolise BDE-99 into several different OH-PBDEs.

It is difficult to define the toxicity of PBDEs as one group as it is congener-specific – each congener has its own biological and toxicological consequences (D'Silva et al., 2004). The different commercial formulations of PBDE contain different congeners and thus different toxicities. For example, PentaBDE contains ca. 60% penta-, 30% tetra- and 5% hexa-brominated congeners, whilst OctaBDE contains ca. 80% hepta- and octa- (La Guardia et al., 2006). The Penta- formulation can activate the aryl hydrocarbon (Ah) -receptor (Gu et al., 2012), cause a reduction in hepatic vitamin A levels and induce various cancers as well as inhibit foetal and neonatal neurodevelopment (D'Silva et al., 2004, Hornung et al., 1996) . The OctaBDE formulation causes developmental toxicity, whilst the DecaBDE formulation is believed to be the least toxic as it contains higher molecular weight congeners that cross membranes less easily and are broken down more readily (D'Silva et al., 2004). However, Schreiber et al. (2010) report that BDE-209 is toxic to human HepG2 hepatoma cells, whilst the higher brominated PBDEs are thought to be broken down readily in photolytic reactions to yield more toxic and bioaccumulative penta- and tetra- congeners as well as PBDD/Fs (D'Silva et al., 2004). Using modified chicken DT40 cells, Ji et al. (2011) investigated the genotoxic potential of congeners from all three commercial formulations, along with some OH-PBDEs. They found that tetra-brominated PBDEs were the most potent in causing DNA damage, whilst penta- and hexa-brominated congeners required significantly larger concentrations to cause the same effects. It was also noted that BDE-209 caused no effect on cell growth, concluding that PBDE toxicity decreases with bromination. Interestingly, it was also discovered that OH-PBDEs are more toxic than their parent PBDEs – for example the lowest concentration of 6-OH-BDE-47 required to induce apoptosis of cells after 24 hours was approximately 5 µM compared with 41.2 µM for BDE-47.

The WHO state that there is limited "experimental" evidence of carcinogenicity from BDE-209 and none for any other PBDE mixtures, whilst limited studies have shown that PBDE mixtures are not genotoxic (Joint FAO/WHO Expert Committee on Food Additives (JECFA), 2006). The same authors went on to conclude that for multiple reasons, such as the complexity of PBDEs as a group, along with the limited data on human toxicity that they could not allocate tolerable daily intake (TDI) figures for PBDEs. However some health based limit values do exist. The U.S. EPA has set references doses (RfD) for BDEs -47, -99, -153 and -209 (Table 1.4) whilst Bakker et al. (2008) calculated "No adverse effect levels" (NAEL) for reproductive toxicity (0.23-0.30 ng/kg bw/day) and neurodevelopmental toxicity (18.8 ng/kg bw/ day) for BDE-99. They stated, that whilst the Dutch population were receiving approximately 100 times lower than the NAEL for neurodevelopmental toxicity, individuals exposed via the diet at the 99th percentile, 0.24 ng/kg bw/day, were likely to be at risk of reproductive inhibition as a result of dietary exposure to PBDEs. In the UK Harrad et al. (2010) carried out an exposure assessment for school children based on concentrations of dust they had measured and found that those with a high-end exposure (a dust ingestion rate of 200 mg/day contaminated at the 95th percentile concentration) would be exposed to 4.3 ng BDE-99/kg bw/day and 13000 ng BDE-209/kg bw/day – both considerably over the NAEL and RfD for BDEs -99 and -209 respectively.

Congener	Reference Dose (μg/kg bw/day)
BDE-47	0.1[a]
BDE-99	0.1[b]
BDE-153	0.2[c]
BDE-209	0.7[d]

[a] U.S. EPA. (2008b); [b] U.S. EPA. (2008c); [c] U.S. EPA. (2008d); [d] U.S. EPA. (2008a)

Table 1.4 U.S. EPA reference doses for a selection of PBDE congeners

Henny et al. (2009) found PBDE residues in the muscle tissue of ospreys in Sweden and discovered that they can be embryotoxic and cause eggshell thinning. More recently, Lee et al. (2012) found that PBDEs and UV-treated PBDEs reduce the hatching rates of grass shrimp embryos, with BDE-47 reducing by up to 50%. Koenig et al. (2012) further highlighted the effect of BDE-47 on neurodevelopment when they found that mice exposed to the compound take longer to find the escape hole in a maze at higher exposure levels.

With these effects observed in animal studies, it is unsurprising that, whilst more research is needed, studies have shown that PBDEs, along with their metabolites can cause adverse effects in humans. It has been suggested that children and young adults are more prone to developmental dysfunctions as a direct result of PBDE exposure (Siddique et al., 2012). Low concentrations of PentaBDE (10 μg/mL) have been found to stimulate the release of ^{3}H-arachidonic acid (^{3}H-AA; a signalling molecule found in the brain) leading to learning and memory impairment, whilst OctaBDE was required in concentrations five times higher to cause similar effects, demonstrating the decreased toxicity with increased bromination (Siddiqi et al., 2003). Furthermore, Bradner et al. (2013) evaluated how a PentaBDE formulation (DE-71) affected the nigrostriatal dopamine system. Using HEK293 cells, designed to express human-VMAT2 constructs, they were able to show that exposure to the DE-71 formulation over a 24 hour period can cause a dose-dependent increase in the release of lactate dehydrogenase – an indicator for cytotoxicity – leading to the conclusion that DE-71 is “an efficient neurotoxicant in a dopaminergic cell line”.

Gascon et al. (2012) found a statistically significant association between an increase in maternal PBDE body burdens and a decrease in mental development scores. On the other hand, in Californian post-mortem brain samples, there was no significant difference in concentrations of any PBDE congener measured across control brain samples and those from persons with Autism Spectrum Disorders or Genetic Neurodevelopment Disorders (Mitchell et al., 2012).

Ren and Guo (2013) stated that OH-PBDEs are highly similar in structure to several thyroid hormones, meaning that when humans are exposed to and have metabolised PBDEs there is the potential for various hormone receptor inhibitions leading to reduced thyroid activity. In a different study, out of 35 workers exposed to DecaBDE in a manufacturing plant, 4 exhibited clinical hypothyroidism, whilst none of the 89 unexposed workers had any known issues (Bahn et al., 1980). This is consistent with findings that at doses of 80 mg/kg bw of BDE-209, negative changes to thyroid, liver and kidney morphology in adult animals can occur (Darnerud, 2003). Furthermore, in human T47D breast cancer cells, 11 cells showed oestrogenic potencies, with BDE-100 (which makes up approximately 10% of PentaBDE formulations) the most potent. PBDEs can produce toxic pseudoestrogens upon metabolism that can inhibit T_4 enzymes from binding to transthyretin causing reduced thyroid activity, whilst they have also been found to affect testes development, hepatic enzyme activity and neurobehaviour (Siddiqi et al., 2003).

PBDEs have also been found to cause disruption to the oestrogen receptor pathway (Ren and Guo, 2013) – the inhibition of which has been found to correlate with various diseases including cancer and obesity (Boswell et al., 2012). Sexual development can also be adversely affected as both the androgen and progesterone receptors, vital for the regulation of genes needed for the development and maintenance of the male sexual phenotype, can be inhibited as Stoker et al. (2005) saw that male pre-pubescent rats exposed to PentaBDE had delayed onset of puberty after several PBDE congeners bound to the androgen receptor.

PBDD/Fs

Like PBDEs, PBDD/Fs are also toxic to humans with similar effects, such as neurodevelopment inhibition and endocrine disruption (Ren et al., 2009). However, there are far fewer studies addressing PBDD/F emissions, exposure pathways and toxicology. Furthermore there is just a handful of studies based on humans (Ericson Jogsten et al., 2010). There is a distinct gap in the knowledge of toxicity of PBDD/Fs, especially when compared to their chlorinated analogues (PCDD/Fs) (Birnbaum et al., 2003). There is a limited amount known on various PBDD/Fs, particularly 2,3,7,8-tetrabromodibenzo-*p*-dioxin (TBDD) which is absorbed readily into the body through oral or pulmonary exposure (Birnbaum and Staskal, 2004). PBDD/Fs are metabolised extremely slowly – data suggests a half-life of 2,3,7,8-

TBDD in humans of approximately 5-10 years (Birnbaum et al., 2003). It is known that PBDD/Fs have similar health impacts to PCDD/Fs, which are lethality, wasting, thymic atrophy, teratogenesis, reproductive disturbance, chloracne, immunotoxicity, enzyme induction, T4 vitamin A reduction, and increased hepatic porphyrins – based on experiments in mammalian and amphibian species (Birnbaum et al., 2003). There is little to no published literature on how PBDD/Fs affect humans, but most of the evidence suggests that their mechanisms (and thus toxic effects) are analogous with those of PCDD/Fs (Birnbaum and Staskal, 2004, DeVito et al., 1998). The investigation of the toxicity of PBDD/Fs is now of growing concern as they have been detected in adipose tissue from the Japanese (Choi et al., 2003b) and Swedish public as well as mothers' milk in various countries (Ericson Jogsten et al., 2010). Hornung et al. (1996) performed a study of the toxicity of PBDD/Fs, PBDEs and PBBs based on the early life stage mortality of rainbow trout. Whilst PBDEs did not display acute effects, it was found that PBDD/Fs with bromine atoms substituted in at least 3 of the 2,3,7 and 8 positions caused mortality in rainbow sac fry due to problems including yolk sac edema, pericardial edema, subcutaneous haemorrhages, reduced growth and craniofacial malformations (Hornung et al., 1996). Ericson Jogsten et al. (2010) recently examined the presence of PBDD/Fs in human adipose tissue and plasma from 10 people in comparison to other well-known POPs such as PBDEs and PCDD/Fs. They did not detect PBDDs, but PBDFs such as 2,3,7,8-TeBDF (0.27-2.4 pg g^{-1} lipid) and 1,2,3,7,8-PeBDF (0.23-0.89 pg g^{-1} lipid) amongst others were found. It was discovered using a rainbow trout early life stage mortality bioassay that whilst PBDDs were of equal or lower potency than 2,3,7,8-TCDD (the most toxic PCDD), PBDFs – particularly 2,3,7,8-TBDF – were more toxic than their chlorinated equivalents by up to 9 times (Hornung et al., 1996). This has since been backed up by Matsuda et al. (2010) who found using CALUX® assays for expression of Ah-receptor ligand activity that 2,3,7,8 TBDF had a relative equivalent potency (REP) of 0.83 compared with 0.021 for 2,3,7,8-TCDF. It was also seen that PBDDs are of similar to much lower potencies than equivalent PCDD homologues – the REPs for 2,3,7,8-TBDD and TCDD were 0.8 and 1 respectively, whilst for 1,2,3,7,8- PeBDD and PeCDD they were 0.28 and 0.73 (Matsuda et al., 2010). However, Olsman et al. (2007) stated that PBDD/Fs were overall of similar potencies to PCDD/Fs, although the REP for 2,3,7,8-TBDF was not given.

1.4.1 Toxic Equivalency Factors (TEFs)

The TEF is a method employed by WHO to "facilitate the evaluation of complex mixtures of related chemicals" (World Health Organization (WHO), 1998). It allows a figure to be assigned to a particular chemical or set of chemicals based on its relative toxicity (i.e. the higher its toxicity, the higher its TEF value). This figure is multiplied by the actual concentration of a specific congener to give its toxic equivalent (WHO-TEQ (formerly I-TEQ before updated TEFs)) value, which can be summed with TEQs from other compounds to give a total WHO-TEQ concentration for a given medium – e.g. ng WHO-TEQ m^{-3} for air samples. The World Health Organization (WHO) (1998) state that there are currently no agreed TEFs for PBDD/Fs and so those from their chlorinated homologues (PCDD/Fs) should be used in the mean time. Since then, a joint WHO and United Nations Environment Program (UNEP) consultation occurred that attempted to determine TEFs for PBDD/Fs. It was concluded that due to the limited experimental data in fish, mammals and humans, new TEFs for PBDD/Fs could not be calculated and that the same TEFs as applied to equivalent PCDD/F homologues should continue to be used (van den Berg et al., 2013).

1.5. Environmental levels, behaviour and sources

PBDEs

1.5.1 Outdoor Air

In the last 5-10 years there has been an increasing number of studies measuring PBDEs in outdoor air, especially with regards to BDEs -183 and -209. Table 1.5 summarises a broad selection of the available data for some PBDE congeners in ambient air. Whilst other congeners have been measured (such as BDEs -17; -28; -49; -66; -71; -77; -85; -119; -126; -138; -153; -154; -156; -183; -184; -191; -196; -197; -206; -207; -208) they make up a very small proportion of the total PBDE content, so only those most common in the environment are presented here. Whilst there have been several studies looking at PBDEs in outdoor air, there is a lack of recent data, with the most recent study dating back to measurements made in 2008, whilst there have been many changes in legislation over the last decade, suggesting that updated data on ambient air concentrations are required.

There are no obvious differences between continents with respect to PBDE concentrations and congener patterns; although with the deficiency in BDE-209 measurements in many studies this is extremely difficult to judge. This distinct gap in published data on the higher brominated BDE congeners, emphasises the requirement for updated studies, especially in the UK, where more stringent flame retardancy legislation for furniture has led to substantially greater use of the DecaBDE commercial formulation (Bromine Science Environmental Forum (BSEF), 2007), so it is expected that BDE-209 levels should be higher for the UK than elsewhere.

Data from Asia shows the importance of industry as a source of PBDEs to the environment with mean ∑PBDE concentrations of 3300 pg/m^3 in outdoor air close to industrial sources, compared with 570 pg/m^3 at a control site, whilst sites close to steel production sites in Korea appear to be on average twice those of rural and suburban locations at 25(9-62) pg/m^3 and 12 (7.3-21) pg/m^3 respectively (Choi et al., 2008).

The role of other anthropogenic activities is highlighted by Strandberg et al. (2001) who found average ambient air concentrations of 55 pg/m^3 in Chicago, compared to 11 pg/m^3 at rural sites close to Lake Michigan and 5.6 pg/m^3 at a remote site close to Lake Erie in the USA.

UK & Ireland

Study Location	Year	Land type	N	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
Lee et al. (2003) UK	2001	Rural/Semi-Rural	86	3.9 (0.72-15)	3.1 (0.53-15)	0.68 (0.46-2.90)	0.35 (0.09-1.5)	0.24 (0.09-0.90)	N/A	N/A
Lee et al. (2003) Ireland	2000	Remote	25	1.1 (0.16-1.9)	0.75 (0.28-1.9)	0.20 (0.07-0.43)	0.10 (0.04-0.18)	0.08 (0.05-0.10)	N/A	N/A
Harrad et al. (2004) UK	2002-3	Urban	6	9.4 (3.4-18)	5 (1.6-7.5)	1.3 (0.17-2.8)	2.9 (1.1-6)	1.8 (1.3-2.5)	N/A	N/A
Gioia et al. (2006) UK	2002-4	Rural/remote	5	1.5 (0.54-2.0)	0.48 (0.16-1.0)	0.13 (0.021-0.23)	0.051 (0.011-0.042)	0.058 (0.031-0.091)	N/A	N/A
Harrad and Hunter (2006a) UK	2003-4	Urban/Suburban	66	9.0 (3.1-17)	2.9 (1.2-5.6)	0.84 (0.25-2.7)	0.5 (0.14-2.11)	0.31 (<0.05-0.72)	N/A	N/A
Harrad and Hunter (2006) UK	2003-4	Rural	55	3.1 (0.29-8.0)	1.0 (0.34-2.57)	0.47 (0.07-1.15)	0.15 (0.11-0.2)	0.13 (<0.05-0.64)	N/A	N/A
Wilford et al. (2008) UK	2004	Semi-Rural	28	0.14 (<0.19-1.3)	0.31 (<0.33-1.8)	0.050 (<0.3-0.32)	1.2 (<0.3-15)	0.21 (<0.3-2.5)	4.6 (<0.5-92)	20 (<0.5-100)
Birgul et al. (2012) UK	1999-2010	Urban	33	6.6 (0.51-34)	2.7 (<0.05-9.2)	0.72 (<0.05-3.1)	0.42 (<0.3-3.1)	0.40 (<0.1-2.2)	0.45 (<0.1-2.2)	N/A
Birgul et al. (2012) UK	1999-2010	Rural	40	3.1 (0.12-28)	1.4 (<0.3-7.2)	0.38 (<0.3-1.9)	0.21 (<0.3-0.83)	0.18 (<0.1-1.2)	0.21 (<0.1-0.9)	N/A
Schuster et al. (2010) UK	2004-8	Rural/Remote	10	33 (<0.2-130)	25 (<0.3-86)	4.7 (<0.3-19)	7.9 (<.3-24)	1.4 (<0.3-18)	N/A	N/A

Table 1.5 Mean (range) PBDE concentrations (pg/m^3) in outdoor air around the world from previous studies

Europe & Scandinavia										
Study Location	**Year**	**Land type**	**n**	**BDE 47**	**BDE 99**	**BDE 100**	**BDE 153**	**BDE 154**	**BDE 183**	**BDE 209**
Gioia et al. (2006) Norway	2002-4	Rural/remote	7	0.025 (<0.05-0.27)	0.32 (0.059-0.75)	0.069 (<0.05-0.26)	0.036 (0.011-0.081)	0.24 (<dl-0.082)	N/A	N/A
Schuster et al. (2010) Norway	2004-8	Rural	12	240 (<0.05-550)	130 (<0.05-500)	36 (<0.05-130)	81 (<0.1-150)	6.8 (<0.1-81)	N.A	N.A
Agrell et al. (2004) Sweden	2001-2	Industrial	17	2.3 (1.2-4.5)	3 (0.5-9.7)	1.4 (<0.05-5.1)	0.29 (0.05-1)	0.2 (0.05-0.6)	0.16 (.05-1.1)	20 (<0.05-118.7)
Agrell et al. (2004) Sweden	2001-2	Urban	19	1.6 (0.05-5.7)	2.1 (0.05-13.1)	0.83 (0.05-6)	0.12 (<0.05-0.8)	0.15 (0.05-6)	0.05	40 (<0.05-191
ter Schure et al. (2004) Baltic	2001	Remote	19	1.8 (0.2-5.6)	1.2 (0.2-4.3)	0.7 (0.1-1.7)	N/A	N/A	N/A	6.1 (1.1-74.5)
Vives et al. (2007) Italy	2005	Industrial	1	152	15.7	7.2	1	1	2	16
Castro-Jiménez et al. (2011) France	2007-8	Urban/Industrial	13	89 (70-103)	77 (62-90)	20 (16-23)	4.9 (4.1-5.7)	4.7 (3.9-5.5)	0.13 (0.09-0.2)	1.2 (0.78-1.4)
Jaward et al. (2003) Europe	2002	Urban	25	16 (2.4-79)	16 (4.3-120)	2.9 (0.82-20)	1.8 (0.24-14)	1.2 (0.29-9.1)	N/A	N/A
Jaward et al. (2003) Europe	2002	Rural/remote	46	7.5 (2.4-43)	11 (4.4-72)	2.0 (0.82-13)	1.2 (0.23-7.8)	0.84 (0.29-5.1)	N/A	N/A
Iacovidou et al. (2009) Greece	2006	Remote	26	1.8 (<0.1-4.2)	0.8 (<0.1-4.5)	0.2 (<0.1-0.7)	0.2 (<0.1-0.6)	0.1 (<0.1-0.9)	N/A	N/A
Mandalakis et al. (2009) Greece	2006	Urban	8	8.3 (2-24)	6.1 (0.8-11.6)	1.4 (0.5-2.4)	0.65 (0.2-0.8)	0.60 (0.1-1.0)	0.46 (<0.1-0.9)	N/A

Table 1.5 Mean (range) PBDE concentrations (pg/m^3) in outdoor air around the world from previous studies

Asia										
Study Location	**Year**	**Land type**	**n**	**BDE 47**	**BDE 99**	**BDE 100**	**BDE 153**	**BDE 154**	**BDE 183**	**BDE 209**
Takigami et al. (2009) Japan	2006	Suburban	2	2.8	1.1	0.27	0.15	<0.15	N/A	N/A
Chen et al. (2006) China	2004	Industrial	16	82	570	120	23	18	8.9	2500
Chen et al. (2006) China	2004	Urban	8	29	21	3	6	3	4.5	260
Chen et al. (2006) China	2004	Background	8	30	35	5.5	7.2	3.9	4.3	480
Zhang et al. (2009a) China	2006-7	Rural	2	1.9 (<20-0.9)	2.8 (0.6-7.9)	0.8 (<20-4.7)	2.5 (0.5-6.5)	1.5 (0.3-6.6)	5.9 (2.2-18)	330 (49-1158)
Gevao et al. (2006) Kuwait	2005	Background	14	4.6 (1.3-17)	3.3 (0.9-11.4)	0.7 (<0.1-2.3)	0.3 (<0.1-0.92)	0.3 (<0.6-0.96)	0.1 (<0.6-0.89)	<0.6
Muenhor et al. (2010) Thailand	2007-8	E-Waste	10	17 (2.9-46)	19 (1.4-73)	4.8 (0.17-12)	4.6 (<0.05-20)	0.24 (< 0.05-0.082)	N/A	N/A
Xiao et al. (2012) Tibet	2006-2008	Remote	15	0.69 (0.32-1.2)	0.61 (0.21-1.2)	0.13 (0.049-0.24)	0.058 (0.011-0.16)	0.034 (0.0073-0.091)	0.14 (0.011-0.60)	0.15 (0.0021-0.51)
Choi et al. (2008) South Korea	2006	Industrial/ Steel	6	10 (4.7-18)	7.8 (1.6-21)	1,8 (0.6-4.7)	1.5 (0.3-5.4)	0.78 (0.2-2.6)	2.4 (0.4-7.2)	N/A
Choi et al. (2008) South Korea	2006	Rural/suburban	12	6.3 (3.3-11)	2.6 (1.6-7.5)	0.88 (0.6-1.8)	0.32 (0.1-1.0)	0.30 (0.10-0.90)	0.39 (0.10-1.20)	N/A

Table 1.5 Mean (range) PBDE concentrations (pg/m^3) in outdoor air around the world from previous studies

North America										
Study Location	**Year**	**Land type**	**n**	**BDE 47**	**BDE 99**	**BDE 100**	**BDE 153**	**BDE 154**	**BDE 183**	**BDE 209**
Strandberg et al. (2001) USA	1997-1999	Urban	12	33	16	2.0	0.53	0.41	N/A	0.3
Strandberg et al. (2001) USA	1997-1999	Rural	24	6.1	4.1	0.6	0.22	0.13	N/A	<0.10
Strandberg et al. (2001) USA	1997-1999	Remote	12	2.9	2.1	0.29	0.13	0.088	N/A	<0.10
Hoh and Hites (2005) USA	2002-3	Urban/suburban	66	11 (1-42)	6.1 (0.3-15)	1.3 (0.15-3.6)	N/A	N/A	N/A	27 (0.14-878)
Hoh and Hites (2005) USA	2002-3	Remote	61	6.5 (0.51-27)	4.2 (0.25-23)	1.6 (0.03-41)	N/A	N/A	N/A	2.0 (0.05-21)
Hoh and Hites (2005) USA	2002-3	Agricultural	30	9.2 (1.2-42)	5.4 (0.87-35)	1.2 (0.17-6.1)	N/A	N/A	N/A	9.0 (0.05-135)
Schecter et al. (2010) USA	2006	Urban	2	43	15	4.1	2.8	2.0	3.1	42
Wilford et al. (2004) Canada	2002-3	Urban	7	0.87 (<0.1-1.9)	1.1 (<0.3-1.9)	0.11 (<0.3-0.38)	N/A	<0.5	N/A	N/A
Harner et al. (2006) Canada	2000-1	Urban/rural	23	7.7 (1.5-16)	3.4 (0.53-7.3)	0.94 (0.17-2.36)	0.27 (<dl-0.61)	0.21 (0.03-0.5)	0.19 (0.06-0.58)	N/A
Xiao et al. (2012) Canada	1992-2008	Remote	78	2.7 (0.25-12)	0.65 (0.060-5.3)	3.2 (0.20-31)	0.21 (0.05-1.8)	0.22 (0.03-1.9)	0.11 (0.04-1.5)	N/A

Table 1.5 Mean (range) PBDE concentrations (pg/m^3) *in outdoor air around the world from previous studies*

Rest of the World										
Study Location	**Year**	**Land type**	**n**	**BDE 47**	**BDE 99**	**BDE 100**	**BDE 153**	**BDE 154**	**BDE 183**	**BDE 209**
Cetin and Odabasi (2008) Turkey	2004-5	Industrial	13	14	3.8	18	2	2.8	N/A	43
Cetin and Odabasi (2008) Turkey	2004-5	Urban/suburban	47	10	12	2.9	2.1	1.5	N/A	28
Toms et al. (2009b) Australia	2005	Urban	2	<3.2	<1.4	<0.4	<0.1	<0.1	0.1	3.6
Wurl et al. (2006) Indian Ocean	2004-5	Remote	10	4.3 (1.1-12.7)	2.3 (0.2-5.4)	0.4 (0.1-0.7)	0.13 (<dl-1.3)	N/A	<0.1	<0.1

Table 1.5 Mean (range) PBDE concentrations (pg/m^3) in outdoor air around the world from previous studies

1.5.2 Soils

As with outdoor air, data on PBDEs in soil has increased over the last 5 years. However, there is a gap of nearly 10 years since the last report of UK concentrations (Harrad and Hunter, 2006a) with no UK data for BDE-209 at all. Table 1.6 summarises a selection of studies that have investigated the concentrations of PBDEs in soils – only those giving specific congener concentrations are included. This summary highlights a huge range of concentrations for each measured congener with Eljarrat et al. (2008) demonstrating that sludge treated agricultural soils are more contaminated than those that go untreated – this is further backed up by Swedish data (Sellstrom et al., 2005).

PBDE levels from China demonstrate that e-waste treatment sites can increase local soil concentrations more than 100-fold, although it must be noted that there was a 5 year period between sampling of e-waste soils and those from a remote location (Wang et al., 2005, Chen et al., 2012, Labunska et al., 2013). Moreover, a single soil sample taken from a landfill site in Beiyang Bridge, Wuhan, China was measured for BDE congeners -47; -99 and -100 and was found to contain 300000 pg/g highlighting how easy it is for PBDEs to migrate from their original products into the environment (Xiao et al., 2007). Harrad and Hunter (2006a) also found that concentrations of PBDEs in urban soils (1150 pg/g) can be five times those detected in rural location (230 pg/g).

Given the above, it is clear that there are various sources of PBDEs to the outdoor environment, and with a high organic carbon:water partition coefficient (K_{OC}) PBDEs are likely to accumulate in soils. Also, taking into account the increased UK usage of BDE-209, it is vital that some data is obtained to see what effect this has had on its environmental levels.

Cetin and Odabasi (2007) highlighted the effect that the steel industry can have on PBDE levels in soil when they found concentrations of 2200 pg/g within the vicinity of a steel-works in Izmir, Turkey compared with an average of 840 pg/g in soil from a nearby suburban site. Further studies by the same group found ∑PBDE concentrations to be 4 times higher when including BDE-209 measurements in soil close to steel production (37000 pg/g) than in suburban locations (9900 pg/g) (Odabasi et al., 2010). These studies highlight the steel industry as a potential source of PBDEs to the environment, but there is still a lack of data, especially in the UK, which is discussed below in Section 1.6.

Study Location	**Year**	**Sample Site Description**	**N**	**BDE 47**	**BDE 99**	**BDE 100**	**BDE 153**	**BDE 154**	**BDE 183**	**BDE 209**
Eljarrat et al. (2008) Spain	2005	Sludge Treated Soils	6	1300 (590-33000)	1400 (540-27000)	1500 (570-6300)	1200 (<dl-3700)	1,200 (770-3400)	5,900 (2700-30000)	250000 (2.5 x 10^4 -10.8 x 10^5)
Eljarrat et al. (2008) Spain	2005	Untreated Agricultural Soil	1	690	630	1080	940	930	1870	14600
Chen et al. (2012) China	2008	Rural/Remote	22	2.1	2.3	2.1	2	0.68	2.1	290
Hassanin et al. (2003) UK	2003	Rural/Remote	42	280 (7-1400)	590 (78-3200)	73 (8-470)	141 (19-1200)	100 (8-940)	48 (10-7000)	N/A
Hassanin et al. (2003) Norway	2003	Rural/Remote	24	250 (12-860)	360 (63-1400)	58 (18-230)	51 (11-270)	47 (9-170)	25 (9-130)	N/A
Harrad and Hunter (2006)[a] UK	2003-4	Urban/Suburban	66	270 (60-909)	520 (100-1700)	120 (25-390)	130 (25-410)	110 (<0.5-410)	N/A	N/A
Harrad and Hunter (2006)[a] UK	2003-4	Rural	55	60 (35-70)	110 (88-130)	20 (17-25)	22 (13-30)	15.1 (<0.5-38)	N/A	N/A
Wang et al. (2005)[a] China	2003	E-Waste	2	130	310	45	130	40	420	N/A
Leung et al. (2007) China	2005	E-waste	4	38000	75000	11000	25000	11000	45000	420000
Yun et al. (2008) USA[a]	2002-4	Floodplain Soils	26	590 (<10-270)	530 (<10-270)	120 (<10-60)	50 (<10-20)	150 (<0.5-520)	N/A	4700 (<10-48000)

[a] mean (median not given); [b] n = 12; [c] n = 3; [d] <10 = below detection limit of 10 pg/g

Table 1.6 – Median (range) PBDE concentrations (pg/g) of soils from previous studies

Sellstrom et al. (2005)[a] Sweden	2000	Sludge Treated Soils	5	120	170	33	28	16	<10	530[b]
Sellstrom et al. (2005)[a] Sweden	2000	Untreated Agricultural Soil	5	35	44	12	3.5	4.9	<6	480b
Odabasi et al. (2010)[a] Turkey	2008	Industrial/Steel	17	220	400	70	150	110	N/A	36000
Odabasi et al. (2010)[a] Turkey	2008	Suburban	3	90	120	30	50	60	N/A	9500
Xiao et al. (2007) China	2007	Landfill Site	1	170000	19000	100000	N/A	N/A	N/A	N/A
Ma et al. (2009)[a] China	2006-7	e-waste	10	27000 (610-165000)	46000 (660-23000)	5100 (90-25000)	8700 (<0.5-25,000)	3300 (<0.5-11000)	N/A	1800000 (72000-5700000)
Ma et al. (2009)[a] China	2006-7	Urban/rural	5	30	34 (<0.1-90)	0 (<0.1-10)	<0.5	<0.5	N/A	380 (<5-790)
Ma et al. (2009)[a] China	2006-7	Chemical Complex	12	70 (<0.1-20)	90 (<0.1-240)	10 (<dl-50)	50 (<0.5-580)	<0.5	N/A	40,000 (1900-270000)
Parolini et al. (2013) Tanzania	2011	Background	20	200 (27-510)	42 (13-170)	24 (7-110)	3.9 (1.1-32)	3.3 (0.8-38)	7.5 (1.2-65)	N/A
Labunska et al. (2013) China	2005	E-waste	6	89000 (8000-350000)	155000 (4000-360000)	14000 (14000-360000)	54000 (6500-1400000)	18000 (200-380000)	47000 (3400-2800000)	6900000 (530000-150000000)

[a] mean (median not given); [b] n = 12; [c] n = 3; [d] <10 = below detection limit of 10 pg/g

Table 1.6 – Median (range) PBDE concentrations (pg/g) of soils from previous studies

1.5.3 Sediments & Sludge

Sediments are both an important sink and source of PBDEs within the aquatic environment as their hydrophobic physicochemical properties cause PBDEs released into aquatic/marine environments to partition into sediments. Once in the sediment they can bioaccumulate in fatty tissues of benthic filter-feeders, such as bivalves, and magnify up the food chain (Moon et al., 2007). It is therefore important to monitor PBDEs in sediments as a non-invasive indicator of their fate in other biota. PBDEs have been found in sediments for some time, with Nylund et al. (1992) finding concentrations in sediment cores dated from 1946-1987 in concentrations of 0.03-2.9 ng/g of ignitable content (IG) for just 3 PBDE congeners (BDEs-47, BDE-99 and an unknown penta-BDE). Since then, more studies have taken place investigating PBDEs in sediments, whilst also investigating their concentrations in biota from the same sites. Eljarrat et al. (2004) found sediment $\sum_{40}$PBDE concentrations from 4 sites in Spain to be 2.4, 2.6, 41.7 and 39.8 ng/g dry weight respectively. Both in fish muscle and liver tissue, they found the mean PBDE concentrations to be highest in the sites 3 and 4 (muscle: 280 and 96 ng/g wet weight; liver: 260 and 75 ng/g wet weight respectively) whilst sites 1 and 2 were comparatively low (muscle: 1.3 and 4.5 ng/g wet weight; liver: 0.2 and 0.4 ng/g wet weight respectively). Sellström et al. (1998) found the same general trend in Sweden, with sediment concentrations of <3-28 ng/g IG with a general increase in PBDE concentration in fish tissue with sediment concentrations (43-1500 ng/g lipid weight). The UK has seen some of the highest sediment concentrations with an average of 287 ng/g (range: 1-2,337 ng/g) found in the Clyde Estuary (Vane et al., 2010). Allchin et al. (1999) measured sediment samples in the north of England between 1995-1996, along with fish and shellfish samples. Sampling locations were close to known point sources of PBDEs. They found mean $\sum_{\text{tetra-penta}}$PBDE concentrations in sediments of 120 ng/g dry weight, whilst muscle tissues of fish and shellfish were all found to contain up to 27 ng/g wet weight further emphasizing sediment as an indicator of the presence of PBDEs within aquatic ecosystems. This is not limited to Europe and PBDEs have been detected in sediments and consequently biota worldwide. Liu et al. (2005) measured PBDEs in sediment (2.4-53.6 ng/g dry weight) and mussels (33.8-83.7 ng/g dry weight) from Hong Kong and whilst the same trend was not found, the PBDE congener profiles were found to be similar in sediments and mussels at sites where both were taken. Median sediment concentrations from 16 samples across China were found to be 2.45 ng/g dry weight, although one site contained 2800 ng PBDE /g dry weight (Wang et al., 2009), whilst Wang et al. (2005) found 27 ng PBDE /g dry weight in sediment close to an e-waste recycling facility in Guangdong, China. BDE-209 was detected in sediments in concentrations from <25-11600 ng/g dry weight between 1988-89, stated to be the highest concentration known at that time (Environmental Agency Japan, 1991). Several other studies from other countries have also measured PBDEs in sediments such as from North America close to a PUF manufacturing plant (up to 132 ng/g dry weight (Hale et al., 2002)); and Australia (median 1.1 ng/g dry weight (Toms et al., 2008)), where sediment concentrations were used to highlight how urban and industrial areas are more vulnerable to PBDE contamination with concentrations of 2.2-61000 ng/g dry weight in Port Phillip (industrial/urban) as well as the potential of sewage sludge as a source (sediment upstream of a sewage treatment plant was 0.36 ng/g dry weight compared with downstream, where it was 7.7 ng/g dry weight).

The effect of sewage sludge has also been highlighted by others. For example, Table 1.5 demonstrates that sludge treated soils can contain PBDE concentrations that are more than 10 times higher than those from untreated soils from a similar area – in Spain ∑PBDEs were 260 ng/g dry weight in treated soils compared with 20 ng/g dry weight in untreated, whilst mean sludge samples measured 580 ng/g dry weight for PBDEs (Eljarrat et al., 2008). As with other media, PBDEs have been consistently found in sludge from many countries, such as the USA (up to 1400 ng/g (North, 2004)) and Kuwait (up to 1600 ng/g (Gevao et al., 2008)). These studies highlight not only the effect of sewage sludge on agriculture, but also that sewage treatment plants are likely to be a source of PBDEs to aquatic environments, through the discharge of sewage effluent into rivers, where PBDEs will preferentially accumulate in substances high in organic carbon (sediment) or fat (biota).

1.5.4 Long-term Temporal Trends in PBDE levels

Between 1970 and 2000, PBDE concentrations increased significantly in human tissue, serum and breast milk with Noren and Meironyte (2000) finding concentrations in Swedish breast milk samples to be their lowest (0.07 ng/g lipid) in 1972 and at their highest in the last sample taken in 1997 (4.01 ng/g lipid). This study was enhanced by the meta-analysis of Hites (2004) who compiled data from studies between 1970-2002 and stated that over 30 years there was an exponential increase in human PBDE concentrations with a doubling time of 5 years. More recent studies have suggested a decline in human PBDE exposure with Fangstrom et al. (2008) finding that, whilst there has been an overall increase in human PBDE concentrations since 1980, these concentrations peaked between 1995-2001 and there has been a gradual decline since. This theory is supported by Ma et al. (2012) who found median concentrations of 0.54 ng/g lipid in 130 Chinese placenta samples taken between

2005-2007. There has also been a decline in PBDE contamination of human breast milk samples in the Philippines between 2004 and 2008 with median concentrations of 7.2 ng/g lipid (Malarvannan et al., 2009) and 1.8 ng/g lipid respectively (Malarvannan et al., 2013).

Several studies have looked at long-term time-trends for tri-hepta PBDEs in various environmental media, in the last 5-10 years, which have seen similar patterns that coincide with historical increased/decreased PDBE usage and legislation. Hassanin et al. (2005) looked at semi-rural grassland samples from the UK (40 km north of London) and found that until the mid-1970s, concentrations were negligible but increased from around 500 pg/g dry weight to 2500 pg/g dry weight during the 1980s and 90s, before decreasing again to around 500 pg/g dry weight between 2001-2004. However, again, BDE-209 was not measured in this study. Similar trends were found in Canadian suspended sediment samples in which there was a slow increase from low ppb concentrations in 1980-1988 before a rapid increase post-1988 where concentrations reached as high as 35 ng/g dry weight (BDE-209 the dominant congener), before a small decrease between 2001-2 (15-24 ng/g dry weight) (Marvin et al., 2007); whilst Hale et al. (2012) found an almost identical pattern for tri-decaBDE congeners in Chicago sewage sludges and biosolids. Finally Kohler et al. (2008) saw similar patterns, again in sediment cores taken from a lake close to Zurich, Switzerland, which found that BDE-209 increased steadily from 1.1 ng/g dry weight in the 1970s to 7.2 ng/g dry weight in 1999-2001, with Penta- congeners following the same trend at lower concentrations.

In areas where PBDE time-trends have been studied, the patterns of PBDE concentration has reflected the local patterns of usage and legislation as outlined in Section 1.3. However, for BDE-209 there is still a lack of data in more than one location with no temporal trends recorded for BDE-209 in the UK, and no temporal trends recorded for any PBDEs in Australia, showing that understanding of the environmental fate and behaviour of PBDEs remains incomplete.

1.5.4.1 Investigating historical trends in PBDEs using sediment cores

As mentioned in 1.5.3, monitoring the concentrations of PBDEs in sediments can be a useful indicator for their levels in biota and the food chain, and possibly human exposure. Therefore, measuring the concentrations in dated layers from sediment cores can show important historical trends in PBDE levels. Over the last 10-15 years, there have been many studies looking at temporal trends of PBDEs using sediment cores. These can be important in areas of known sources of PBDEs to see how these sources affect nearby aquatic and marine ecosystems over time, but also in areas away from these sources in order to investigate long-distance transport of PBDEs since their introduction in the 1970s. These papers have shown that, due to the high rates of sediment formation in rivers, estuaries, lakes and harbours, their concentrations in sediments can be reflective of their usage at a particular time.

In Switzerland, sediment cores taken from Lake Thun close to wastewater treatment plants showed a linear increase in PBDE concentrations from minimal levels in 1980 to approximately 100 ng/g organic carbon (OC) in 2005 (Bogdal et al., 2008), whilst Lake Greifen close to the city of urban Zurich showed a similar trend with levels of 1.1 ng/g dry weight in 1975 to 7.2 ng/g dry weight in 2000 for BDE-209, and 0.36 and 1.6 ng/g dry weight for tri-hepta BDEs in the same years respectively (Kohler et al., 2008).

The Clyde Estuary, UK has also been investigated, again with BDE-209 being the dominant congener (Vane et al., 2010, Webster et al., 2008). However, these two studies that took cores within the same year found differing results in terms of sediment concentrations. Both sets of cores were taken from the Clyde Estuary, in 2003, with the highest concentrations being found in the top layer of sediment. Vane et al. (2010) found concentrations of of 1-2645 ng/g dry weight for ∑PBDEs, whilst Webster et al. (2008) detected concentrations for BDE-209 at a range of 33000-98000 ng/g dry weight, whilst both found a linear increase in both tri-hepta PBDEs and BDE-209 from the deepest layers to the surface, which is to be expected given the peak usage of PBDEs towards the end of the 1990s/early 2000s. These two differing figures in the top layers of sediments from the two studies in similar locations highlight the spatial variation of PBDE concentrations even within short distances. Other European studies have also followed this trend of a linear increase in PBDEs from 1973 onwards, with BDE-209 first appearing in samples from Norway, Holland and Germany in 1975 and becoming the dominant congener in 1978 (Zegers et al., 2003) and peak PBDE concentrations being detected in the top 3 cm in cores from the Scheldt River, Antwerp, Belgium (7,600 and 5,800 ng/g dry weight) (Covaci et al., 2005).

These trends are not limited to the UK and Europe, and Asia has seen some of the highest sediment concentrations in the world with ∑PBDE concentrations increasing exponentially from 2200 ng/g dry weight in 1953-55 to almost 80000 ng/g dry weight in 1992-1999 in Tokyo Bay, with BDE-209 again dominant (Choi et al., 2003a). Again spatial variation is seen within Tokyo Bay as Minh et al. (2007) found similar temporal trends as above, with BDE-209 making up around 50% of the total PBDE content, but ∑PBDE concentrations peaked at 40-200 ng/g dry weight in 1998. Elsewhere in Asia sediment cores have been taken from areas of the Pearl River Delta, China on multiple occasions (Mai et al., 2005, Zhang et al., 2009b, Chen et al., 2007). Chen et al. (2007) found that whilst the mean ∑PBDE concentration increased from 3.9 to 13 and then to 21 ng/g dry weight for core slices dating from the pre-1990s, 1990s and 2000s respectively; the tri-hepta PBDE concentrations decreased and levelled from 2.51 to 1.31 and 1.48 ng/g dry weight, whilst the BDE-209 contribution rose from 36% pre-1990s to 90% and 90% in the 1990s and 2000s respectively. Although their cores were not dated, Mai et al. (2005) found that tri-hepta PBDEs were present at 2-6 ng/g dry weight in the deeper layers, but typically <1 ng/g in the top 20 cm, whilst BDE-209 concentrations were 1-2 ng/g dry weight in the deeper layers of the core, and 2.5-34 ng/g dry weight in the top 14 cm. Zhang et al. (2009b) took two sediment cores 2-3 years later than the previous two studies in 2006. They found that BDE-209 levels were much higher in the bottom layers of the cores with peak concentrations of approximately 500 and 900 ng/g dry weight, before levels tailed off to around 200 and 600 ng/g dry weight towards the top layers. The tri-hepta PBDE concentrations are similar to those previously reported, suggesting that the previous studies possibly underestimated BDE-209 concentrations in sediment cores. Sediment cores have also been taken from South China (Jin et al., 2008), India (Binelli et al., 2007) and Masan Bay, Korea in 2005, where tidal currents in the inner section of the bay are weak meaning a long residence time for pollutants (Hong et al., 2010). Increases in PBDEs in the lower layers of sediment cores are attributed to their use shortly after the PCB ban in the 1980 where they increase from <1 ng/g dry weight to 15 ng/g dry weight in 1990. In 2003 the levels increased dramatically to 72 ng/g shortly after a typhoon, “Maemi” is thought to have brought a large amount of industrial and urban waste into the bay (Hong et al., 2010). Johannessen et al. (2008) also found that PBDEs in sediment cores were reflective of their usage trends in the Strait of Georgia, an inland sea subject to discharge of industrial and urban waste such as municipal wastewater. They found that PBDEs were first elevated in sediments corresponding to 1978, close to when PBDEs were first introduced as PCBs were banned, whilst there was a linear increase to 0.27-13 ng/g in surface sediments representative of 2002-3.

North America has been studied fairly extensively, in terms of vertical distribution of PBDEs in sediments, with the Great Lakes being paid particular attention (Song et al., 2004, Song et al., 2005a, Song et al., 2005b, Zhu and Hites, 2005, Qiu et al., 2007). Concentrations of both tri-hepta PBDEs and BDE-209 were found to increase from low levels in sediment from the

10 cm layer to 0.5-3 and 6-18 ng/g dry weight respectively in the top 2 cm in Lake Superior, where samples were taken away from known point sources of PBDEs (Song et al., 2004), whilst Lakes Ontario and Erie showed a similar but more erratic pattern with an overall rise of minimal tri-hepta PBDEs at 16-18 cm depth to 2-7 ng/g dry weight at the surface; whilst BDE-209 rose from non-detectable at 6-8 cm to 50-250 ng/g dry weight in surface sediments. The irregular changes in concentrations with core depth is attributed to the lower water retention of the lakes, combined with an increased flow through them (Song et al., 2005a). Zhu and Hites (2005) calculated doubling times for PBDEs in Lakes Michigan and Erie. Tri-hepta PBDEs doubled every 11 and 6.4 years, whilst BDE-209 doubled every 7.5 and 5.3 years in sediments in Lakes Michigan and Erie respectively, which is similar to the doubling time for tri-hepta PBDEs found in the Rocky Mountains of 5.4 years (Usenko et al., 2007) – showing the more recent dominance of the DecaBDE technical mix compared to Penta- and Octa- is also true of North America.

Whilst PBDE levels in the Arctic are much lower than in populated and industrial cities and countries, they are still found in sediment cores (Stern et al., 2005), indicating that long distance transport of PBDEs continues. Even BDE-209, which is thought to be less capable of long-distance transport has been found in the top layers of Arctic lakes, such as AX-AJ Lake (0.075 ng/g dry weight) and Char Lake (0.042 ng/g dry weight), whilst the overall fluxes in PBDEs have shown an increased input into these lakes over time (De Wit and Muir, 2004), whilst sediment cores taken in 2001 from Ellasjøen in the Norwegian Arctic contained 0.73 ng/g dry weight in surface layers with concentrations estimated to have increased 10-fold over 50 years (Evenset et al., 2007).

This section shows that in all areas of the world that PBDEs have been measured in sediment cores from different water-based environments, they have shown a historical trend of increased input from the late 1970s/early 1980s, with a peak in the mid-late 1990s/early 2000s. Whilst sediment cores have been investigated for PBDEs in many countries across multiple continents, they have not been examined in Australia and many other Southern Hemisphere countries, showing a lack of understanding of temporal trends of PBDEs in those countries. Furthermore, it is evident from the above studies that long-distance transport of PBDEs has been taking place since their introduction, based on the detection of PBDEs in Arctic areas, where sources of PBDEs are scarce/non-existent.

1.5.5 The Role of Cities as Sources of PBDEs

It has previously been suggested, that with the vast amount of urbanization, cities themselves can be considered sources of PBDEs due to the huge number of flame retarded items, such as office carpets, furniture and computers as well as the actual building materials themselves (Butt et al., 2003). In spite of this theory, there are still only a handful of studies that have examined this possibility. Butt et al. (2003) measured the PBDE concentrations in organic films from window surfaces in Ontario, Canada and found that ∑PBDE concentrations in urban sites (9 ng/m^2 mean concentration (n=6)) were 10-fold those in suburban (1.1 ng/m^2) and rural sites (0.56 ng/m^2). Off the back of this study Gouin et al. (2005) discovered that PBDE concentrations in ambient air in Ontario were of a similar pattern at five times those of rural locations. Harrad et al. (2006) also found evidence of an "urban pulse" for PBDEs in the West Midlands, UK in both air and soil with the highest concentrations being in the three sampling sites closest to the centre of Birmingham. However, to the author's knowledge, the only urban pulse study to have measured BDE-209 is that of Gevao et al. (2011) who examined an urban-rural transect across Kuwait for PBDEs in soils. They found a total range of ∑PBDE concentrations of 290-8,000 pg/g dry weight with concentrations in Kuwait City significantly higher than those in sites outside the city. In every sample, BDE-209 was the dominant congener making up 84-99% of ∑PBDEs (BDEs -28; -47; -100; -99; -154; -153; 183; -209).

PBDD/Fs

Studies on environmental levels of PBDD/Fs are extremely limited, with only a very small number published on their background concentrations. Wang et al. (2008) measured air concentrations of PBDD/Fs in rural, urban and industrial areas as well as a science park. The rural areas were at the lowest at 11 fg m^{-3} whilst the highest was the Science Park at 95 fg m^{-3}. However, Li et al. (2008) found mean ambient concentrations for 2,3,7,8-PBDD/Fs to be as high as 8,031 fg m^{-3} in Shanghai, China. Ma et al. (2009) detected average PBDD/F concentrations of 799 (range: 46-3700) pg TEQ /g in soil from an e-waste site (n=10), but they did not detect PBDD/Fs in soils from urban, rural and agricultural reference sites (n=11), highlighting e-waste sites as important point sources of PBDD/Fs. There are no other studies which appear to have monitored background concentrations. This is probably due to expense and limitations with regards to their measurement. Table 1.7 shows a selection of concentrations from various compartments taken from available literature.

Study (Location)	**Year**	**n**	**Sample Description**	**PBDD/F Concentration**	**Units**
Takigami et al. (2008) (Japan)	2005	5	Dust from inside Japanese TVs	0.9	ng WHO-TEQ/g
Suzuki et al. (2007) (Japan)	2005	19	Household dust	0.19	ng CALUX-TEQ/g
Suzuki et al. (2007) (Japan)	2005	14	Office dust	0.37	ng CALUX-TEQ/g
Takigami et al. (2009) (Japan)	2006	8	Hotel dust	0.034	ng WHO-TEQ/g
Tue et al. (2013) (Vietnam)	2008	20	Household dust close to e-waste site	0.13	ng WHO-TEQ/g
Tue et al. (2013) (Vietnam)	2008	11	Urban household dust	0.011	ng WHO-TEQ/g
Ma et al. (2009) (China)	2007	5	Dust from e-waste Site	1.5	ng WHO-TEQ/g
Litten et al. (2003) USA	2001	2	Urban run-off in New York City following 9/11 disaster	0.54	ng WHO-TEQ/L
Terauchi et al. (2009) (Hong Kong)	2004	6	Marine sediments from urban locations	0.0039	ng WHO-TEQ/g
Terauchi et al. (2009) (Korea)	2005	8	Marine sediments from industrial locations	0.0039	ng WHO-TEQ/g
Wang et al. (2008) (Taiwan)	2005	5	Rural outdoor air	2.7	fg WHO-TEQ/m^3
Wang et al. (2008) (Taiwan)	2005	7	Urban outdoor air	6.4	fg WHO-TEQ/m^3
Wang et al. (2008) (Taiwan)	2005	5	Industrial outdoor air	12	fg WHO-TEQ/m^3
Wang et al. (2008) (Taiwan)	2005	2	Outdoor air from vicinity of science park	31	fg WHO-TEQ/m^3
Li et al. (2008) (China)	N/A	25	Outdoor air from various locations across city of Shanghai	214	fg WHO-TEQ/m^3
Ma et al. (2009) (China)	2007	10	soils from e-waste Site	0.8	ng WHO-TEQ/g
Ma et al. (2009) (China)	2007	12	soils from chemical complex	0.00048	ng WHO-TEQ/g
Ma et al. (2009) (China)	2007	4	Soils from close to copper mine	0.018	ng WHO-TEQ/g

Table 1.7 Environmental Levels of PBDD/Fs in various media from available literature

Li et al. (2007) highlighted the role of the treatment of waste electrical and electronic materials as a source PBDD/F emissions by collecting air samples in an electrical waste dismantling site in Guiyu, China as well as at sites 9 km away (Chendian) and 450 km away (Guangzhou). The highest PBDD/F concentrations were in Guiyu with 2,3,7,8-PBDD/F concentrations of 8.1-461 pg m^{-3}. This was 12-18 times higher than concentrations from Chendian and 37-133 times higher than those from Guangzhou and it was concluded that Guiyu has the highest PBDD/F concentrations reported globally to date (Li et al., 2007). It was also found, in the same study, that there were seasonal variations in PBDD/F air concentrations that may be due to their susceptibility to photolysis. So in an area of high emission such as Guiyu, concentrations in the winter are significantly higher than in summer (Li et al., 2007).

1.6 The Integrated Steel Industry as a source of PBDEs and PBDD/Fs

1.6.1. Processes in the Integrated Steel Industry

The steel industry consists of several processes, which involve extremely high temperatures. There are currently four routes used globally for steel production. These are the integrated route (blast furnace/basic oxygen), direct melting and extraction of liquid iron and scrap in electric arc furnaces (EAFs), smelting reduction, and direct reduction (European Commission, 2010). These processes all involve huge amounts of energy, and materials can reach temperatures close to 1500 ºC for extended periods of time (Ooi et al., 2008).

The most complex route is the integrated steelmaking route. It occurs in large industrial complexes covering areas of several square kilometres. Integrated steelworks are made up of large networks of interdependent production units, with huge flows of energy both within and between them. These production units are sinter plants, pelletisation plants, coke oven plants, blast furnaces and basic oxygen steelmaking plants (European Commission, 2010). The routes of these processes are shown in Figure 1.8. In all of these process, many different materials are used (350 Mt of input materials will produce 200 Mt of crude steel, along with 150 Mt of waste outputs, such as off-gases and solid residues), whilst extremely high inputs and outputs of energy are involved.

A vital part of the integrated steel making process is iron-ore sintering. Coke is produced via the dry distillation of coal in the coke ovens. Next, three components: coke, iron ore and fluxes (limestone), plus recycled iron-containing materials from the blast furnace are ground, mixed and pelletised via means of a large rotating "balling drum" along with the addition of water, drying and re-watering to obtain "pellets" of iron ore, approximately 9-16 mm in size. Following this, a 400-600 mm layer of pellets is loaded onto a large cast iron grate, on top of

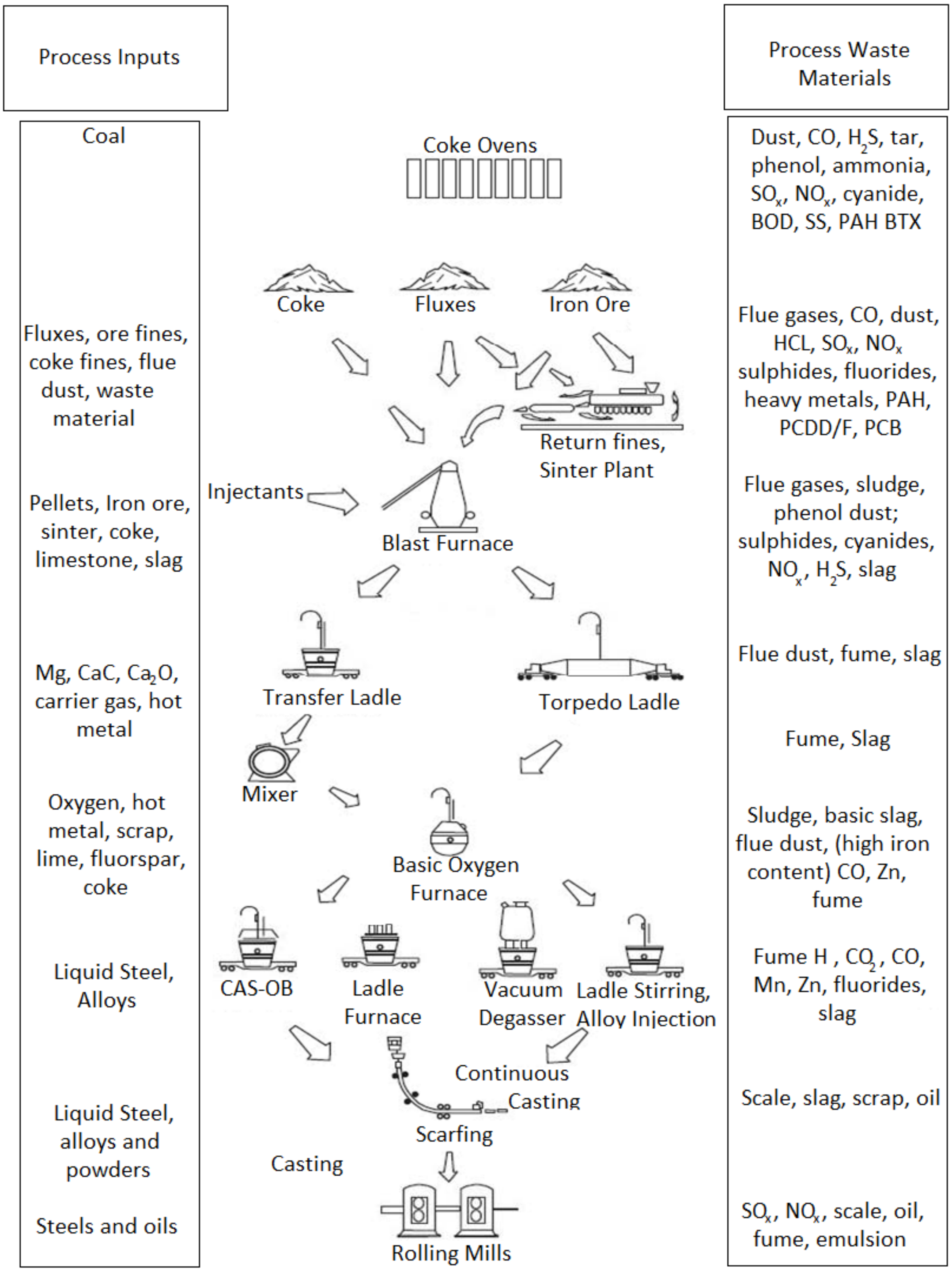


Figure 1.8 An overview of the process routes of an integrated steelworks. Reproduced from European Commission (2010)

a 30-50 mm deep layer of recycled sinter to prevent pellets falling through the grate, before coke breeze is added for ignition. Once ignited temperatures of 1300-1480 °C are attained during combustion which causes reduction of the iron ores to form metallic iron particles. The sinter is then cooled by forcing air through the sinter layer, producing up to 1500 m^3 of waste gas per tonne of sinter at a temperature of up to 300 °C. Finally, the cooled sinter is transferred to screens to separate the pieces used in the blast furnace (approximately 4-50 mm in size) (European Commission, 2010).

The sintering process is alreadya known source of POPs such as PCDD/Fs and PCBs (Aries et al., 2008). Considering the fact that both PBDEs and PCBs have found use as flame retardants (potentially in the conveyor belts used in the steelmaking process) and chemically behave in a very similar way, it is plausible that they would be present in the steel industry too, and at the temperatures experienced, could represent precursors of PBDD/Fs. There are many other processes within the steel industry that have already been documented as potential sources of PBDEs and PBDD/Fs (such as EAFs) however the sintering process remains relatively unstudied. Hence this section focuses on iron ore sintering as a potential source of PBDEs and PBDD/Fs.

1.6.2. PBDEs in the steel industry

Although to date, literature is still limited as to whether the steel industry is a source of PBDEs to the environment, there is strong, growing evidence to suggest that this is the case. Choi et al. (2008) investigated atmospheric concentrations of PBDEs and found a gradient with its peak in and around a steel complex and decreasing with distance away from the complex. Concentrations of PBDEs within the complex were at least double those anywhere else in the study. Further exploration showed that EAFs may well be a source of PBDEs as scrap metal from manufacturing equipment such as automobiles containing technical PBDE mixtures is sometimes utilised. However the authors noted that the sites within the steel complex with the highest PBDE concentration were those downwind from thermal processes i.e. – sintering, coke production and the blast furnace (Choi et al., 2008). Odabasi et al. (2009) support this hypothesis by stating that 32% of the world’s steel requirement is produced from ferrous scrap metals in EAFs. They state EAFs are a source of various particle-bound pollutants and that the quantity and composition of emissions is dependent on the composition of the scrap used as feedstock and the type of furnace activity. Ferrous scrap contains impurities such as plastic and polyurethane foam that will contain significant concentrations of PBDE which will then be released into the atmosphere when heated in the furnace, and can also undergo thermolysis and form PBDD/Fs in *de novo* reactions (Odabasi et al., 2009).

Cetin and Odabasi (2007) measured PBDE concentrations in both ambient air and soil of PBDEs in various areas around Izmir, Turkey. The air samples were taken from 3 sites, which the authors labelled suburban, urban and industrial. The soil samples were taken from 13 different sites falling under the same categories and a bag filter dust sample from an EAF was taken from a steel works. Ambient air concentrations of PBDEs ranged from 6.2 pg m^{-3} (suburban) to 148.8 pg m^{-3} (industrial) with a clear dominance of BDE-209. With respect to soil the 3 most contaminated sites were from the electronic industry site, Bozkoy industrial site and the steel plant, which had concentrations of 2.84×10^6, 9.83×10^4 and 4.41×10^4 ng PBDE kg^{-1} dry weight respectively. The bag filter dust was also found to contain 2.05×10^5 ng PBDE kg^{-1} dry weight (Cetin and Odabasi, 2007).

Odabasi et al. (2009) investigated this further by measuring stack gas emissions for various POPs including PBDEs from steel plants with EAFs in Aliaga, Izmir, Turkey. They measured stack gas concentrations from 4 plants without scrap pre-heating and of 1 with scrap pre-heating as well as ambient air samples from the surrounding area of Aliaga. Mean PBDE concentrations of the plants without pre-heating were found to be 33 ng/m^3 whilst the one with pre-heating was almost three times higher at 91 ng/m^3. The ambient PBDE concentrations in Aliaga were considered significantly elevated 1.45 ng/m^3. The authors concluded that steel plants with EAFs are “hot spots” for PBDEs as well as other POPs and even more so if the scrap metal receives pre-heating too (Odabasi et al., 2009).

Wang et al. (2010b) investigated emissions of PBDEs and PBDD/Fs in metallurgical facilities and found that raw scrap materials in an aluminium recycling plant had PBDE concentrations of 245-67450 ng/g. They also found that BDE-209 was the most abundant congener across the metallurgical facilities and was dominant in air and soil samples, whilst Fang et al. (2012) also found BDE-209 to comprise up to 91% of PBDEs in dry deposition samples within the vicinity of a Korean steel complex (up to 110 ng PBDE m^{-2} day^{-1} compared with upwind rural areas 7.9 ng PBDE m^{-2} day^{-1}).

1.6.3. PBDD/F emissions from the steel industry

A large number of studies have taken place examining PCDD/Fs within the steel industry with Rappe (1992) ranking iron and steel production as the most significant source of PCDD/Fs in Sweden. Before the introduction of ESPs, waste gas concentrations in German sinter plants were as high as 68 ng I-TEQ/m^3 (see Section 1.4.1 for definition of I-TEQ), but it was suggested that ESPs could reduce this to 5-10 ng I-TEQ/m^3 (Lahl, 1994). More recently, Buekens et al. (2001) stated that huge flows of flue-gases are generated in iron ore sintering which can contain up to 30 ng/I-TEQ generated via de novo formation. They stated that although measured PCDD/F formation rates are relatively low, the vast throughput of flue gas (500000 m^3/h) means a large amount of PCDD/Fs may be emitted from the sintering process. However, around a similar time, Anderson and Fisher (2002) stated that mean waste stack gas emissions from UK-based sintering plants are much lower at 1.2 ng I-TEQ/m^3 (n=94) resulting in the annual release to the UK atmosphere of 38 g I-TEQ per annum, which they equate to a similar mass released by bonfire night alone based on a study by Dyke et al. (1997). However, they also state that the iron-ore sintering process is the "only noteworthy source of PCDD/Fs in the UK". Working on the theory that PBDD/Fs are formed and released into the environment via similar mechanisms to PCDD/Fs then it could be suggested that they too could be emitted significantly from the steel industry through *de novo* reactions at high temperatures (such as in EAFs) (Choi et al., 2008). Considering the evidence mentioned in 1.6.2 that precursors such as PBDEs have been detected in significantly high levels within a steel-works, and the high temperatures involved in various processes (such as sintering and EAF) there is strong evidence to suggest that PBDD/Fs could be formed within the steel-manufacturing process. Wang et al. (2010b) provided further evidence to consolidate this theory when they found PBDD/F concentrations to be 4 times higher around a steel complex, when compared to rural areas nearby. Despite these early indicators that the steel industry could be a source of PBDD/Fs to the environment, this hypothesis has yet to be explored fully. It is important that the formation of PBDD/Fs within the steel-manufacturing process is investigated further, due to the above concerns regarding toxicity, combined with the logic that they should behave in a similar way to their chlorinated analogues and therefore the steel-making process could also provide conditions for their formation.

1.7 PBDE Congener Profiles

As previously stated, the different commercial formulations produced for PBDEs contain very different proportions of each congener. As a result, the way they behave and affect the environment is highly variable. For example, the lower vapour pressures of the higher brominated compounds such as BDE-209 mean that they preferentially partition to the particle phase. This combined with a higher K_{OC} means that they are more persistent in particle phase compartments such as soils, sediments and dusts, with respect to the lower brominated congeners (Wania and Dugani, 2003).

Harrad et al. (2008b) demonstrated via a principal component analysis (PCA) how different commercial formulations can affect the congener profiles of PBDEs using dust from North America (Canada and USA) and the UK (Figure 1.9). Two principal components (PC) were used. A negative score for PC1 in the majority of UK samples demonstrated a strong influence

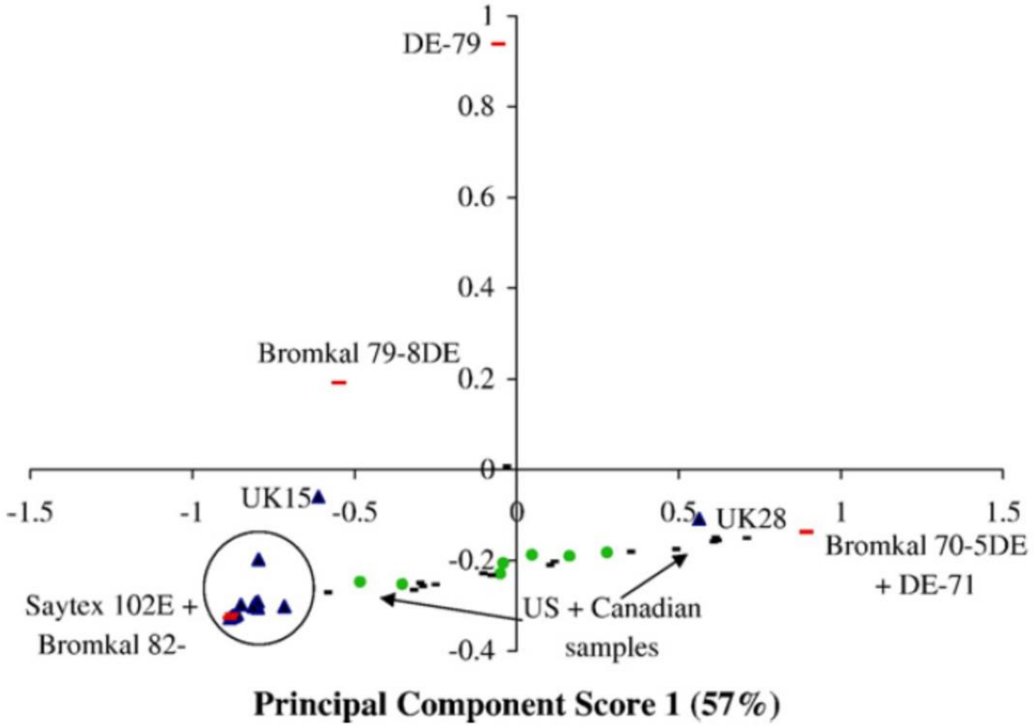


Figure 1.9 PCA results for UK, US & Canadian dust samples along with the different commercial formulations – taken from Harrad et al. (2008b)

of Deca-BDE based congeners, whilst a negative score in PC2 demonstrated little influence of Octa-BDE based congeners. North American samples also all had negative scores for PC2, whilst samples were distributed from partially negative to partially positive scores for PC1, implying an influence of both DecaBDE and PentaBDE formulations (Harrad et al., 2008b).

Whilst the congener profiles of environmental samples are primarily influenced by the specific commercial formulations used to treat their original source of release into the environment, there are various factors that can lead to distinguishable changes in congener profile once released. For example, Hassanin et al. (2003) found that in soils from the UK and Norway measured for BDEs$_{17:190}$ the congener profile was very similar to that of the PentaBDE formulation. They claimed this to be evidence that PentaBDE based congeners undergo efficient "source-air-soil transfer" with little weathering or degradation during either atmospheric transport, or movement through soil. However, higher brominated congeners have been found to undergo degradation in the presence of UV light to form PentaBDE based congeners BDEs -47, -99 , -100, -153 and -154 as well as other higher brominated congeners typical of OctaBDE and PBDFs (Söderström et al., 2003).

Furthermore, Gouin et al. (2005) found that atmospheric concentrations of lower brominated congeners (particularly BDE-47) are likely to be higher in spring and summer than winter and autumn, due to increased temperatures. This was also demonstrated by Shi et al. (2013) in Beijing, China. The authors showed that the contribution to total PBDEs of BDEs -28 and -47 was higher during the spring and summer than in the autumn and winter. Conversely, BDE-209 was found to be far more variable with overall lower concentrations in the spring and summer and increases in the autumn and winter. This is consistent with the aforementioned potential of BDE-209 to undergo photolytic degradation.

It is clear from these studies that the PBDE congener profiles are likely to be extremely variable both spatially and temporally due to a number of factors. Firstly, there are discernible differences between different commercial formulations (Figure 1.10) – both between Penta-, Octa- and DecaBDE, as well as between variations of the specific product itself – DE-79 and Bromkal 79-8DE were found to have considerably different congener profiles despite both being labelled as OctaBDE (La Guardia et al., 2006). Secondly, there is evidence to suggest that different congeners will behave differently under various conditions such as weathering and degradation of higher brominated congeners, as well as clear differences in physicochemical properties leading to differing levels of persistence and partitioning into vapour or particle phase.

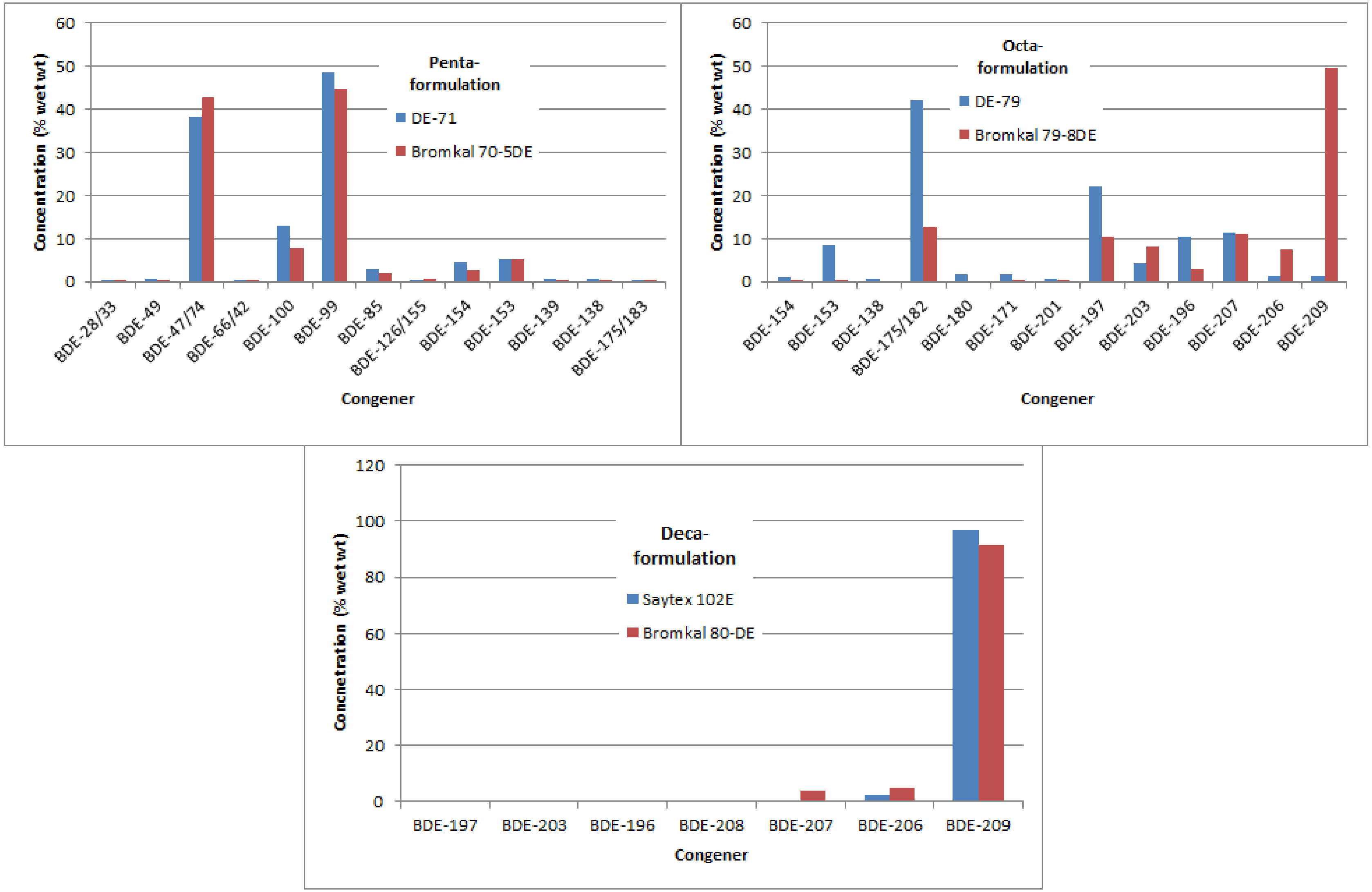


Figure 1.10 Congener profiles of commercial formulations for penta (DE-71 & Bromkal 70-5DE); octa (DE-79 & Bromkal 79-8DE); and deca (Saytex 102E & Bromkal 82-0DE) taken from La Guardia et al. (2006)

1.8 Aims and Objectives

It is clear from the above that there are several research gaps with respect to the environmental presence, fate and behaviour of PBDEs and PBDD/Fs both in the background environment and the steel industry. It is important to try to place into context the environmental impacts of PBDE emissions from the steel industry. Moreover, international variations in PBDE usage volumes and patterns render international comparisons of environmental contamination vital, with a distinct lack of data available for the Australian environment. Furthermore, continuing monitoring of UK levels are needed to evaluate the efficacy of recent actions to restrict PBDE manufacture and new use. Moreover, there are currently no published data for BDE-209 in UK soil or outdoor air – a significant omission given the widespread use of the DecaBDE commercial formulation of which BDE-209 is the principal constituent. In order to try and address these gaps, this project will:

1. Test the hypothesis that the steel industry (specifically the iron ore sintering process) in the UK is a source of PBDEs to the environment via measuring them in emissions such as stack gas and electrostatic precipitator (ESP) dust samples.
2. Attempt to identify the source of PBDEs within the iron ore sintering process to the environment by measuring them in raw input materials (such as iron ores and coke) as well as outputs. This will be conducted both on a production plant and controlled laboratory experiment scale.
3. Measure ambient air PBDE concentrations within the integrated steel-making process to make a preliminary occupational exposure assessment.
4. Test the hypothesis that the iron ore sintering process is a source of PBDD/Fs
5. Test the hypothesis that PBDEs act as precursors to PBDD/F formation within the iron ore sintering process.
6. Evaluate the impact of the steel industry on contamination of outdoor air with PBDEs. This will be achieved by comparing concentrations in samples from the vicinity of a steel-making plant, with those from the West Midlands of the UK.
7. To examine the role of cities as sources of PBDEs (particularly BDE-209). This will be achieved by comparing ambient air and soil concentrations along an urban-rural transect from 8 sites across the West Midlands, UK from Worcester to Tamworth, passing through Birmingham.
8. To evaluate whether any temporal trends in PBDE levels have occurred in response to recent legislation to reduce PBDE usage. This will be achieved by comparing the

concentrations of PBDEs in ambient air and soil samples obtained in 2012/13 at various UK locations those measured in similar locations taken between 2003-2005. Sediment cores taken in 1999 from Port Jackson, Sydney Harbour, Australia will also be measured for PBDEs to monitor temporal trends in Australia up until a time close to legislative action.

9. To evaluate the effects of land-use on environmental levels of PBDEs in Australia. This will be done by comparing concentrations of soil samples taken in 2003 across the entire country according to land-use (urban, agricultural, industrial, and remote).

Chapter II

Sampling and Analytical Methodology

This study required determination of PBDEs in several different classes of sample matrices: iron ores, fluxes (i.e. limestone), fuels, reverts (flue dust from blast furnace re-used in the sintering process), sinter products, sinter plant emissions, electrostatic precipitator (ESP) dusts, passive air samples and soils. The four main stages of measurement for all samples were: sampling, extraction, clean-up and analysis. For all classes, except for soil the same overall analytical methodology was used, whilst soils underwent simultaneous in-cell extraction and clean up. These methods were validated against stringent quality assurance/quality control measures that are outlined in this chapter.

2.1 Sampling.

2.1.1. Sinter Plant Raw Material Sampling

Sintering is an "agglomeration process" of iron ores to provide feedstock for the blast furnace in the manufacture of steel (Ooi et al., 2008). The full process is shown in Figure 2.1. Raw material samples were collected at various stages at the beginning and end of the sintering process.. Samples consisted of a combination of several sub-samples taken from different areas of their containers in attempt to create a representative sample accounting for any heterogeneous distribution of contaminents. Samples were thoroughly mixed in a rotating drum before being stored in amber jars below 5 °C. These samples consisted of iron ores (n = 29), reverts (n = 20), fluxes (n = 5), fuels (n = 4), raw sinter mix (RSM) – the final combination of iron ores, reverts, fluxes and fuels used for sintering (n = 6), sinter product (n = 6), and ESP dusts (n = 8).

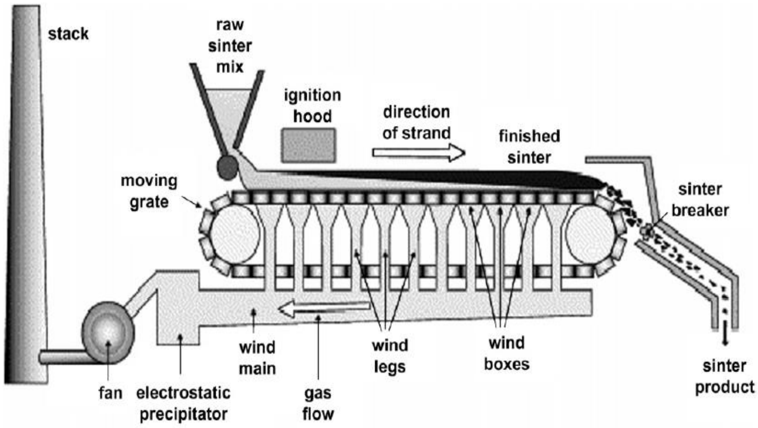


Figure 2.1 – Schematic diagram of a typical sinter plant (Ooi et al., 2008)

All raw materials - except for sinter product - were collected as coarse dusts and were transferred straight to amber jars ready for extraction and clean-up. Sinter product samples were taken from the centre of the sinter and crushed into dusts using a Tema T750 k laboratory disc mill, prior to collection in sealed amber glass jars.

2.1.2. Sinter Plant Stack Emission Sampling

Stack emission samples were taken by Tata Steel using the “filter/condenser method” (Figure 2.2) according to their own sampling protocol, which is in accordance with British and European standards (BS EN 1948). Samples (gas and particle phase) were taken isokinetically (i.e. at a flow rate where the velocity and direction of the gas entering the sampling nozzle matches those of the gas in the duct at the sampling point) using pre-extracted glass fibre filters, adsorbent traps containing pre-cleaned XAD-2 resin (Supelpak-2, Supelco, Sigma Aldrich, USA) and solvent washings of sample probes (toluene and acetone). The filter is placed downstream of the sampling nozzle (in the stack) and probe (outside the stack) and kept at below 125 °C (in order to avoid chemical reactions on activated surfaces). If there is a high dust load expected then a quartz wool filter (not analyzed) is incorporated into the “sampling train” before the sample collection filter to prevent overloading of dust. Particulate phase analytes are retained on the glass fibre sample collection filter. A condenser is attached to cool the sampled gas to below 20 °C, followed by the XAD-2 resin adsorbent traps which retain the gaseous phase analytes. The glass fibre sample collection filters and resin traps were all stored in pre-cleaned amber jars until extraction.

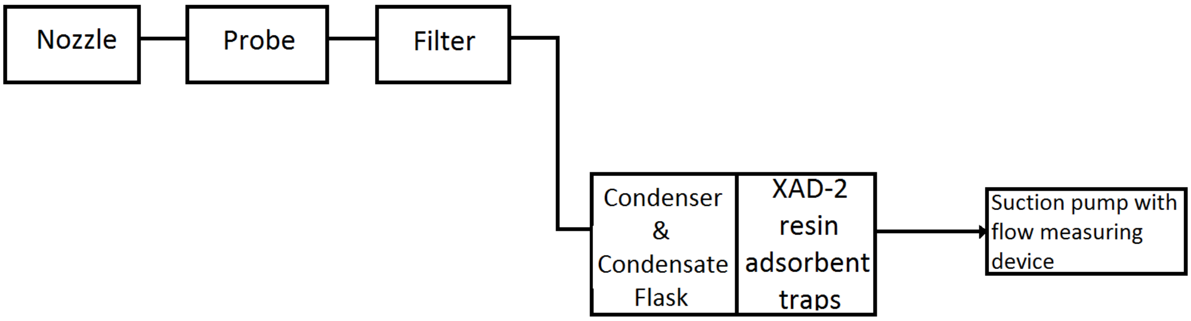


Figure 2.2 Schematic representation of the “filter/condenser” method used for stack emission sampling

2.1.3. Sinter Pot Samples

The Sinter Pot (SP) is an apparatus designed to mimic the sintering process on a laboratory scale. Approximately 1 kg of RSM is produced and sintered with a total emission sample being collected allowing for a complete mass balance of the sintering process to be calculated. Details of this method are outlined below. RSM samples were collected (using the same methods as in 2.1.1.) before pelletizing into pre-cleaned amber jars. Sinter product was sampled from the centre and crushed as in 2.1.1 before collection in amber jars. Volatile emissions from the sinter pot were collected on pre-extracted PUF plugs fitted on the SP "exit" line along with solvent washings from within the sinter pot.

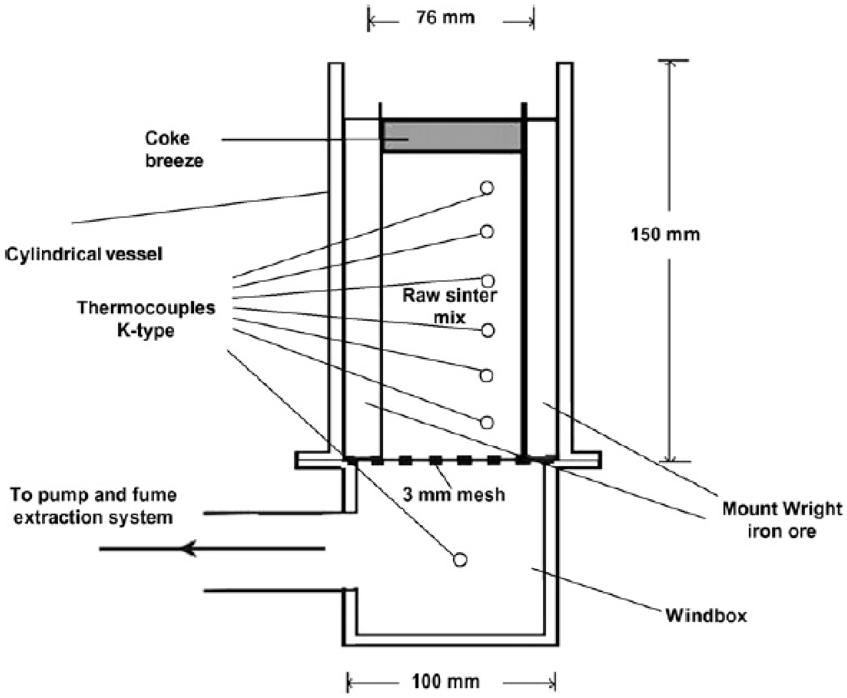


Figure 2.3 – Schematic diagram of the sinter pot apparatus (Ooi et al., 2008)

2.1.3.1. Sinter Pot Methodology

A "base case" of all the components of a typical RSM was produced, containing ores, coke, fluxes and reverts. This was mixed thoroughly in a rotating drum. Different – additional – components, depending on the required experimental conditions were added afterwards in the same manner (i.e. potassium chloride, potassium bromide, PBDE technical solutions). For those containing PBDE technical solutions, the two solutions – Penta- (Bromkal 70-5DE), and Deca- (Bromkal 82-0DE) (Cambridge Isotope Laboratories (CIL), Andover, MA, USA) – were each diluted into 25 mL methanol and added, drop by drop, to the base case mixture in a rotating drum, before being left covered overnight to allow solvent to evaporate, before mixing again for 2 hours in the rotating drum to attempt complete homogenization of the PBDEs throughout the RSM. Moisture content and total mass were then determined before the mixture was returned to the mixing drum which was turned very slowly whilst the correct volume of distilled water was added slowly (2-3 mL every 30 seconds) to pelletize the mixture with a moisture content of ~6.5% (±0.2%). The volume of water was calculated using *Equation 2.1* assuming a density of 1 g/mL of water at atmospheric pressure and temperature. The moisture content was then measured 3 times to ensure it was correct.

$$V = M \times (m_T - m_I) \qquad \text{(Equation 2.1)}$$

Where V is the volume of distilled water to be added (mL); M is the total mass of the RSM (g); m_T is the target moisture content (%); m_I is the initial moisture content (%)

Approximately 1 kg of the required RSM was packed into the cylindrical vessel of the SP and was surrounded by Mount Wright ore (which does not oxidise and therefore will not sinter in the process) and a layer of coke breeze over the top. The coke breeze was then ignited using propane gas that was fed into the vessel for 3 minutes. The propane supply was stopped whilst the RSM sintered. Pipes surrounded by condensers (fed by an external water pump circulating ice cold water through them) channelled all emissions through to the PUF plug. The apparatus was left to cool for an hour before being dismantled. The PUF was collected and stored in a sealed jar whilst all individual parts and pipes were rinsed with solvent (toluene and acetone) that was collected in large pre-cleaned amber jars. The outer layer of the sinter was "chiselled" and discarded, whilst samples were taken from the centre before being crushed ready for extraction and clean-up as in 2.1.1.

2.1.4 Passive Air Sampling

Passive air samples (PAS) were taken from eight locations across the West Midlands conurbation as well as at five locations within the Scunthorpe Sinter Plant site and one at Swinden Technology Centre in Rotherham. Whilst PBDD/Fs would ideally have been measured in outdoor air samples, this was not possible during the life-span of the project, as high volume active samplers are required in order to gain a large enough sample volume to overcome instrumental detection limits. All passive air samples were collected with the same basic configuration using a PUF disc (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g cm^{-3} density, PACS, Leicester, UK) and a glass fibre filter ((GFF) 125 mm diameter, 1 µm pore size, Whatman, UK) as the sampling media. The configuration (Figure

2.4) is the same as that developed by (Abdallah et al., 2009) as it samples both gaseous and particulate phase allowing for detection of higher molecular weight congeners such as BDE-209. The PUF disc(s) and filter are sheltered between two stainless steel housings (top housing - 23 cm diameter, two litre volume; and bottom housing - 18 cm diameter, one litre volume). The inner surface of the top housing was coated with aluminium foil and washed with hexane and dichloromethane to try to minimize its particle-scavenging potential (Abdallah et al. 2010). The GFF is suspended in the middle of the sampler, supported by a wire mesh. The sampler was designed so that air would flow over the GFF and the particulate phase would be sampled by the upper facing side of the GFF by a combination of gravitational settling and turbulent deposition.

For samples taken at the Scunthorpe Sinter Plant site, PUF discs were pre-extracted via soxhlet extraction with hexane for 6-8 hours. PLE would have been preferred. However at the time of sampling at Scunthorpe, a pre-extraction method was not in place that maintained the shape of the PUF discs. A method was later developed using PLE (pressurised liquid extraction) (ASE-350 (Dionex)) with 3:2 dichloromethane (DCM):hexane (90°C and 1500 psi; flush time – 5 minutes; static cycle – 4 minutes; purge time – 120 s; 1 static cycle) that did not damage the PUFs and so this was used for all samples taken in the West Midlands transect study. GFFs were baked for 5 hours at 500 °C before the samplers were assembled and deployed. Shelters were also thoroughly rinsed with hexane and acetone before each sampling period to avoid potential cross-contamination.

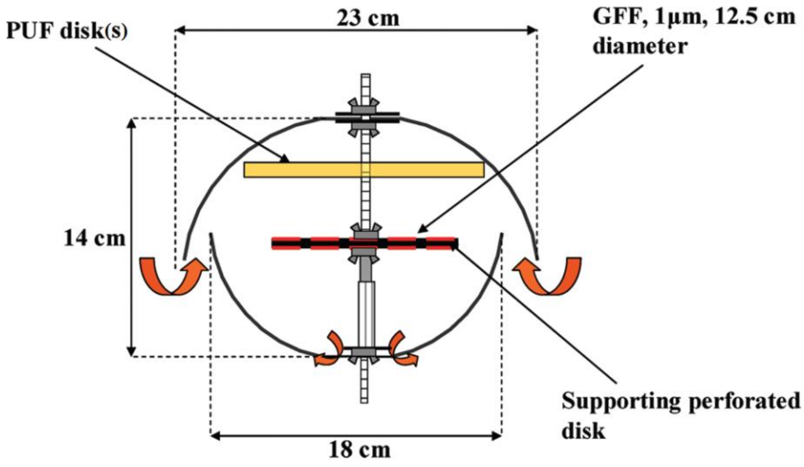


Figure 2.4 Configuration of Passive Air Samplers used to sample PBDEs in outdoor ambient air (Abdallah and Harrad, 2010)

2.1.4.1 Calibration of passive air samplers.

As this configuration had not hitherto been used to sample outdoor air, the sampling rate was unknown. PAS were calibrated against active samplers to determine the volume of air sampled and therefore the actual concentrations (pg PBDE m^{-3} air).

2.1.4.1.1 Experimental conditions.

The calibration used the same basic method as that used by (Abdallah and Harrad, 2010) for indoor air. PBDEs were monitored in outdoor air using the PAS over five different exposure times, whilst also being monitored in low volume active air samples from a known volume of air (approximately 100 m^3, n=5). PAS were deployed (n=8) for 50 days at the Elms Road Observatory Site (EROS, University of Birmingham, Edgbaston, UK). Samplers were then collected at 10 day intervals over the 50 days with three samplers being collected after 10 days and two after 20 days and combined to ensure detectable masses at both sampling intervals.

2.1.4.1.2 Passive samplers' uptake rates

The following equation (2.2) was used to calculate estimated volumes of air sampled for each PAS used in the calibration study.

$$V_e = \frac{M_{PAS}}{C_A} \qquad \textbf{(Equation 2.2)}$$

Where V_e is the effective total volume of air sampled, M_{PAS} is the mass of the compound detected in the passive sample (pg) C_A is the concentration of the compound in the active air sample (pg m^{-3}). V_e was then plotted against sampling period (days) and the sampling rate calculated from the slope of the line.

Figures 2.5 a, b and c show the correlation between the estimated air volume sampled and time for BDEs -99, -100 and -209 respectively. Good correlations were found for BDE-209 and BDE-100 (both >0.99), and for BDE-99 (0.984). The average sampling rate was calculated from these graphs by calculating the slope of the trend line providing estimated sampling rates of 2.26 m^3/day, 3.92 m^3/day and 3.92 m^3/day for BDEs -209, -99 and -100 respectively. Therefore a sampling rate of 2.26 m^3/day was applied to all PAS for BDE-209. A sampling rate of 3.92 m^3/day was applied for all tri-hepta BDE congeners from BDE-99 and BDE-100 data. Theoretically there should be no differences between sampling rates for different congeners as the same sample (and therefore volume of air) is used for the analysis of all congeners. However, as with other studies (Shoeib and Harner, 2002; Hazrati and Harrad, 2007) differences were seen between congener-specific sampling rates in the present study. Hazrati and Harrad (2007) attribute these differences to the “the combined effect of environmental conditions, the physicochemical properties and the passive sampler design”. For example, if the air sampled contains low levels of particulate matter, then there will be a lower rate of deposition of particles on the GFF. Congeners such as BDE-209, which are found almost entirely in the particulate phase (due to their low vapour pressures) will have a lower effective volume than those found primarily in the vapour phase like BDEs -99 and -

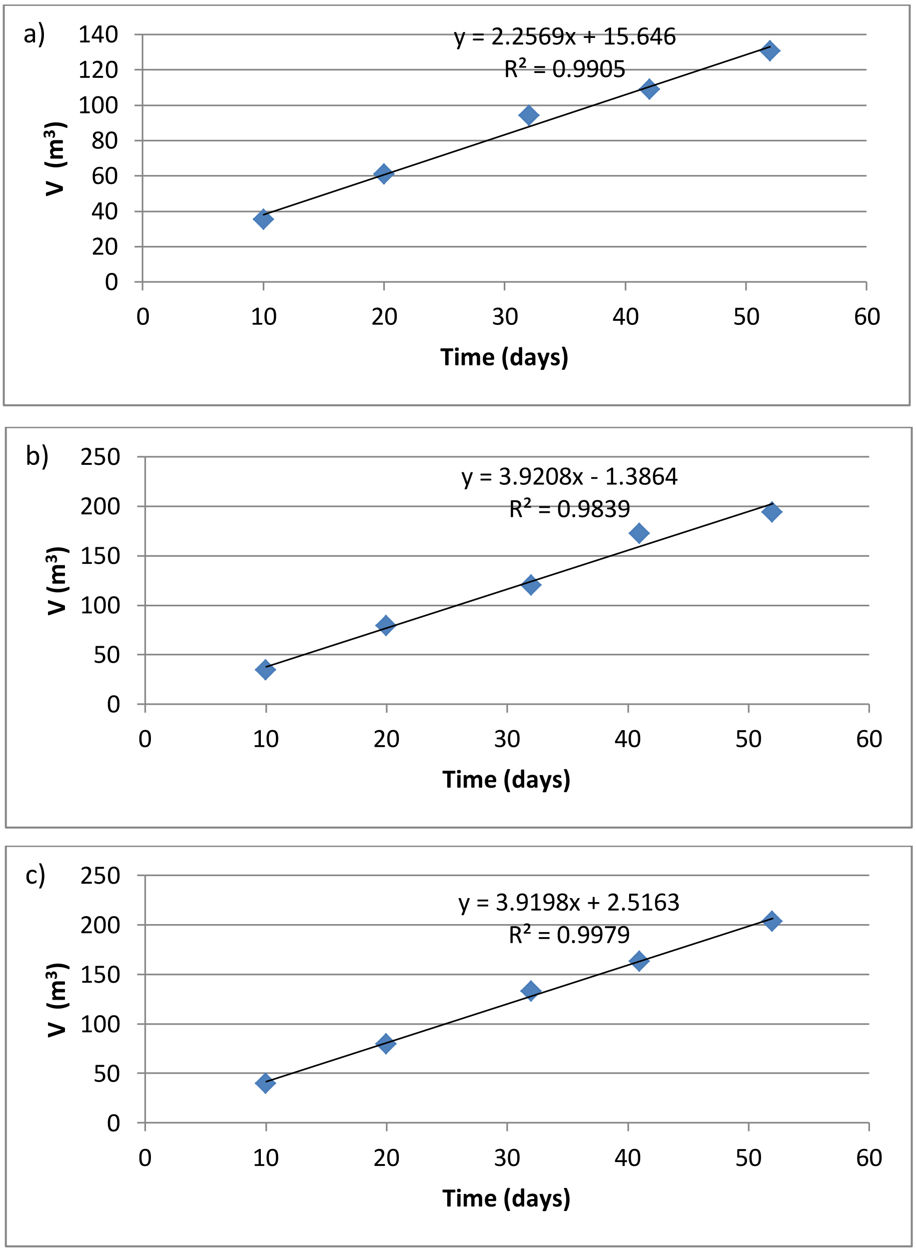


Figure 2.5 Calculated volume of air sampled in PAS used in calibration study from a) BDE-209; b) BDE-99; and c) BDE-100

100 (Hazrati and Harrad, 2007), thus explaining their lower sampling rate..BDE-47 was not monitored in the PAS calibration study as there were sensitivity issues with the LC-APPI-MS/MS at the time of analysis meaning that it was not detected in all samples.

2.1.5 Soil Sampling

2.1.5.1 – Australian Soil Samples

Australian soil samples were originally taken for the National Dioxin Program in 2003. The sampling strategy was based on that of Buckland et al. (2005) where each sample was made up of 18 soil cores from three sub-sampling sites. A triangular sampling configuration was employed at each sub-sampling site with each core taken to 10 cm depth, and wrapped in foil. All 18 cores were then combined, homogenised and freeze-dried in the laboratory. Samples were stored in glass jars in a dark, dry area.

2.1.5.2 – UK Soil Samples

New UK soil samples were taken using the same method as archived UK soils initially taken as part of a different study in 2005 (Evans, 2007). Three sub-samples were taken at each location, at least 1 m apart, within a 1 m^2 area. Sub-samples were from the top 5 cm of surface soil and taking the soil immediately beneath the surface and storing in sealed amber jars. The three sub-samples were combined and homogenised for analysis. Ideally the archived samples would have been spiked with a C^{13}-labelled standard to monitor any loss of target analytes during storage. However this was not possible and it was assumed that there was 100% recovery up until extraction.

2.1.6 – Sediment Core Samples

Sediment core samples were initially taken in 1998/99 as part of another study (Taylor et al., 2004). Cores were taken in shallow-water areas (<8 m) in locations close to stormwater drains, which have been identified previously as a major source of contaminants (Birch and Taylor, 1999), using a piston corer (up to 1.5 m) designed to reduce compaction, provide good core recovery and to avoid physical disturbance. Each core was then cut into 2 cm layers up to 10 cm, and then another 2 cm was taken every 10 cm. Samples were freeze-dried and sieved to particle sizes of less than 62.5 µm (Taylor et al., 2004). Sedimentation rates were determined by Taylor et al. (2004) based on previously used methods using the exponential decay of ^{210}Pb to levels supported by ^{226}Ra (Goldberg, 1963, Nriagu et al., 1979).

2.2 Extraction

2.2.1 Extraction for PBDE analysis

2.2.1.1 Raw material and sinter pot samples

Raw material and sinter pot (SP) samples were all provided as dusts ready for PLE as previously used by others for extraction of soils, sediments and dusts (de la Cal et al., 2003, Lagalante and Oswald, 2008). Approximately 10 g sample was mixed with pre-extracted hydromatrix (Varian inc., UK) and added to pre-cleaned 66 mL extraction cells. Hydromatrix was added to fill the remaining volume of the cells. They were then spiked with 60 ng of internal standard (IS, $^{13}C_{12}$-labelled BDEs -28, -47, -99, -153 and -209 (BDE-28 was used for analysis via GC/MS only, whilst BDE-209 was only analysed on LC-MS/MS). The cells were then extracted with dichloromethane (DCM):hexane (3:2 v/v) at 90°C and 1500 psi (heating time 5 minutes, static time 4 minutes, 3 static cycles, purge time 120 s, flush volume 50%)

2.2.1.2 Passive Air Samples

2.2.1.2.1 PAS from Tata Steel

Although PLE was generally preferred, at the time of sampling, PUFs could not be pre-extracted via PLE without being damaged and were extracted via Soxhlet. Therefore the same method was used for extraction of samples to avoid any extraction of interfering compounds that were not pre-extracted before sampling. PUFs and GFFs were loaded into a Soxhlet apparatus and spiked with internal standards (as in 2.2.1.1). They were then extracted with hexane for 8 hours as reported previously (Harrad et al., 2006).

2.2.1.2.2 PAS from West Midlands Locations and Calibration Study

PUFs and GFFs were loaded into 66 mL extraction cells and spiked with internal standards and extracted as described in 2.2.1.1.

2.2.1.3 Soil & Sediment Samples

Soil and sediment samples underwent simultaneous in-cell extraction and clean-up as outlined in 2.3.1.2.

2.2.2 Extraction for PBDD/F analysis

The sample extraction and clean-up methods for PBDD/Fs were based on methods used in accordance with ENV PES 100 v12 (an in-house clean-up method developed by Tata Steel

Environmental Laboratories for the analysis of PCDD/Fs). The methods were the same for QC5 (Tata steel internal quality control ESP dust samples) and for all emission samples analysed in this study.

The sample was spiked with internal standards ($^{13}C_{12}$-2,3,7,8-TBDD, $^{13}C_{12}$-1,2,3,7,8-PeBDD, $^{13}C_{12}$-1,2,3,7,8,9-HxBDD, $^{13}C_{12}$-2,3,7,8-TeBDF and $^{13}C_{12}$-1,2,3,7,8-PeBDF), loaded into Dionex ASE extraction cells and subjected to PLE on either an ASE 200 or an ASE 100 with toluene (90°C, 1500 psi, heating time 5 minutes, static time 4 minutes, 3 static cycles, purge time 120 s, flush volume 50%).

2.3 Clean-up

2.3.1 Clean-up for PBDE analysis

All samples except for soil samples underwent the same clean-up methods for PBDE analysis, (based on US EPA method 1614 (EPA, 2007)) adapted from previous work within the group (Harrad et al., 2006, Harrad et al., 2004).The extract was concentrated to 0.5 mL under a gentle stream of nitrogen using a Zymark Turbovap® II concentration workstation (Hopkinton, MA, USA) then transferred to 10 mL conical test tubes containing 2 mL 95% concentrated sulfuric acid and mixed thoroughly. The two layers were left for 24 hours to separate. The top (hexane) layer and three subsequent washings were collected and passed through to a column containing 1 g florisil (60-100 mesh, Sigma Aldrich, UK) and 1 g sodium sulfate. The acid layer was discarded. 20 mL hexane was also passed through, the total eluate collected in 50 mL Turbovap® tubes and concentrated under nitrogen to near-dryness using a Turbovap® II (Biotage, Uppsala, Sweden). 60 ng $^{13}C_{12}$-BDE-100 was added as a recovery determination standard and the sample made up to 50 µL with either nonane (GC/MS) or methanol (LC-MS/MS). Final sample extracts were sonicated for 30 s and transferred into autosampler vials using an Eppendorf 100 µL micropipette.

2.3.1.2 Soil & Sediment Samples

The method in this section was developed based on the above methods for clean-up of extracts for PBDE analysis. The aim was to carry out all clean-up within the cell at the same time as PLE, thereby reducing the number of glassware transfers to only 2, increasing sample recovery and reducing the risk of contamination during clean-up.

UK samples had not been freeze dried and so 10 g aliquots from homogenised soil samples were mixed with 5-10 g sodium sulphate in a pre-cleaned beaker (acetone and hexane) to remove water content. Australian samples had been freeze dried so a 10 g aliquot from homogenized samples were weighed in disposable measuring boats. Samples were added to either 66 mL or 100 mL Dionium® (A zirconium alloy able to tolerate highly acidic and basic conditions) ASE cells that had been pre-cleaned and loaded with the following components from the bottom upwards (Figure 2.6): two microfibre filters (Dionex, UK), silica gel (Sigma Aldrich, UK), 5 g florisil (60-100 mesh, Sigma Aldrich, UK), 3 g diatomaceous earth (Sigma Aldrich, UK), microfibre filter, 10 g acid impregnated silica (44% sulfuric acid), microfibre filter, 5 g copper powder, 2 g hydromatrix, 2-10 g sample mixed with hydromatrix. The remaining volume of the cell was filled with hydromatrix and internal standards (as in 2.2.1.1). The ASE cells were extracted with DCM and hexane (1:1 v/v) at 90°C and 1500 psi (heating time 5 minutes, static time 5 mins, 3 static cycles, flush volume – 50%, purge time – 120 s). The extract was concentrated to near-dryness using a Zymark Turbovap® II concentration workstation (Hopkinton, MA, USA). 60 ng $^{13}C_{12}$-BDE-100 (recovery determination standard) was added and the final volume adjusted to 100 µL with methanol. The sample was sonicated for 30 s and transferred to autosampler vials using an Eppendorf 100 µL micropipette.

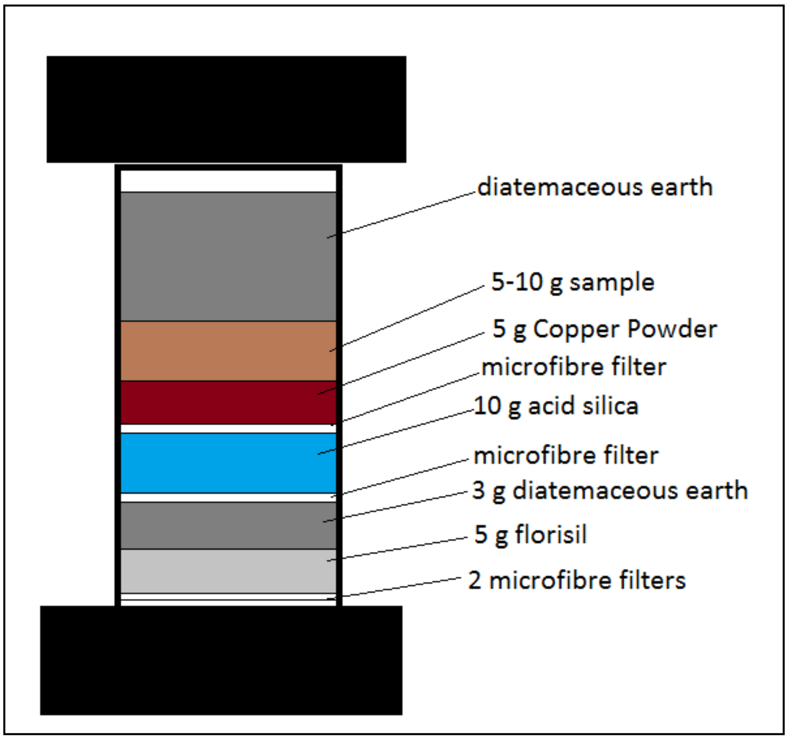


Figure 2.6 – Schematic of a Dionium ASE cell used for in-cell clean-up of soils and sediments for PBDEs

2.3.2 Clean-up for PBDD/F Analysis

The extracts were concentrated using nitrogen gas and a water bath to ca. 0.5-1.0 mL before being passed through a multi-layered silica column (380 mm x 24 mm i.d. (York Glassware Services) containing silica gel (Davisil, grade 633, 200-425 mesh (Sigma Aldrich) and then through an activated florisil column (containing pre-extracted florisil (Sigma Aldrich) and anhydrous sodium sulfate – Analar (VWR or Farenheit) to remove interfering compounds. The eluate was then transferred, along with washings, into turbovap tubes and concentrated under a stream of nitrogen gas to dryness. Nonane and recovery standards ($^{13}C_{12}$-2,3,4,7,8 -PeBDF) were added up to a volume of 50 µL and mixed using a micropipette. The tips of the tube were then sonicated before the solution was transferred into a 1.0 mL glass vial and capped with a crimp seal.

2.4 Analysis

2.4.1 GC/MS analysis of PBDEs

2.4.1.1 Sinter Plant Raw Materials

Tri-hexa PBDEs were measured in the sinter plant raw materials (RSM, ESP dust, sinter product and emission sample) at the University of Birmingham using the following method. Samples were analysed on an Agilent 5975 MS coupled with an Agilent 6850 GC.

Time (min)	**Analyte**	**Quantifier**	**Qualifier**
7.00-9.80	Tri-brominated diphenyl ether	405.9	407.9
	$^{13}C_{12}$ Tri-brominated diphenyl ether	417.9	419.9
9.80-11.00	Tetra-brominated diphenyl ether	325.9	327.9
	$^{13}C_{12}$ Tetra-brominated diphenyl ether	337.9	339.9
11.00-15.00	Penta-brominated diphenyl ether	403.9	405.9
	$^{13}C_{12}$ Penta-brominated diphenyl ether	415.9	417.9
11.00-15.00	Hexa-brominated diphenyl ether	483.9	481.9
	$^{13}C_{12}$ Hexa-brominated diphenyl ether	495.9	493.9

Table 2.1 – Target masses and retention times for the identification and quantification of PBDEs via GC/MS with a DB-XLB column

An Agilent DB-XLB column (30 m x 0.25 mm internal diameter x 0.10 µm film thickness) was used for GC/MS analysis of PBDEs. Helium was used as the carrier gas with a constant flow of 1.0 mL/min. The inlet was run in splitless mode. The GC oven had an initial temperature of 100°C and held for 5 minutes. The temperature was then increased by 20°C/min to 310°C and held for 15 minutes. PBDE calibration solutions (CS1-CS5, Cambridge Isotope Laboratories (CIL)) were injected and the GC/MS was run in total ion chromatogram (TIC) mode to determine retention time windows and target ion masses to be monitored. An acquisition file was then created based on those retention times and ion masses (Table 2.1) and the calibration solutions were injected in single ion monitoring (SIM) mode. A full 5-point calibration showed good response factors with a low relative standard deviation.

2.4.1.2 Other UK samples

All other GC/MS analyses of UK samples (SP, outdoor air and soils) took place on the same instrument as above to measure tri-hepta PBDEs. An Agilent DB-5ms column was used, 30 m (length) x 0.25 mm (internal diameter) x 0.25 µm (film thickness). Helium was used as the carrier gas with a constant flow of 1.0 mL/min. The inlet was run in splitless mode. The GC oven had an initial temperature of 70°C which was held for 2 minutes and then increased by 20°C/min to 270°C and held at this temperature for 53 minutes. The MS was run in SIM mode scanning for the masses show in Table 2.2.

Time (min)	Analyte	Quantifier	Qualifier
0.00-27.00	Tri-brominated diphenyl ethers	405.8	407.8
	$^{13}C_{12}$ Tri-brominated diphenyl ether	417.8	419.8
27.00-37.00	Tetra-brominated diphenyl ethers	485.8	483.8
	$^{13}C_{12}$ Tetra-brominated diphenyl ether	497.8	495.8
37.00-45.80	Penta-brominated diphenyl ethers	403.9	405.9
	$^{13}C_{12}$ Penta-brominated diphenyl ether	415.9	417.9
45.80-63.50	Hexa-brominated diphenyl ethers	483.9	481.9
	$^{13}C_{12}$ Hexa-brominated diphenyl ether	495.9	493.9
	Hepta-brominated diphenyl ethers	723.8	721.8

Table 2.2 – Target masses and retention times for the identification and quantification of PBDEs via GC/MS with a DB5-ms column

2.4.1.3 HRGC/HRMS analysis of Australian Soil and sediment samples

Australian soil samples were analysed for BDE-47 at the National Research Centre for Environmental Toxicology (EnTox), University of Queensland, Australia using HRGC/HRMS with an HP 5890 II GC coupled to a Micromass Autospec HRMS. A Zebron ZB-5ms column was used, 10 m (length) x 0.18 mm (internal diameter) x 0.18 µm (film thickness). The inlet was run in splitless mode at a temperature of 280 °C. Ultra-high purity helium was used as the carrier gas with a constant flow of 1.0 mL/min. The GC oven was held at an initial temperature of 110 °C for 3 mins and increased by 30 °C/min to 200 °C and then 20 °C/min to 330 °C and held for 1 min. BDE-47 was measured using ions 485.8 (quantifier) and 483.8 (qualifier), whilst $^{13}C_{12}$- BDE-47 was measured using ions 497.8 (quantifier) and 495.8 (qualifier).

2.4.2. Analysis of PBDEs via LC-MS/MS

2.4.2.1 LC-APPI-MS/MS analysis of PBDEs in UK Samples

Sinter plant outdoor air samples and RSM components were measured for all target analytes (BDEs – 47, 85, 99, 100, 153, 154, 183, 209) at the University of Birmingham using LC-APPI-MS/MS. Analytes were separated using a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan) with a SIL-209A autosampler, a DGU-20A3 vacuum degasser, and a Varian Pursuit XRS3 C_{18} reversed phase analytical column at room temperature (250 mm x 4.6 mm i.d., 3 µm particle size).

A 10 µL injection volume was used. A mobile phase program based upon 1:1 methanol/water (mobile phase A) and 1:4 toluene/methanol at a flow rate of 0.4 mL/min was used for the elution of target compounds, starting at 85% mobile phase B and increased gradually to 100% over 15 minutes. Mobile phase B is held at 100% for another 15 minutes. After 30 minutes mobile phase B is reduced sharply to 85% and held for 5 minutes to equilibrate the column for the next sample. The LC-APPI-MS/MS parameters are detailed in Table 2.3.

The elution order of PBDEs was already known (Abdallah et al., 2009). Therefore calibration solutions were made from dilutions of pure standards (Wellington Laboratories), the most concentrated (1000 ng/mL) were injected and the instrument operated in multiple reaction monitoring (MRM) mode. The retention times were recorded for the appropriate mass to charge (m/z) ratios (Table 2.4). A full 5-point calibration of standards ranging from 50-1000 ng/mL was performed producing response factors close to 1.0 with a low relative standard deviation in accordance with quality assurance protocol detailed in Section 2.5. An excellent range of linearity was seen between the relationship between peak area and concentration with R^2 values above 0.99 for all congeners.

Parameter	**Value**
Curtain Gas	25 psi
Collision Gas (CAD)	11 psi
Ion Transfer Voltage (IS)	1250 V
APPI Temperature	400 °C
Probe nebulizer gas	60 psi
Auxillary Gas	30 psi
Declustering Potential	-8.0 V
Focussing Potential	-365.0 V
Entrance Potential	-12.0 V
Collision Energy	-75.0 eV
Collision Cell Exit Potential	-8.0 V

Table 2.3 – LC-APPI-MS/MS Parameters

BDE Congener	Precursor (m/z)	Fragment (m/z)
BDE-47	420.9	78.6
$^{13}C_{12}$ BDE-47	432.9	78.6
BDEs -85, -99, -100	500.8	78.6
$^{13}C_{12}$ BDEs -99, -100	512.8	78.6
BDEs -153, -154	578.8	78.6
$^{13}C_{12}$ BDE-153	590.8	78.6
BDE-183	658.6	78.6
BDE-209	486.6	78.8
$^{13}C_{12}$ BDE-209	498.6	78.8

Table 2.4 MRM values for LC-APPI-MS/MS analysis of PBDEs

2.4.2.2 LC-APCI-MS/MS analysis of PBDEs in Australian soil and sediment samples

Penta-deca-BDEs were determined in Australian soils and sediments at EnTox by HPLC-MS/MS using an AB/Sciex API5500Q mass spectrometer (ABSciex, Concord, Ontario, Canada) equipped with an atmospheric pressure chemical ionisation (APCI) source coupled to a Shimadzu Prominence HPLC system (Shimadzu Corp., Kyoto, Japan).

Separation was achieved using a 3 micron 50 mm x 2.0 mm Phenomenex Gemini NX C18 column (Phenomenex, Torrance, CA) run at 45^{o}C, and a flow rate of 0.3 mL/min with a linear gradient starting at 85% B, ramped to 100% B in 6 minutes then held at 100% for 4.0 minutes followed by equilibration at 85% B for 4 minutes. (A = 5% methanol in HPLC grade water, B = 95% methanol in HPLC grade water). The mass spectrometer was operated in the negative ion, multiple reaction-monitoring mode using nitrogen as the collision gas. Mass spectrometer parameters were as Table 2.5.

Analyte	Precursor (m/z)	Fragment (m/z)	Declustering Potential	Entrance Potential	Collision Energy	Cell Exit Potential
Penta-BDE	500.7	78.9	-40 V	-8 V	-100 eV	-10 V
	500.7	80.9				
$^{13}C_{12}$ Penta-BDE	512.7	78.9	-40 V	-8 V	-100 eV	-10 V
	512.7	80.9				
Hexa-BDE	578.6	78.9	-60 V	-7 V	-100 eV	-10 V
	578.6	80.9				
$^{13}C_{12}$ Hexa-BDE	590.6	78.9	-60 V	-7 V	-100 eV	-10 V
	590.6	80.9				
Hepta-BDE	658.5	78.9	-40 V	-8 V	-120 eV	-10 V
	658.5	80.9				
$^{13}C_{12}$ Hepta-BDE	670.5	78.9	-40 V	-8 V	-120 eV	-10 V
	670.5	80.9				
Deca-BDE	894.2	78.9	-40 V	-8 V	-132 eV	-10 V
	894.2	80.9				
$^{13}C_{12}$ Deca BDE	908.2	78.9	-40 V	-8 V	-132 eV	-10 V
	908.2	80.9				

Table 2.5 – MRM values and LC-APCI-MS/MS parameters for PBDE analysis in Australian soils and sediments.

2.4.3 HRGC/HRMS analysis of PBDD/Fs

This was conducted at the Swinden Technology Centre (Tata Steel, Moorgate, Rotherham, UK). Samples were analysed using an Autospec Ultima (Waters). Using the calibration solution (CS4) from a set of PBDD/F calibration solutions CS1-CS5 (CIL), several runs were carried out to monitor primary and secondary ions for tetra- through to hepta- PBDD/Fs (see Table 2.6) using an Agilent DB-5MS column 30 m (length) x 0.25 mm (in diameter) x 0.1 µm (film thickness). Helium was used as the carrier gas with a constant flow of 1.0 mL/min. The inlet was run in splitless mode. The GC oven was held at an initial temperature of 140 °C for 1 minute. The temperature was then increased to 200 °C at a rate of 20 °C/min and held for 6 minutes. It was then increased to 280 °C at 5 °C/min and held for 4 minutes.

Time (min)		**Quantifier**		**Qualifier**	
	Analyte	**Mass**	**Ion**	**Mass**	**Ion**
13.0 – 17.0	Tetrabromodibenzofurans	483.6954	M+4	481.6974	M+2
	$^{13}C_{12}$ tetrabromodibenzofuran	495.7357	M+4	493.7377	M+2
	Tetrabromodibenzo-p-dioxins	499.6903	M+4	497.6923	M+2
	$^{13}C_{12}$ tetrabromodibenzo-p-dioxin	511.7306	M+4	509.7326	M+2
	PFK Lock Mass	**492.9697**			
17.0 – 21.0	Pentabromodibenzofurans	561.6059	M+4	563.6039	M+6
	$^{13}C_{12}$Pentabromodibenzofuran	573.6462	M+4	575.6442	M+6
	Pentabromodibenzo-p-dioxins	577.6008	M+4	579.5988	M+6
	$^{13}C_{12}$ Pentabromodibenzo-p-dioxin	589.6411	M+4	591.6391	M+6
	PFK Lock Mass	**566.9665**			
21.0 – 26.0	Hexabromodibenzofurans	641.5144	M+6	639.5164	M+4
	$^{13}C_{12}$ Hexabromodibenzofuran	653.5546	M+6	651.5566	M+4
	Hexabromodibenzo-p-dioxins	657.5093	M+6	653.5113	M+4
	$^{13}C_{12}$ Hexabromodibenzo-p-dioxin	669.5495	M+6	667.5515	M+4
	PFK Lock Mass	**654.9601**			

Table 2.6 Ions monitored for PBDD/F determination

The retention times for each compound are listed in Table 2.5. After having identified the retention times of all the PBDD/F compounds present in CS4 calibration solution, each group of compounds was separated into 4 functions (F1- tetraBDD/Fs; F2- pentaBDD/Fs; F3-hexaBDD/Fs; F4-heptaBDD/Fs). Although heptaBDD/Fs were detected, the peaks were extremely small and close to the limits of detection. A single HpBDF peak was detected in an emission sample with high concentrations, but it was unquantifiable. Therefore, in other samples no attempt was made to quantify HpBDF. Once the correct retention time windows were determined, a full 5-point calibration was performed using CS1-CS5. The calibration (See Figure 2.4) showed good response factors with a very low relative standard deviation.

2.5 Validation and QA/QC Criteria

There is a set QA/QC protocol within our research group, which was used to form the basis of QA/QC for this project (Appendix 5). Ideally, for all samples, 2 replicates would have been analysed and the average figures used. However, due to time restrictions on this project, one sample was used for each analysis presented.

2.5.1 Analyte identification and Quantification criteria

The elution orders for both sets of compounds for GC/MS, LC-APPI-MS/MS, LC-APCI-MS/MS and HRGC/HRMS were already known from previous work within the relevant research groups at which these analyses were conducted. Therefore, mixtures of solutions containing each individual target compound, were injected to perform a full 5-point calibration with a concentration range of 50-1000 ng/mL to determine exact retention times and the linearity of the MS response. Calibration curves (and standards) were only accepted if R^2 values were more than 0.99.The same ^{13}C-labelled isomers added to samples prior to extraction were used as internal standards. The peak areas from the 5-point calibration were used to determine relative response factors (RRFs) for each target compound. The RRF is defined as the instrument response for a unit amount of target pollutant relative to the instrument response obtained for the same amount of the internal standard (IS). RRFs were calculated using Equation 2.3.

$$RRF = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{IS}}{C_{NAT}} \qquad \textbf{(Equation 2.3)}$$

Where A_{NAT} is the peak area for the “native” (naturally occurring ^{12}C) compound in the standard; A_{IS} is the peak area of the ^{13}C-labelled internal standard in the standard; C_{NAT} is the concentration of the “native” compound in the standard; and C_{IS} is the concentration of the internal standard in the standard. The relative standard deviation (RSD) of the RRFs calculated for each target compound at the 5 points of its calibration curve did not exceed 5%.

A single calibration standard was injected before and after each batch of samples and the average RRFs were calculated. To be acceptable these had to be within ±25% of the average RRFs from the initial 5-point calibration and were used for calculating the concentrations of target compounds in samples using Equation 2.4.

$$Concentration = \frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS} \qquad \textbf{(Equation 2.4)}$$

Where A_{IS} is the peak area of the internal standard in the sample; A_{NAT} is the peak area of the target compound in the sample; RRF is the relative response factor for the target compound; M_{IS} is the mass of internal standards (ng) added to the sample; and SS is the sample size (g or m^{-3}).

The following criteria had to be met to ensure that a given peak was a target pollutant in a sample:

1. The signal to noise ratio (S/N) must exceed 3:1.
2. The relative retention time (RRT) of the peak in the sample must be within ±0.2% of the average value determined for the same congener in the 2 calibration standards ran before and after each batch of samples.
3. The bromine isotope ratios must be within ±20% of the average for the 2 calibration standards run before and after each sample batch.

2.5.2 Recovery Determination Standard

The recoveries of internal standards during sample extraction and clean-up were determined relative to the recovery determination standard (RDS) added to the samples prior to MS analysis – $^{13}C_{12}$-BDE 100, whilst for HRGC/HRMS analysis of PBDD/Fs the standard used was 2,3,4,7,8-PeBDF. The IS recoveries for each sample were calculated using Equation 2.5

$$\%\, IS\ Recovery = \left[\left(\frac{A_{IS}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{IS}}\right)_{STD} \times \left(\frac{C_{IS}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{IS}}\right)_S\right] \times 100 \ \textbf{(Equation 2.5)}$$

where $(A_{IS}/A_{RDS})_S$ = ratio of internal standard peak area to recovery determination standard peak area in the sample; $(A_{RDS}/A_{IS})_{STD}$ = ratio of recovery determination standard peak area to internal standard peak area in the calibration standard (the average of values obtained for both calibration standards run for a batch of samples is used); $(C_{IS}/C_{RDS})_{STD}$ = ratio of concentration of internal standard to concentration of recovery determination standard in the calibration standard; and $(C_{RDS}/C_{IS})_S$ = ratio of concentration of recovery determination standard to concentration of internal standard in the sample. Table 2.7 shows a summary of internal standard recoveries across all samples analysed in this study. Samples were only accepted if they had a recovery within the range of 35-150% as stated in our research group's quality assurance document (Appendix 5).

PBDD/F Emissions (n=25)	**Mean**	**SD**	**Median**	**Min.**	**Max.**
$^{13}C_{12}$-1,2,3,7,8-PeBDF	90	19	81	69	118
$^{13}C_{12}$-2,3,7,8-TeBDF	60	19	60	36	87
$^{13}C_{12}$-2,3,7,8-TBDD	59	13	58	41	83
$^{13}C_{12}$-1,2,3,7,8-PeBDD	96	25	85	69	130
$^{13}C_{12}$-1,2,3,7,8,9-HxBDD	103	26	91	80	145
PBDE Raw Materials (n=102)	**Mean**	**SD**	**Median**	**Min.**	**Max.**
^{13}C-BDE 47	94	33	101	37	141
^{13}C-BDE 99	89	26	88	39	127
^{13}C-BDE 153	103	37	95	36	149
^{13}C-BDE 209	74	29	64	42	124
PBDE Soils & Sediments (n=80)	**Mean**	**SD**	**Median**	**Min.**	**Max.**
^{13}C-BDE 47	93	26	92	48	132
^{13}C-BDE 99	86	20	85	52	125
^{13}C-BDE 153	85	19	86	49	114
^{13}C-BDE 209	81	20	82	47	110
PBDE Ambient Air (n=48)	**Mean**	**SD**	**Median**	**Min.**	**Max.**
^{13}C-BDE 28	55	15	52	36	110
^{13}C-BDE 47	68	16	68	42	110
^{13}C-BDE 99	79	23	73	42	137
^{13}C-BDE 153	53	17	48	35	118
^{13}C-BDE 209	87	29	91	38	133

[a] SD = Standard Deviation; Min. = minimum; Max. = maximum

Table 2.7 – Descriptive statistics of IS recoveries (%) across all studied samples

2.5.3 Accuracy and Precision

The accuracy and precision of PBDE analysis conducted at Birmingham and EnTox was assessed via replicate analysis (n=12) of a standard reference material (SRM 2585, organic contaminants in house dust, NIST). The results (Table 2.8) were consistent (indicated by low relative standard deviation) and comparable to the certified values for PBDEs.

There is no reference material for PBDD/Fs, but internal quality control samples (QC5, an electrostatic precipitator dust certified for PCDD/Fs, n=5) from Tata Steel were used to evaluate reproducibility (Table 2.9).

	Average ± standard deviation (n=12)		**Relative Standard Deviation (RSD) (%) of measured values**
	Measured	**Certified**	
BDE-47	464 ± 10.5	497 ± 46	2.3
BDE-85	42.5 ± 1.4	43.8 ± 1.6	3.3
BDE-99	783 ± 68.8	892 ± 53	8.8
BDE-100	138 ± 38.2	145 ± 11	27.7
BDE-153	124 ± 11.7	119 ± 1	9.4
BDE-154	75.1 ± 7.7	83.5 ± 2.0	10.2
BDE-183	44.3 ± 2.2	43.0 ± 3.5	5.0
BDE-209	2410 ± 189	2510 ± 190	7.8

Table 2.8 Concentrations (ng g^{-1}) of PBDEs measured in NIST SRM 2585 compared to certified values

	Measured value ± SD	**RSD (%)**
Tetra-furans	790 ± 108.9	13.8
Penta-furans	2923 ± 1304	44.6
Hexa-furans	2899 ± 1095	37.8
Tetra-dioxins	14.9 ± 2.9	19.7
Penta-dioxins	14.9 ± 4.7	31.3
Hexa-dioxins	34.4 ± 12.1	35.2

Table 2.9 – Measured PBDD/F concentrations (pg g^{-1}) in QC5 samples from Tata Steel

2.5.4 Analysis of blanks, LODs and LOQs

Instrumental limits of detection (LODs) were calculated for all studied compounds based on a 3:1 signal to noise ratio. The sample limits of quantification (LOQ) were then calculated using Equation 2.6:

$$LOQ = \frac{LOD \times F_{EV}}{V_{FEI} \times SS} \times \frac{100}{\%\, IS\ Recovery} \qquad \textbf{(Equation 2.6)}$$

Where F_{EV} is the final extract volume (µL); V_{FEI} is the volume of final extract injected (µL); SS = sample size (g or m^3); % IS Recovery = percentage recovery of the internal standard used to quantify the target pollutant in a particular sample. None of the target compounds were found in method blanks for soils, or raw materials. However, BDE-209 was detected in field blanks for passive air samples. Field blanks were used as a control for air samples and consisted of a pre-extracted PUF and baked glass fibre filter.

	UK Soil & Sinter Pot	**Australian Soil/Sediment**	**UK Air**	**Iron Ore Sintering Raw Materials**	**Stack Emission Samples**	
Compound	**pg/g**	**pg/g**	**pg/m^3**	**pg/g**	**Compound**	**pg/m^3**
BDE 17	2.6	-	0.21	-	2,3,7,8-TBDF	2.1
BDE 28	2.7	-	0.23	-	1,2,3,7,8-PeBDF	2.9
BDE 49	3	-	0.25	-	2,3,4,7,8-PeBDF	2.8
BDE 47	3.6	1.4	0.3	20	1,2,3,4,7,8-HxBDF	9.9
BDE 66	5.4	-	0.45	-	2,3,7,8-TBDD	2.2
BDE 100	5.4	2.6	0.45	3.4	1,2,3,7,8-PeBDD	2.4
BDE 99	5.9	2.1	0.49	2.7	1,2,3,4,7,8/1,2,3,6,7,8-HxBDD	7.6
BDE 85	8.9	2.6	0.74	6	1,2,3,7,8,9-HxBDD	8.3
BDE 154	11	2.1	0.89	5		
BDE 153	14	1.6	1.1	4.3		
BDE 183	18	1	1.5	3.8		
BDE 209	14	5	2.2	21		

Table 2.10 – Limits of quantification (LOQs) for various sample matrices

The level of BDE-209 detected in these samples was usually less than 5% of the amount found in samples from the same batch and thus no action was taken. However, on two occasions (sampling months two and three for PAS at Scunthorpe sintering plant, Tata Steel) field blank concentrations for BDE-209 were 10% and 11% respectively of the lowest concentration in the sample batch. In these cases, the mass of BDE-209 was subtracted from the mass detected in those particular samples, prior to the calculation of concentrations. Table 2.10 shows the LODs and LOQs for sample matrices based on typical sample sizes, internal standard recoveries and volume of final extract injected.

2.6 Statistical Analysis

A variety of statistical analyses were used to examine the data produced from the various studies in this project. Where it was possible individual data (as opposed to averages) were used for data comparison. For example, PBDE concentrations of the individual components of raw sinter mix were transformed to percentage contributions to total PBDE content and ranked to highlight any components contributing any significant PBDE contamination towards the raw sinter mix (Chapter 3). However, in some cases arithmetic mean values were used for ease of comparison with data both from within this thesis and the previous literature. When datasets are highly skewed, arithmetic averages can be misleading. When this is a potential issue in the thesis, a more robust measure of the central tendency, the median (as well as the interquartile ranges) are also reported.

In the majority of cases, variability within and between datasets was such that parametric statistical tests were unsuccessful/inappropriate. As a result, graphical (e.g. scatter plots, bar charts and box plots) and tabulated presentation of data was used extensively to demonstrate the results of this study, whilst principal component analysis and mass balances were used where appropriate.

Air samples are presented as mean concentrations for each location, with the ranges also presented. This is not the most statistically robust way to represent the central tendency and spread of a dataset, but is in line with practice in the discipline. For skewed distributions of the kind presented below it is more appropriate to use the interquartile range, or 5th and 95th percentiles for comparison, the absolute minimum and maximum values were usually used to demonstrate the large spatial and temporal variations of concentrations found in samples – especially those close to industrial and urban sources. Attempts were made to compare samples with any previous data on a like-for-like basis. For example, air samples from the same months were compared when investigating long-term temporal trends (thereby minimising comparability issues due to any potential seasonal variations in concentrations), whilst soils were compared based on organic carbon content when this was possible to do so.

Where possible, mean values were used for comparison, with t-tests and analysis of variance (ANOVA) applied to data to test for any significant differences between means. Non-parametric tests were also used to compare datasets (e.g. Mann-Whitney U Test) in cases where parametric tests were not appropriate. However, comparisons were also made using individual data for each sample as Pearson product-moment correlations were used to test for any linear trends that were indicated by graphical data.

Statistical analysis of data was carried out using a combination of Microsoft Excel (Microsoft Office versions 2007 and 2010) and SPSS for Windows (version 19.0). All confidence limits were set to 95% (i.e. significance (p) level of 0.05) for all statistical tests (t-test, ANOVA and Pearson product-moment correlation).

Chapter III

PBDEs and PBDD/Fs in the Sintering Process

3.1 Synopsis

In this chapter, concentrations of tri-hexa PBDEs were measured in raw material samples in 5 sinter beds from either Scunthorpe (SSP) or Port Talbot (PTSP) sinter plants (both in the UK). For each sinter bed, PBDEs were measured in input samples (raw sinter mix (RSM) n=6), as well as in output samples (Electrostatic Precipitator (ESP) dust (n=8) and Sinter Product (n=5). A single stack emission sample was also taken from sinter bed 719. The individual components of the raw sinter mix (input samples comprising 29 iron ores, 20 reverts, 4 fuels and 5 fluxes) are reported for tetra-deca PBDEs, along with ambient outdoor air samples from various locations around SSP. PBDD/Fs (tetra-hexa) are also reported in 15 stack emission samples (8 from SSP and 7 from PTSP) to investigate their presence within the iron-ore sintering process. The overall presence of PBDEs within the steel industry will be studied based upon mass balance measurements to quantify total PBDE inputs and outputs to and from the sintering process. The ambient air samples (using PAS) are designed to evaluate the impact of PBDE outputs from the Scunthorpe plant. Finally, the presence of PBDD/Fs will be studied in an effort to study the potential for their formation during the sintering process.

3.2 Sampling Strategy

3.2.1 Raw Material Sampling

Raw material samples were taken between 2009-2011 from either SSP or PTSP. The full sampling process of raw materials is outlined in 2.1.1. RSM samples were taken after all materials required for sintering had been homogenized, but before moisture had been added for pelletizing. ESP dust samples were taken directly from the ESP collection bags. The raw materials were sampled again after being sintered (sinter product was ground and homogenized). All samples were taken by Tata Steel and sent to the University of Birmingham for extraction, clean-up and analysis. Individual RSM component samples were also taken by Tata Steel just before mixture and homogenization.

3.2.2 Stack Emission Sampling

3.2.2.1 PBDEs

The stack emission sample was taken (as outlined in 2.1.2) in 2010 by Tata Steel at SSP and its raw extract (in toluene) was sent to the University of Birmingham for clean-up and analysis.

3.2.2.2 PBDD/Fs

Stack emission samples were taken in 2009-10 and had already been extracted and cleaned up (as described in 2.3.2) by the laboratories at Tata Steel and measured for PCDD/Fs via HRGC/HRMS. The PBDD/F results in this chapter are therefore semi-quantitative as internal standards (as in section 2.2.2) were added directly to the already cleaned extracts, meaning a potential underestimation of concentrations as internal standard recovery throughout the clean-up method is not taken into account. The method was checked for precision by using the steel company's internal quality control sample (QC5) which produced acceptably reproducible results for 5 replicate analyses (Table 2.9 in Section 2.5.3).

3.2.3 Outdoor Air Sampling of PBDEs

PAS were used (as outlined section in 2.1.4) to sample PBDEs in outdoor air within the vicinity of SSP. Five locations were chosen (Figure 3.5 in Section 3.4) both up- and downwind of SSP within the entire steel manufacturing plant along with a control site (Swinden Technology Centre, Rotherham) – a typical urban environment approximately 70 km southwest from SSP.

3.3 Concentrations of PBDEs in Raw Materials

3.3.1 Inputs and Output of PBDEs in Sintering Process

Raw material samples were classed into either input (RSM) or output (ESP dust, sinter product, stack emission) samples. Table 3.1 shows the concentrations of PBDEs in each sample. The concentrations of the input samples show that there is a clear contamination in the RSM before the sintering process has begun with a mean ∑PBDE concentration of 10,500 ng/kg. This finding contrasts with that of Wang et al. (2010b) who stated that PBDEs were formed in the sintering process based on there being no PBDE contamination in the raw materials. To further investigate this, a complete mass balance was carried out for all sinter beds to see whether the total mass for ∑PBDEs was higher before or after the process had taken place (N.B. as a stack emission sample was procured only for Bed 2272, an estimated ∑PBDE output via stack emission was estimated for all other beds using Equation 3.1)

$O_e = C_{E2272} \times (t \times S)$ (**Equation 3.1**)

Where O_e = Estimated output via stack emission; C_{E2272} = ∑PBDE concentration of stack emission sample from bed 719 (142.8 ng/m^3); t = duration of sintering process in the bed in question (s); and S = stack emission sampling rate (348 m^3/s).

Mass balance calculations (Figure 3.1) showed that in all cases there was a reduction in the total amount of ∑PBDEs after the sintering process had taken place, with a mean percentage reduction of 86% (range: 69-96%). These figures suggest that PBDEs are destroyed in the sintering process. However in view of the evidence mentioned in section 1.3.3 that PBDEs could act as precursors of PBDD/Fs within the sintering process, it cannot be ruled out that the PBDE reduction leads to an increase in PBDD/F formation.

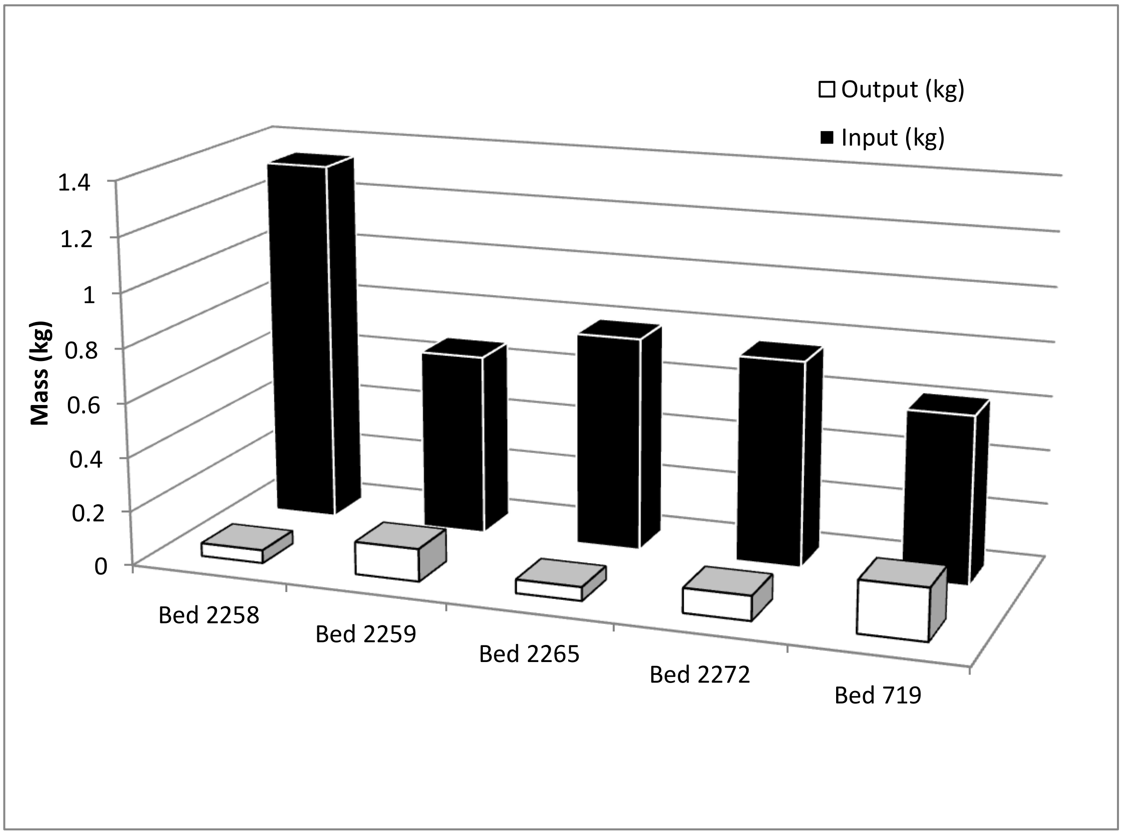


Figure 3.1 PBDE Inputs and Outputs for each sinter bed based on mass balance calculations

Input Samples

	Bed 2258	Bed 2259	Bed 2265	Bed 2272	Bed 719	
Congener	**RSM 1**	**RSM 2**	**RSM 3**	**RSM 4**	**RSM 5**	**RSM 6**
BDE-17	150	69	83	21	9.9	13
BDE-28	390	190	230	180	35	42
BDE-49	2000	940	1100	940	170	191
BDE-47	3800	1900	2300	2300	240	770
BDE-85	1000	570	540	710	0	0
BDE-100	1400	760	200	710	200	340
BDE-99	10000	5100	6500	5600	920	1100
BDE-153	2600	1300	1700	1400	330	400
BDE-154	500	270	390	620	97	110
∑PBDEs	**22000**	**11000**	**13000**	**12000**	**2000**	**3000**

Output Samples

	Bed 2258	Bed 2259	Bed 2265	Bed 2272		Bed 719		
	ESP 1	**ESP 2**	**ESP 3**	**ESP 4**	**ESP 5**	**ESP 6**	**ESP 7**	**ESP 8**
BDE-17	89	78	120	230	89	29	22	80
BDE-28	250	250	330	790	360	86	67	80
BDE-49	1300	1400	1500	5000	2200	460	510	530
BDE-47	2400	2500	2700	11000	4800	1600	1400	2200
BDE-85	850	980	820	5500	2700	530	90	0
BDE-100	1600	1700	1300	5000	3100	1600	1400	1600
BDE-99	9300	11000	7700	53000	25000	4200	2600	2900
BDE-153	5300	4900	4300	23000	12000	2400	1600	2000
BDE-154	1100	1200	1000	5200	2500	500	500	660
∑PBDEs	**22000**	**24000**	**20000**	**110000**	**53000**	**11000**	**8200**	**10000**

	Bed 2258	Bed 2259	Bed 2265	Bed 2272	Bed 719		Bed 719
	Sinter Product 1	**Sinter Product 2**	**Sinter Product 3**	**Sinter Product 4**	**Sinter Product 5**		**Stack Emission[b]**
BDE-17	1.6	20	6.1	0	13		2.3
BDE-28	3.7	27	7.8	24	14		1.9
BDE-49	14	54	16	260	20		0
BDE-47	78	760	190	270	280		31
BDE-85	160	160	13	250	9.3		5.9
BDE-100	130	260	130	0	33		11
BDE-99	130	310	80	86	86		39
BDE-153	0	270	83	240	67		13
BDE-154	0	300	53	93	61		39
∑PBDEs	**520**	**2200**	**580**	**1200**	**580**		**140**

[a] all values are to 2 significant figures and therefore ∑PBDEs may not be the same value as the sum of the above congeners; [b] stack emission sample is in ng/m^3; all others are ng/kg

Table 3.1 – Concentrations of PBDEs in input and output samples of the sintering process

3.3.2 Raw Sinter Mix Components

As a result of identifying substantial PBDE contamination in all RSM input samples, it was important to attempt to identify which RSM component(s) contribute towards this contamination. All components of the mixture were analysed for PBDEs (BDEs -47, -85, -99, -100, -153, -154, -183 and -209). RSM is made up of four main component groups – iron ores; reverts (recycled sinter mix from the blast furnace); fuels (coke); and fluxes (limestone). Specific proportions of materials from each of these are used to create a homogenised RSM, an example of which is shown in Table 3.2.

Bed 2275	**Tonnes**	Contribution (%)
Ore 4	18320	29.7
Ore 9	10534	17.1
Ore 13	5453	8.8
Revert 3	1267	2.1
Revert 7	1797	2.9
Revert 8	1414	2.3
Revert 12	2254	3.7
Revert 14	3010	4.9
Revert 15	2498	4.1
Revert 17	8024	13.0
Fluxes 1	250	0.4
Fluxes 4	2760	4.5
Fluxes 2	1602	2.6
Fuel 2	2437	4.0
TOTAL	61620	100.0

Table 3.2 – The complete make up of RSM used for Sinter Bed 2275 at PTSP

Every component used by the UK based steel company (as in Section 3.1) was analysed for PBDEs. In the majority of cases, BDE-209 was the dominant congener. All components were ranked within their component groups by both their ∑PBDE concentration and BDE-209 concentration (Table 3.3). There is a clear variation in the levels of contamination within each component group with extremely wide ranges (iron ores – 19-120000 ng/kg, reverts – 110-32000 ng/kg, fuels – 840-18000 ng/kg, fluxes – 87-1500 ng/kg), meaning that the level of contamination within a specific sinter bed is highly dependent on which specific components are used from each group.

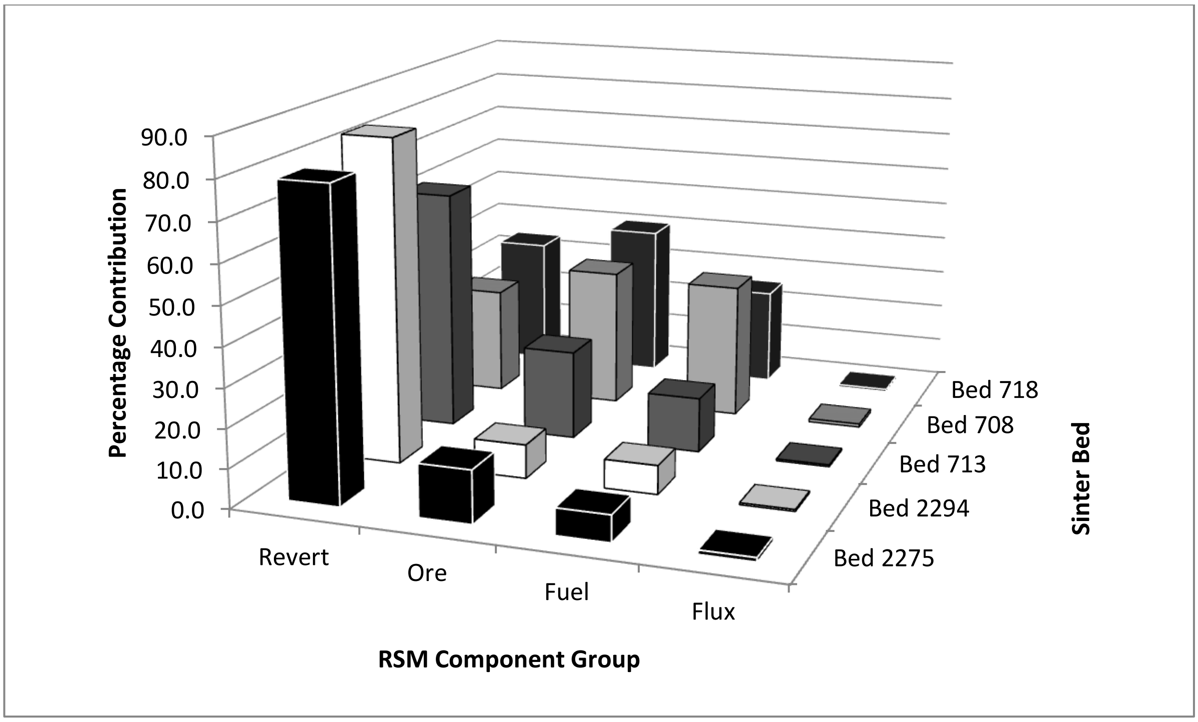


Figure 3.2 The percentage contribution of each component group to PBDE input in different sinter beds.

The proportions shown in Figure 3.2 demonstrate the variability of the original source of PBDEs within the RSM, with only fluxes contributing comparatively insignificant amounts of PBDEs.

With reverts being the only component that is sourced internally, this study shows that up to 60% of the ∑PBDE content in RSM can come from externally sourced materials (iron ores and fuels). When comparing the iron ore ∑PBDE concentrations (19-120000 ng/kg) to those reported for soils as cited in Chapter 1, in locations as diverse as Spain (Eljarrat et al., 2008), China (Chen et al., 2012), USA (Yun et al., 2008) and Sweden (Sellstrom et al., 2005) it was found that all 29 ores fall within the range of concentrations reported previously for soils (140-260000 ng/kg), as do the fuels and fluxes. Moreover, as the reverts are recycled metallic flue dusts from the blast furnace (which only uses the materials prepared by the sintering process), this contamination must also originate from the same external sources suggesting that the majority of PBDE contamination within the sintering process comes from external sources, before the process has even begun. The higher concentrations of reverts is, at this stage, unexplained, however it could be due to the concentration of contaminated particulate matter as the flue dust is extracted from the blast furnace. However, more tests are required as formation or another source of contamination within the blast furnace has neither been identified nor eliminated.

Input Component	**∑PBDE Conc.**	**Rank**	**BDE-209 Conc.**	**Rank**	**Input Component**	**∑PBDE Conc.**	**Rank**	**BDE-209 Conc.**	**Rank**
Ore 1	3800	4	2800	4	Revert 1	1817	12	770	15
Ore 2	670	15	267	17	Revert 2	1037	16	1600	12
Ore 3	250	25	61	25	Revert 3	1800	13	1000	13
Ore 4	1090	12	900	8	Revert 4	2300	11	2000	11
Ore 5	81	27	39	27	Revert 5	17000	3	6200	8
Ore 6	470	18	390	14	Revert 6	660	17	310	17
Ore 7	520	16	120	21	Revert 7	17000	4	15000	3
Ore 8	260	24	130	20	Revert 8	110	20	80	20
Ore 9	1800	9	540	11	Revert 9	11000	7	8500	6
Ore 10	290	22	79	23	Revert 10	3800	10	3400	10
Ore 11	350	21	100	22	Revert 11	6100	9	4900	9
Ore 12	2900	5	2600	5	Revert 12	7900	8	7600	7
Ore 13	390	20	200	18	Revert 13	32000	1	30000	1
Ore 14	720	14	670	10	Revert 14	32000	2	22000	2
Ore 15	1900	7	370	15	Revert 15	1300	14	900	14
Ore 16	420	19	320	16	Revert 16	14000	5	14000	4
Ore 17	77	28	46	26	Revert 17	12000	6	12000	5
Ore 18	107	26	65	24	Revert 18	530	18	214	18
Ore 19	2700	6	1700	6	Revert 19	370	19	157	19
Ore 20	19	29	19	29	Revert 20	1100	15	680	16
Ore 21	4500	3	2800	3	Fuel 1	18000	2	9800	2
Ore 22	1900	8	1100	7	Fuel 2	9000	3	4100	3
Ore 23	280	23	190	19	Fuel 3	22000	1	20000	1
Ore 24	1200	10	780	9	Fuel 4	840	4	800	4
Ore 25	830	13	390	13	Fluxes 1	240	3	190	2
Ore 26	1100	11	25	28	Fluxes 2	1500	1	580	1
Ore 27	22000	2	12000	2	Fluxes 3	87	5	74	5
Ore 28	120000	1	94000	1	Fluxes 4	270	2	82	3=
Ore 29	480	17	480	12	Fluxes 5	104	4	82	3=

Table 3.3 – Concentrations of ∑PBDEs and BDE-209 (ng/kg) in all input components along with their rank from highest to lowest for each value.

3.3.3 Congener profile of raw material components

The mean congener profiles in each group of RSM components used in the beds mentioned in Figure 3.2 was calculated. In reverts, fluxes and fuels BDE-209 was the predominant congener (comprising 97%, 44%, 54% of ∑PBDE respectively), whilst it made up only 39% of ∑PBDEs in ores, albeit second only to BDE-47 (46%). Figure 3.3 shows the mean congener profiles of all groups with BDE-209 excluded (∑PBDE$_{47:183}$). The profile suggests that there is an input of congeners prevalent in all three commercial formulations present in all 4 components of the RSM, with Deca-BDE-like contamination predominant, followed very closely by that akin to Penta-BDE dominating ∑PBDE input. Moreover, the presence – albeit at low levels – of BDEs -153, -154 and -183 suggests a small minor input of Octa-BDE. Considering the raw materials for the sintering process are sourced from all continents, this very much reflects the global usage of PBDEs mentioned in Chapter 1, whilst it further suggests that PBDEs are present in the inputs to the sintering process and are thus perhaps not formed as a result of it. The source of this PBDE contamination to the sintering process is currently unknown, although it is assumed that the contamination occurs at some point between the mining of iron ore and coal, storage, transportation and preparation for the commercial sintering process. However, with almost 30 different sources of iron ore sourced and transported across the world from many different countries and continents (along with a similar setting for coal), locating this source was not feasible during the lifespan of this study.

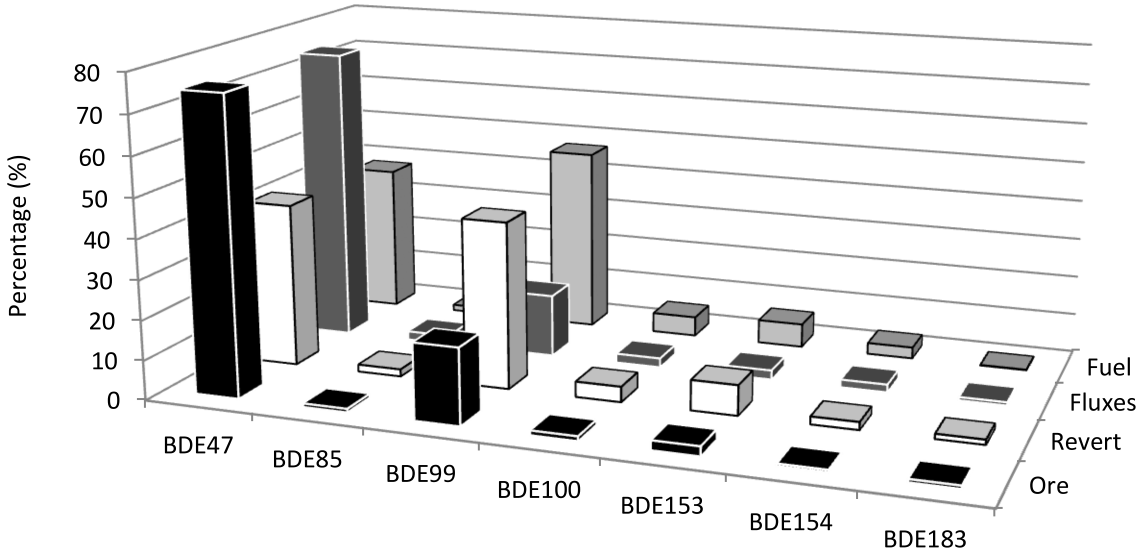


Figure 3.3 Mean ∑PBDE$_{47:183}$ congener profile in RSM component groups

Using data on tonnages provided by Tata Steel such as that in Table 3.2, the congener profile of the total PBDE input was calculated for each sintering bed. Whilst BDE-209 was the most commonly detected congener in the 5 beds monitored (60-96% contribution), there was also a noticeable contribution from congeners typical of the Penta-BDE formulation with BDEs -47 and -99 contributing 6.8-15% and 7.8-18% of the total PBDE input into the sintering process. Figure 3.4 demonstrates the contribution of Penta-BDE congeners to total PBDE input within the sintering process. The figure also demonstrates that there is a variation in congener profiles between each sinter bed, with BDE-209 making up 96% of total PBDE content for Bed 2294. This is due to the large number of different ores, fuel, reverts and fluxes used to create different RSMs meaning that the congener profile is completely dependent upon the tonnages and PBDE concentrations of each RSM component used for each sintering bed.

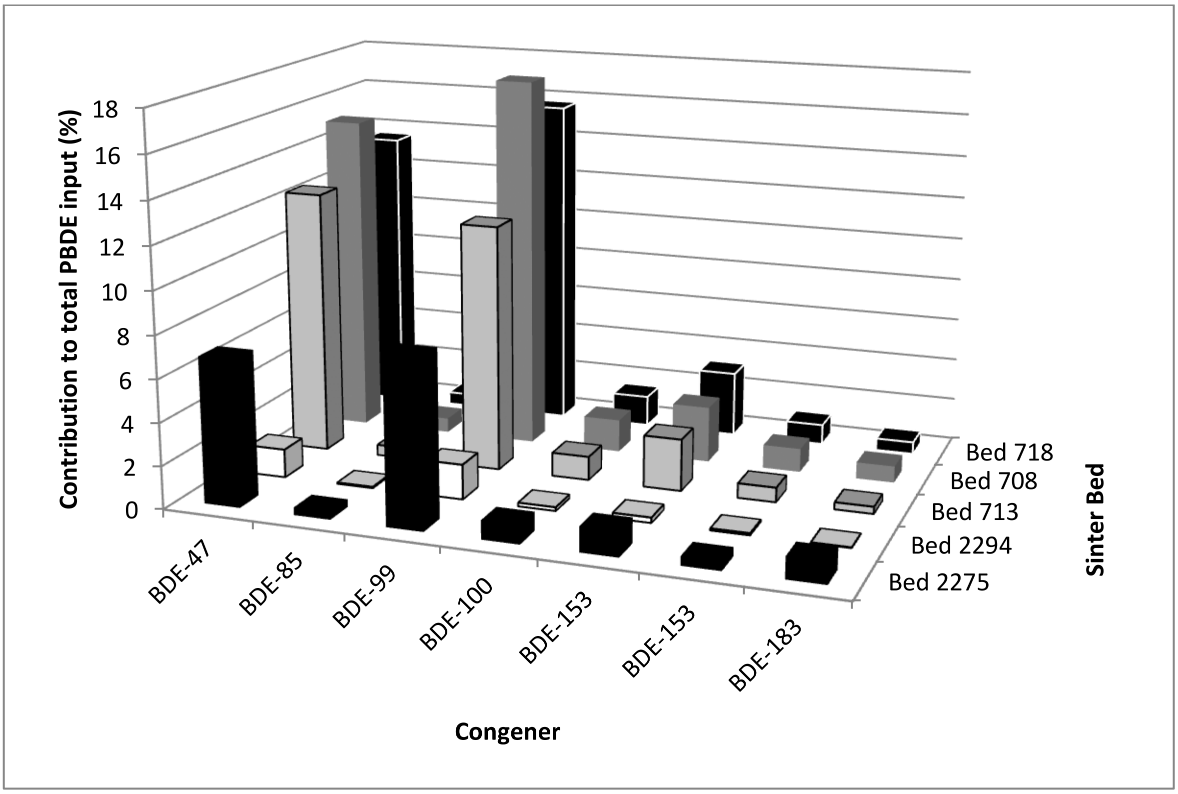
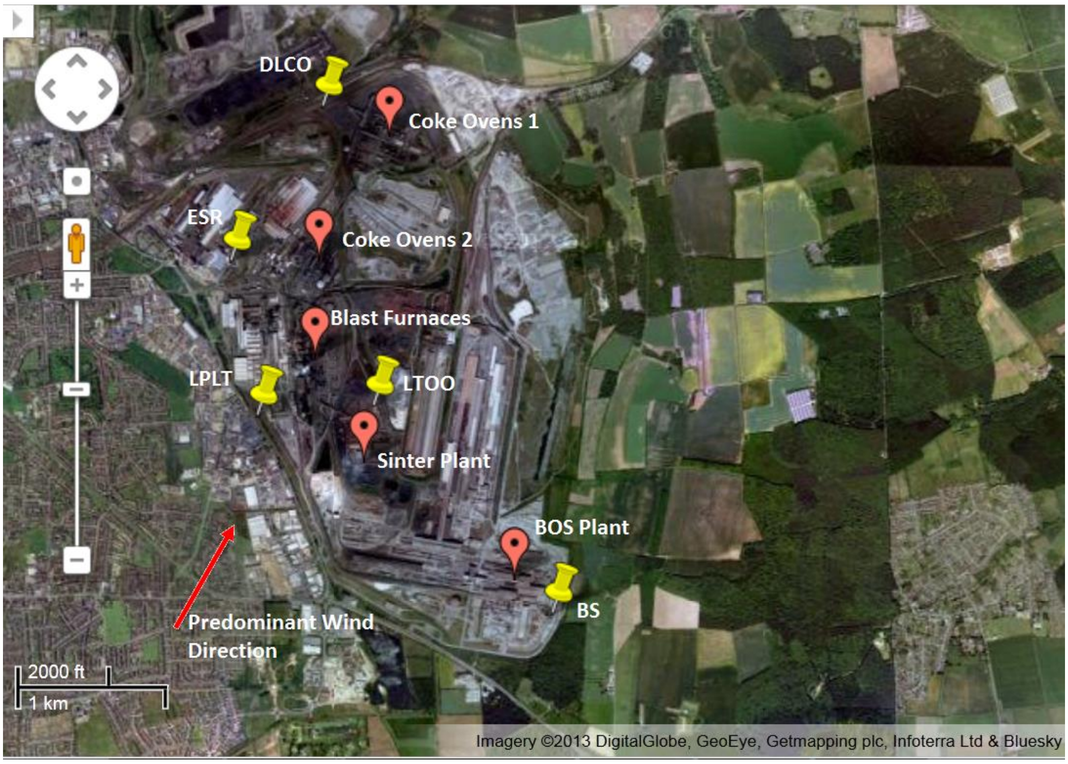


Figure 3.4 Contribution of BDEs $_{47:183}$ to total PBDE input in various sinter beds

3.4 Ambient Air Concentrations in the vicinity of a sinter plant

The average PBDE concentrations in PAS were calculated (Table 3.4) based on the PBDE masses detected in each sampler and the air sampling rates derived from the calibration experiment described in Chapter 2.

Ambient air samples all contained detectable levels of BDE-209, including the control site away from the sinter plant. However, ∑PBDE concentrations increased from background levels upwind of the sinter plant (Broughton Substation – 550 pg/m^3) to more than 6 times higher downwind (DLCO – 3,400 pg/m^3). A t-test showed that the mean ∑PBDE concentration downwind of the sinter plant ((LTOO, LPLT, ESR, DLCO) 2800 pg/m^3) was significantly higher than that of the control site (AT (Swinden Technology Centre, Rotherham), p = 0.009) and of the upwind sampling site (BS, p = 0.003).



Yellow pins = sampling locations. BS = Broughton Substation; LTOO = Lighting Tower Opposite Office; LPLT = Lorry Park Lighting Tower; ESR = Environmental Services Roof; DLCO = Dawes Lane Coke Ovens; Red markers show locations of key processes around the steel works

Figure 3.5 PAS locations up and downwind of SSP in Scunthorpe Integrated Steelworks.

The PBDE concentrations in Table 3.4 indicate that there would be an increased daily intake of PBDEs by employees working in and around sinter plants, especially directly downwind from the sinter plant itself. Using the following equation, adapted from that used by many other authors over the past decade (Besis and Samara, 2012, Harrad et al., 2004, Harrad et al., 2006, Gevao et al., 2006, Mandalakis et al., 2008), the estimated occupational exposure for PBDEs can be estimated as

$$Intake_{air}\ (pg/hour)\ = (C_w F_w) \times R_R$$

where R_R is the average respiration rate; C_w is the concentration of air from the work place; F_w is the time spent in the work place (to get an hourly rate a value of 1 is applied here). An adult based R_R of 0.67 m^3/hour was calculated based on a recommended figure of 16 m^3/day by the US Environmental Protection Agency (U.S. EPA (2011)).

	PBDE concentrations - mean (range) pg/m^3					
Sample Site	**Broughton Substation (BS)**	**Lighting Tower opposite Office (LTOO)**	**Lorry Park Lighting Tower (LPLT)**	**Environmental Services Roof (ESR)**	**Dawes Lane Coke Ovens (DLCO)**	**Swinden Technology Centre (Control)**
n	5	3	1	2	5	3
BDE-47	12 (0-26)	51 (24-93)	8.5	59 (48-70)	860 (184-1500)	6.5 (2.0-11)
BDE-85	1.4 (0.30-3.0)	7.2 (3.5-15)	<0.7	4.1 (0.5-7.7)	69 (6.6-180)	1.0 (0.37-2.1)
BDE-99	8.1 (4.0-11))	85 (65-110)	7.3	60 (26-94)	1000 (300-2100)	2.7 (0.15-6.23)
BDE-100	3 (0.4-9.9)	6.3 (3.3-8.0)	0.77	6.2 (2.3-10)	70 (12-170)	0.17 (<0.5-1.0)
BDE-153	2.1 (1.7-3.0)	8.8 (4.2-13)	1.3	9.5 (2.0-17)	160 (47-360)	0.57 (<1.1-1.0)
BDE-154	0.66 (<0.5-1.0)	1.7 (1.1-2.0)	1.5	1.3 (1.3-1.4)	34 (4.0-86)	0.42 (<0.5-0.65)
BDE-183	1.3 (<0.5-2.79)	1.4 (0.26-2.1)	1.2	0.71 (0.16-1.3)	6 (2.6-14.6)	0.58 (<0.5 -1.7)
BDE-209	520 (170-870)	2300 (1600-3000)	2200	2500 (800-4100)	1100 (290-2200)	770 (340-1400)
∑PBDEs	530 (180-890)	2400 (1800-3200)	2200	2600 (880-4300)	3400 (1200-6600)	780 (400-1400)

Table 3.4 – Concentrations of PBDEs in ambient air within the vicinity of SSP and at a control location

Using an average concentration of 2,800 pg/m^3 downwind from the sinter plant, the exposure rate through inhalation of air was calculated as 1,900 pg/hour, which is 4.3 times higher than the average exposure from inhalation at upwind or control sites (470 pg/hour). Using data for the same congeners in ambient air in the West Midlands (presented in Chapter 5), an exposure of 170 pg/hour was calculated, which is more 10 times lower than downwind of the sinter plant. One-sample t-tests confirmed that the PBDE intake through air is significantly raised compared to that upwind ($p = 0.003$), at the control site ($p = 0.009$) or in the West Midlands ($p=0.001$), confirming increased occupational exposure to PBDEs for those working around the sinter plant.

3.4.1 Congener profile of ambient air samples

With the exception of DLCO, mean congener profiles of PAS in the sinter plant are all very similar to that of the control site with BDE-209 constituting in excess of 95% of the total PBDE content. DLCO, however has a very high proportion of BDEs -47 and -99 along with more elevated levels of BDE-100, which is very typical of a commercial PentaBDE source. There are also marginally increased levels of BDEs -153, -154 and -183, which is also an indicator of potential Octa-BDE usage. Whilst the BDE-209 dominance is lower, its concentration remains similar, although slightly lower (1100 pg/m^3), than the other sites at SSP. DLCO samples appear to have a congener profile similar to those of the raw material components in 3.3.1. where there was a mixture of congeners from all three commercial formulations, with a dominance of BDEs -47, -99 and-209. The relatively high levels of BDEs -47, -99 and -153 in RSM demonstrated by Figure 3.4, appear to contribute to the ambient air concentrations at DLCO. A principal component analysis (PCA) was conducted for all measured congeners in all ambient air samples (Figure 3.6). Principal Components 1 and 2 accounted for 80.6 and 12.8 % of the total variance in the data. The rotated component matrix shows the relative contribution of each congener to each principal component score (Table. 3.5). A high score for principal component 1 (PC1) indicated relatively high contributions of the lower brominated PBDE congeners (i.e. BDEs -47, -85, -99, -100 which are indicative of usage of the Penta-BDE formulations), whilst a low or negative score meant a higher proportion of BDE-209 (indicative of Deca-BDE formulations). Principal component 2 (PC2) was driven in a positive direction by higher levels of BDE-183 (dominant of the Octa-BDE formulations (La Guardia et al., 2006)).

	Component	
	1	2
47	.908	.153
85	.966	-.070
99	.973	.076
100	.895	.156
153	.984	.072
154	.983	-.034
183	.064	.996
209	-.979	-.115

Table 3.5 Rotated component matrix score table – reproduced from SPSS output file

As expected, DLCO samples displayed much higher scores for PC1 than all other samples taken within the vicinity of SSP and at the control site, reflecting the dominance of tetra- and penta- brominated PBDE congener in DLCO samples. DLCO also had markedly more positive scores for 3 out of 5 samples PC2, reflecting a greater contribution of BDE-183 to total PBDE content in the DLCO samples than observed in others. The combination of PC1 and PC2 demonstrates the influence of Penta-BDE and perhaps Octa-BDE congeners within the ambient air surrounding DLCO. In contrast, all other samples more upwind of the coke ovens and away from the prevailing wind direction with respect to the sinter plant and coke ovens had negative scores for both PC1 and PC2 reflecting the pre-dominant contribution of BDE-209 to the total PBDE content, very similar to the control site, suggesting ambient air, away from the coke ovens and sinter plant was more in line with background air found in urban locations. Whilst the (log) mean PBDE concentrations in ambient air surrounding SSP are significantly higher than those in the West Midlands outdoor air concentrations presented in Chapter 5 (t-test, $p < 0.05$); the mean congener profile of all SSP samples except DLCO appear to have a similar mean congener profile to that in the West Midlands which is dominated by BDE-209 (97 and 82 % BDE-209 in the SSP (except DLCO) and the West Midlands sample respectively).

These differences in congener profile provide evidence that there is a source of PBDEs within the integrated steel works other than normal diffuse urban sources. This, combined with the increased concentrations downwind of SSP, provides strong evidence to suggest that the iron ore sintering process is the source of elevated PBDEs found in the vicinity of SSP. The differences in congener profile and ∑PBDE concentration at DLCO could possibly be due to one or more of the following reasons: i) LPLT and LTOO are too close to be impacted fully by emissions from the sinter plant ii) ESR is not in line with the typical wind direction from the sinter plant and therefore is less impacted by sinter plant emissions; and iii) DLCO is close to the coke ovens (where the fuels measured in 3.3 are prepared), which may represent the actual source of Penta-BDE like congeners into the atmosphere.

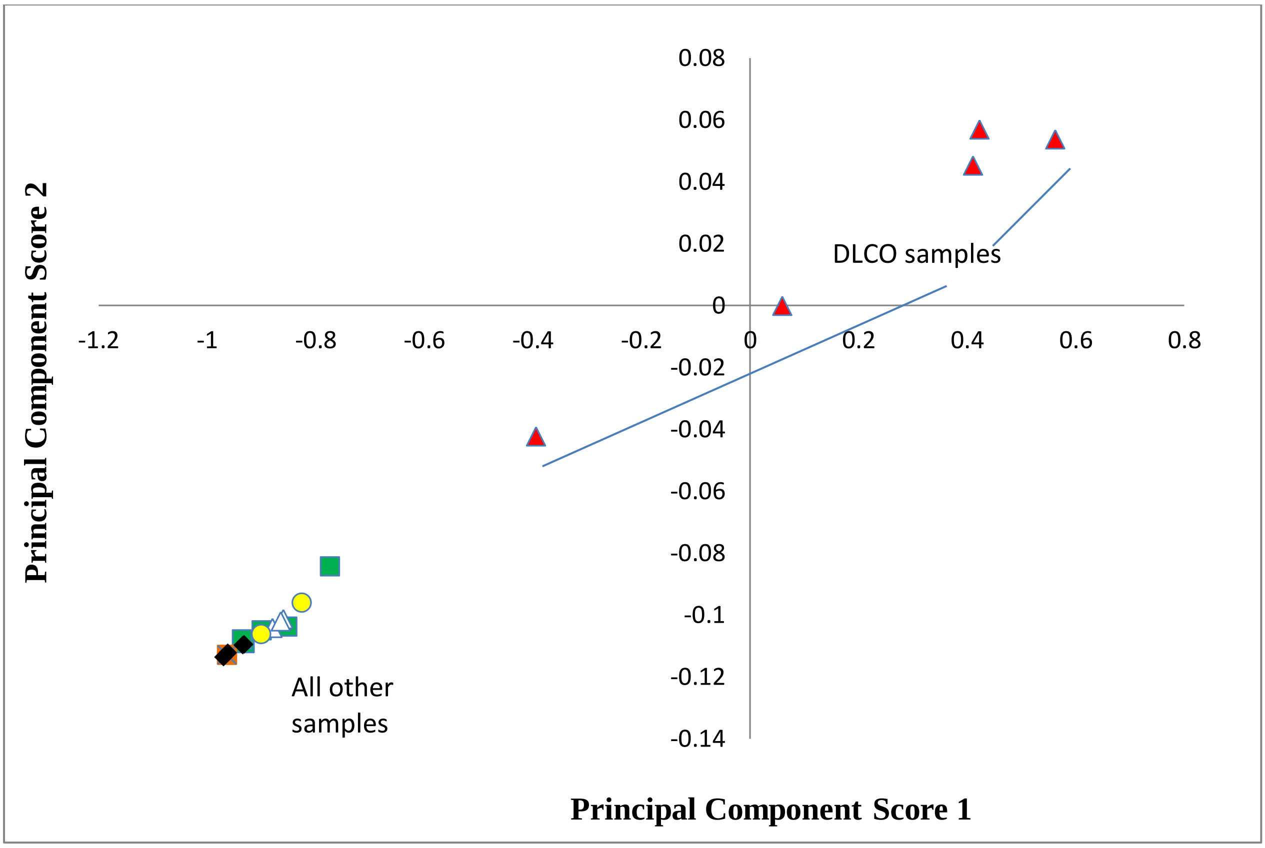


Figure 3.6 Principal component analysis for PBDEs in ambient air samples around SSP and control

Ideally, ambient air concentrations would also have been measured in residential areas close to the integrated steel works. However, this was not feasible during this study. Li et al. (2011) examined the concentrations of PBDEs in ambient air from areas around an integrated steel works in China. They used passive samplers similar to those deployed in this study, however they only employed PUF disks in their samplers and not glass fibre filters, and therefore primarily sampled PBDEs in the gaseous phase, thereby potentially severely underestimating concentrations of BDE-209 and other higher brominated congeners that partition preferentially into the particulate phase. They concluded that there was no significant difference between the concentrations of PBDEs in air from areas around the steel plant (including a sinter plant) and at their control site, meaning that the high levels of PBDEs within the sintering process appeared unlikely to affect local residents. This could be confirmed in future work at our monitoring locations, by measuring PBDE concentrations in passive air samples from residential areas close to SSP to evaluate the existence of increment in concentrations.

3.5 Concentrations of PBDD/Fs in Stack Emission Samples

Table 3.6 shows that PBDD/Fs were detected in all emission samples with PBDFs ten-fold higher than PBDDs (0.12-1.3 ng/m^3 and 0.0052-0.13 ng/m^3 respectively), confirming that PBDDs and PBDFs are emitted in the sintering process, particularly PBDFs.

The mean PBDD/F WHO-TEQ (0.14 ng WHO-TEQ/m^3) concentrations were on average 10 times lower than those for PCDD/Fs, based on the same congeners (range: 3.4-37). These higher concentrations of the chlorinated analogues (shown in Figure 3.7) could be due to the addition of potassium chloride for enhanced sinter densification in “activated sintering”, which is designed to make the sintering process more efficient by providing a lower activation energy for diffusion (Nzihou et al., 2005). It is possible, that if bromide was added in this way, that PBDD/Fs would be formed at a similar rate to PCDD/Fs.

The highest PBDD/F TEQ concentration in this study was 0.39 ng WHO-TEQ/m^3 which is approximately a third of that found by Du et al. (2010a) in stack emissions from a sinter plant in China (1.1 ng WHO-TEQ/m^3). However, they also measured stack emission samples from several other combustion processes (hazardous waste incineration, municipal waste incineration, crematoriums, electric arc furnaces, lead smelting, aluminium smelting, copper smelting and zinc smelting), of which only zinc smelting (1.5 ng WHO-TEQ/m^3) produced higher concentrations than their own measurement of emissions from the sintering process. However, PBDD/F concentrations in stack emissions from lead smelting (0.7 ng WHO-TEQ/m^3) were approximately four times higher than the mean concentration found in this study for iron ore sintering (0.17 ng WHO-TEQ/m^3), whilst EAF and copper smelting were more than double (0.35 and 0.39 ng WHO-TEQ/m^3 respectively).

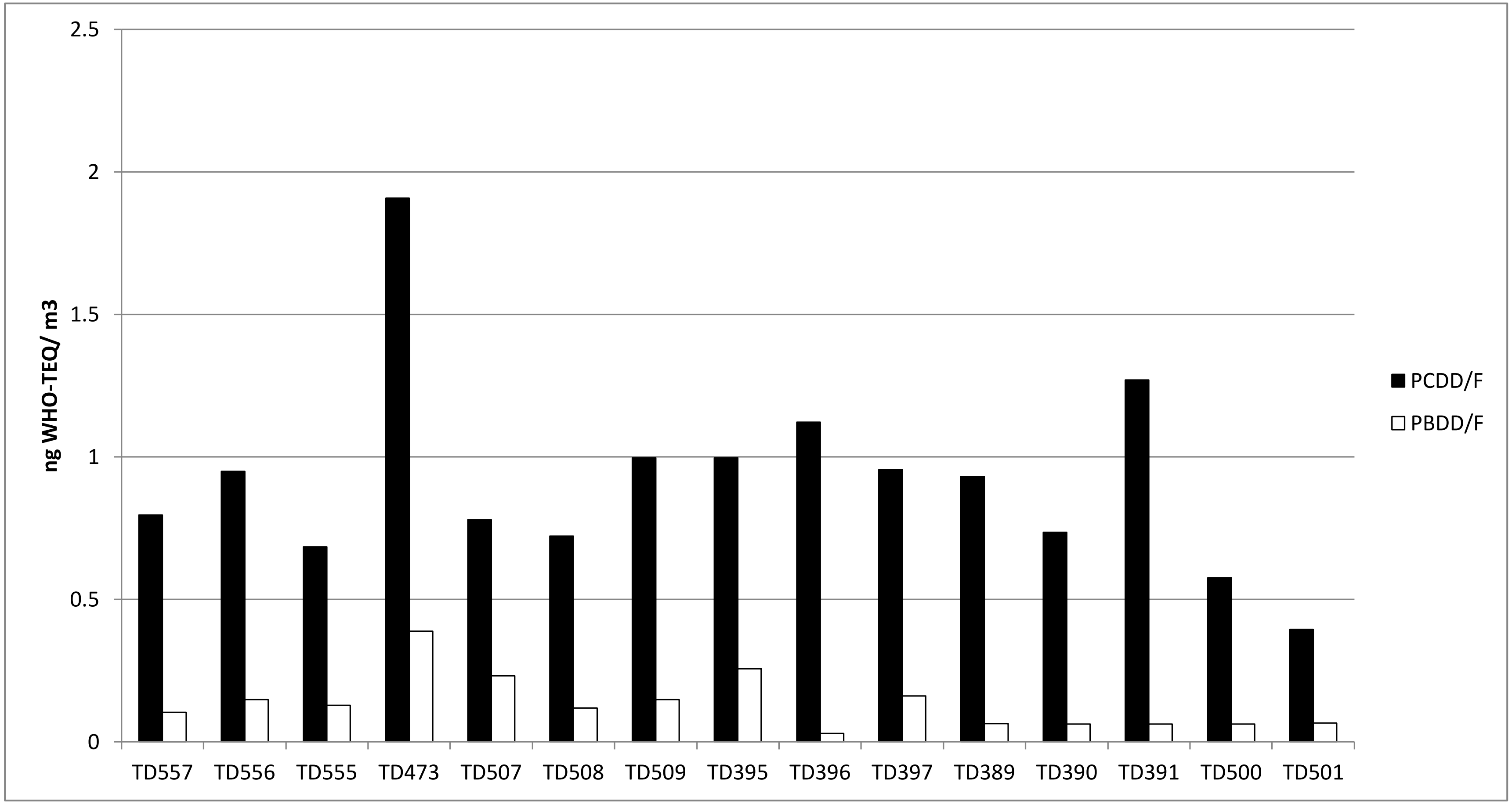


Figure 3.7 WHO-TEQ concentrations (ng/m^3) for PBDD/Fs and PCDD/Fs in sinter plant stack emission samples.

	SSP Emission Samples							
	Concentration (ng/m^3)							
Compound	**TD395**	**TD396**	**TD397**	**TD389**	**TD390**	**TD391**	**TD500**	**TD501**
2378-TBDF	0.28	0.037	0.21	0.077	0.079	0.073	0.11	0.093
12378-PeBDF	0.38	0.048	0.22	0.073	0.065	0.064	0.071	0.075
23478-PeBDF	0.31	0.037	0.19	0.063	0.053	0.069	0.062	0.070
123478-HxBDF	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
∑PBDF	0.97	0.12	0.62	0.21	0.20	0.21	0.24	0.24
2378-TBDD	0.038	0.0026	0.018	0.016	0.021	0.017	0.012	0.013
12378-PeBDD	0.019	0.0026	0.015	0.0047	0.0046	<dl	0.0042	0.0044
123478/123678-HxBDD	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
123789-HxBDD	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
∑PBDD	0.057	0.0052	0.033	0.021	0.026	0.017	0.016	0.017
WHO-TEQ	0.26	0.030	0.16	0.064	0.063	0.062	0.062	0.066

	PTSP Emission Samples						
	Concentration (ng/m^3)						
Compound	**TD557**	**TD556**	**TD555**	**TD473**	**TD507**	**TD508**	**TD509**
2378-TBDF	0.16	0.15	0.14	0.57	0.23	0.17	0.40
12378-PeBDF	0.14	0.16	0.14	0.39	0.30	0.16	0.16
23478-PeBDF	0.12	0.21	0.17	0.34	0.22	0.14	0.14
123478-HxBDF	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
∑PBDF	0.42	0.52	0.45	1.3	0.75	0.47	0.70
2378-TBDD	0.12	0.011	0.013	0.12	0.064	0.014	0.021
12378-PeBDD	0.0090	0.0072	0.0096	0.020	0.017	0.0091	0.0084
123478/123678-HxBDD	<0.002	<0.002	0.0032	<0.002	0.017	<0.002	<0.002
123789-HxBDD	<0.003	<0.003	<0.003	<0.003	0.0056	<0.003	<0.003
∑PBDD	0.13	0.018	0.026	0.032	0.10	0.023	0.029
WHO-TEQ	0.10	0.15	0.13	0.39	0.23	0.12	0.15

Table 3.6 – PBDD/F concentrations (ng/m^3) in emission samples from SSP and PTSP

Figure 3.8 demonstrates that on average PBDFs contributed 93% to the total PBDD/F concentration in stack emission samples with 35, 31 and 28% from 2,3,7,8-TBDF, 1,2,3,7,8 PeBDF and 2,3,4,7,8-PeBDF respectively. Du et al. (2010a) found a similar pattern with PBDFs contributing an average of 75% of total PBDD/F content in a sinter plant stack emission sample. Whilst they detected measurable levels of 1,2,3,4,7,8-HxBDF, the same congener was always below the limits of detection in this study. The overall pattern observed by Du et al. (2010a) appeared to be that PBDFs were formed preferentially to PBDDs with PBDFs comprising up to 92% of total PBDD/F concentrations (Figure 3.9) in the various combustion processes in which they have been measured.

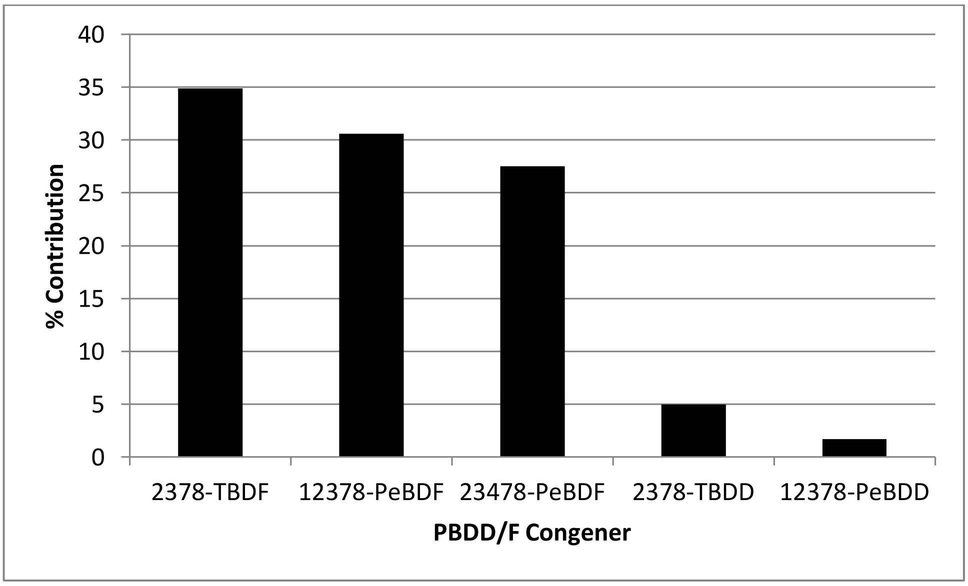
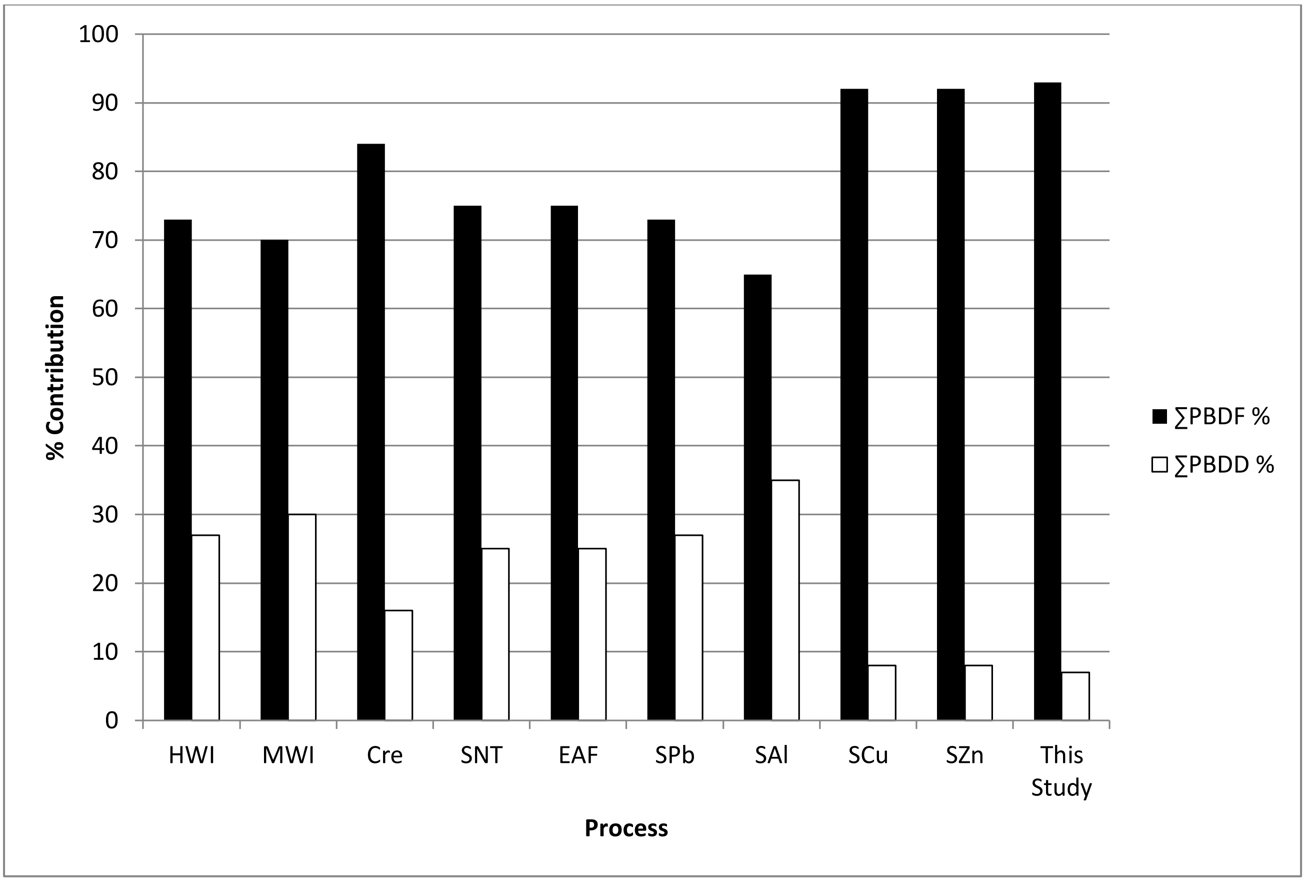


Figure 3.8 Mean % Contribution of each congener to total PBDD/F concentration in stack emissions from the sintering process

This congener pattern has also been observed in air (Figure 3.10) with 44%, 24% and 27% of ∑PBDD/Fs in ambient air from Shanghai coming from 2,3,7,8-TBDF, 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF respectively (Li et al., 2008). Similar patterns have also been observed in Taiwan in air from a mixture of rural, urban and industrial locations (Wang et al., 2008) as well as in Guiyu, China in areas close to e-waste recycling sites (Li et al., 2007). To our knowledge there are no available data on PBDD/Fs in UK air for comparison.



HWI = Hazardous Waste Incineration; MWI = Municipal Waste Incineration; Cre = Cremation; SNT = Iron Ore Sintering; EAF = Electric Arc Furnace; SPb = Lead Smelting; SAl = Aluminium Smelting; SCu = Copper Smelting; SZn = Zinc Smelting

Figure 3.9 Mean % Contribution of PBDFs and PBDDs to total PBDD/F concentration in various processes measured by Du et al. (2010a)

The evidence of this chapter suggests strongly that there is definite contamination by PBDEs within the steel-manufacturing process. However, their overall presence appears to be dramatically reduced as a result of the sintering process as revealed by the mass balance calculations conducted. Whilst the mass of PBDEs decreased on passing through the sintering process, concentrations of PBDD/Fs were detected in stack emission samples. Although these PBDD/F concentrations are much lower than those of their chlorinated analogues, this may indicate their potential formation within the iron ore sintering process. Furthermore, with the PBDD/F congener profile revealing that PBDFs are substantially more abundant than PBDDs in sinter plant emission samples, it is possible that the decrease observed in PBDE levels during sintering is related to PBDD/F formation; as it has been shown previously that PBDFs are preferentially formed over PBDDs during thermal degradation of PBDEs (Weber and Kuch, 2003).

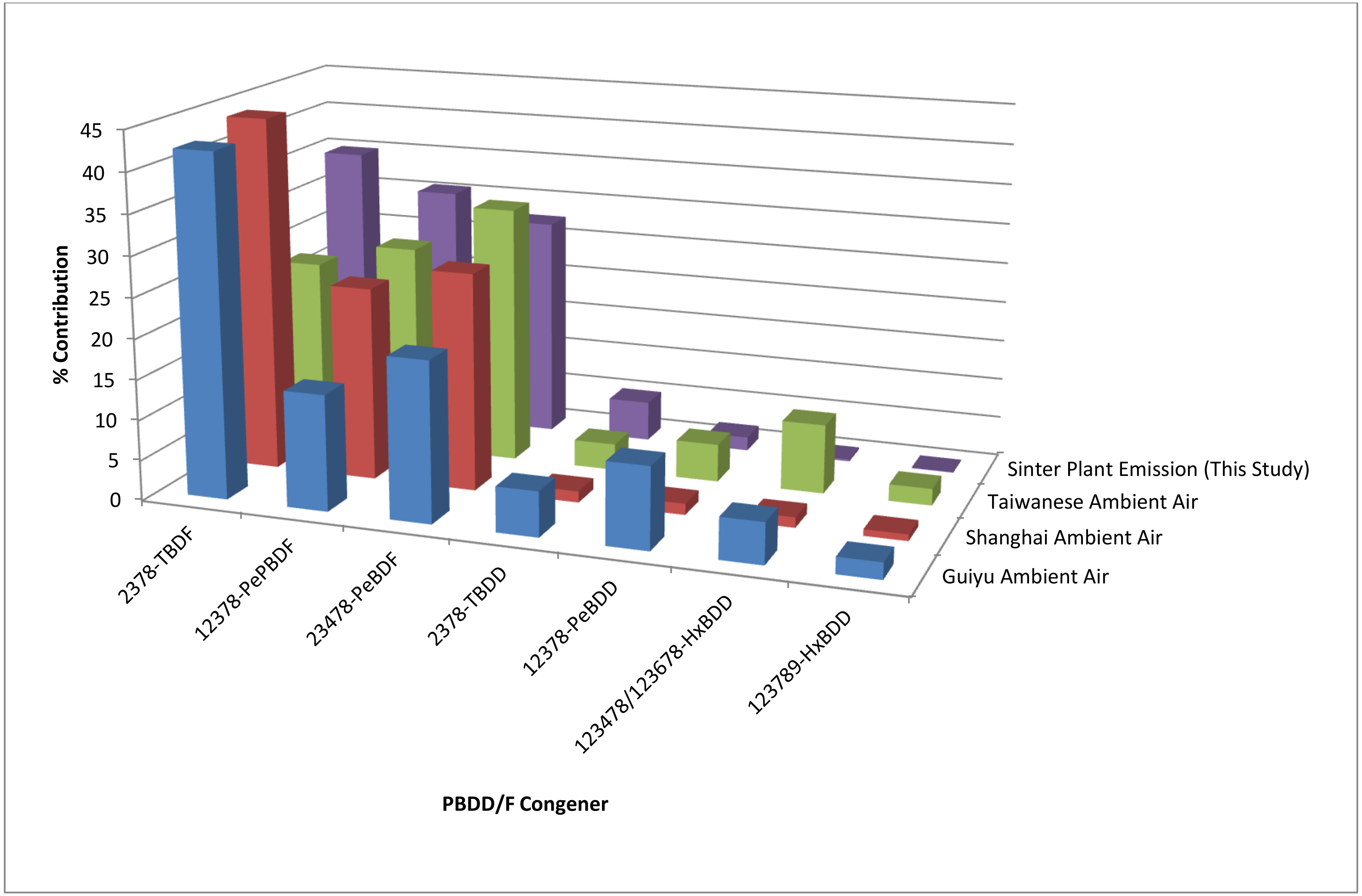


Figure 3.10 Mean PBDD/F congener profiles in air from Guiyu, China (Li et al., 2007), Shanghai (Li et al., 2008) and Taiwan (Wang et al., 2008) along with those from sinter plant stack emissions in this study.

Chapter IV

An investigation into PBDE and PBDD/F formation within the sintering process

4.1 Synopsis

After providing evidence in Chapter 3 that PBDEs and PBDD/Fs are both emitted from the sintering process, this chapter attempts to determine whether they undergo formation within the sintering process. This is investigated by using the sinter pot (SP) which is a laboratory scale apparatus designed to mimic the sintering process, described in full in Section 2.1.3. In this chapter, the SP was used to measure $\sum_{\text{tri-deca}}$PBDE and $\sum_{\text{tetra-hexa}}$PBDD/F concentrations in five different SP experiments involving various input levels and combinations of potassium bromide (KBr) and PBDEs (Table 4.1) to see whether it affected the output concentrations of PBDEs and PBDD/Fs.

Experiment #	**Summary of Conditions**
Experiment 1	"Base Case" – Standard Raw Sinter Mix / no KBr / no PBDE technical mixture
Experiment 2	Standard Raw Sinter Mix + 74.5 mg/kg KBr
Experiment 3	Standard Raw Sinter Mix + 224 mg/kg KBr
Experiment 4	Standard Raw Sinter Mix + 50 µg/kg RSM of each of the Penta-BDE (Bromkal 70-5DE), and Deca-BDE (Bromkal 82-0DE) commercial formulations
Experiment 5	Standard Raw Sinter Mix + 224 mg/kg KBr + 50 µg/kg RSM of each of the Penta-BDE and Deca-BDE commercial formulations

Table 4.1 – SP experimental conditions to study PBDE and PBDD/F formation in iron ore sintering.

The above experiments are designed to achieve objectives 1, 2, 4 and 5 (section 1.7). Measuring the PBDE and PBDD/F concentrations in Experiments 2 and 3 will help determine whether PBDEs and/or PBDD/Fs are formed during the sintering process, whilst Experiments 4 and 5 will help investigate whether PBDEs act as precursors for the formation of PBDD/Fs during the sintering process.

To our knowledge, this will be the first time that the fate and behaviour of PBDEs (including the formation of PBDD/Fs) within the iron ore sintering process has been examined on a controlled laboratory scale basis, with previous studies having only studied individual aspects of the production scale process.

4.2 Sampling Strategy

4.2.1 PBDEs in Input Samples

Input samples were taken after the final mixing stage, before the addition of water for pelletizing for the sintering process and measured for PBDEs as in 2.2.1.1.

4.2.2 PBDEs and PBDD/Fs in Output Samples

The SP was run twice for each experimental scenario listed in Table 4.1 thereby generating one input sample and two output samples for each experiment. All output compounds were either collected using a clean PUF plug (6 cm diameter x 7.6 cm x length, Supelco, UK) which collects total volatilised emissions from the SP, or remained in the residual sinter product. Although there was no PBDD/F sampling evaluation standard available to verify that there was minimal breakthrough, Tata Steel monitor PCDD/F breakthrough in all SP experiments by spiking with a labelled PCDD/F standard ($^{13}C_{12}$-1,2,3,7,8-PeCDF) and confirmed that recoveries were between 70-100% thus confirming that any breakthrough was negligible. This was considered an acceptable indicator due to the vapour pressure of PeCDF (2.5×10^{-4} Pa (Eitzer and Hites, 1998)) exceeding the predicted PBDD/F vapour pressures listed in Table 1.2 (section 1.2). All samples were extracted as in 2.2.1.1, with 10% of the extract from the PUFs used for PBDE analysis and the remainder for the determination of PBDD/Fs. The entire extract from the sinter products was used to determine PBDEs.

4.3 Formation of PBDEs in SP Experiments

Table 4.2 demonstrates that while there is a clear presence of PBDEs in the RSM that did not have any PBDE commercial formulations added to it (Experiments 1-3), the addition of the commercial formulations in experiments 4 and 5 increased the ∑PBDE concentrations by an order of magnitude. Whilst, a combined total of 100 µg of Penta- and Deca-BDE were added for every kg of RSM, values of 43 and 44 µg/kg were measured for experiments 4 and 5 respectively. This is probably due to the difficulty in homogenisation of the mixture, whilst avoiding spoiling the raw materials as the commercial formulations were only available as solutions at the time of conducting the experiment. Moisture content had to be within 0.2% of the target value (6.5%) for effective sintering to take place.

A ∑PBDE mass balance calculation showed that ∑PBDE inputs are 77-97% higher than outputs in the various SP experiments – similar to the mass balance findings in Chapter 3 that examined the production-scale sintering process. Moreover, in Experiments 2 and 3 where KBr was added to the RSM to investigate PBDE formation there is no noticeable difference between ∑PBDE output values and those of Experiment 1. This shows that increasing the availability of bromine (i.e. higher KBr) in the sintering process does not cause an increase in PBDE concentrations, suggesting that net formation of PBDEs in the sintering process does not occur.

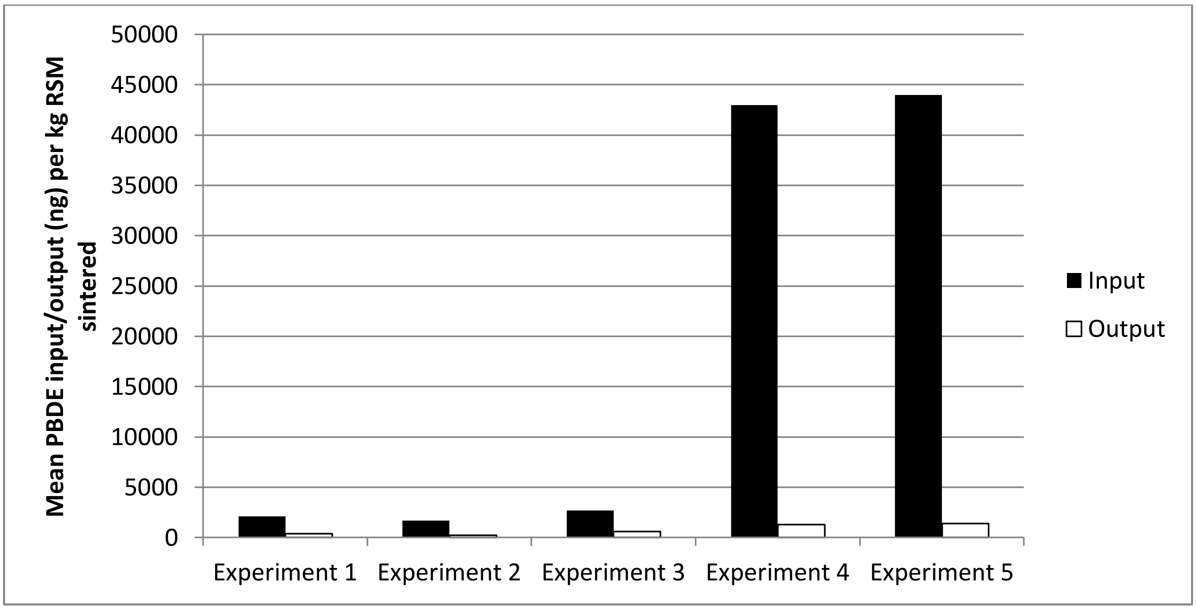


Figure 4.1 – Mean Inputs and Outputs of ∑PBDEs (ng) per kg of RSM sintered in each SP experiment

	Experiment 1		**Experiment 2**		**Experiment 3**		**Experiment 4**		**Experiment 5**	
	Input	**Output**	Input	**Output**	Input	**Output**	Input	**Output**	Input	**Output**
BDE-17	120	**8.3 (6.2-10)**	75	**14 (4.4-23)**	320	**56 (47-65)**	39	**50 (5.9-94)**	41	**23 (19-27)**
BDE-28	85	**5.7 (0-11)**	49	**13 (4.2-21)**	210	**48 (40-55)**	120	**33 (6.8-59)**	120	**29 (22-36)**
BDE-49	100	**17 (0-34)**	71	**8 (0-16)**	<0.001	**28 (1.8-54)**	54	**39 (0-79)**	55	**19 (17-21)**
BDE-47	680	**91 (68-110)**	300	**42 (32-52)**	1300	**130 (100-150)**	9900	**350 (300-420)**	10000	**520 (400-630)**
BDE-100	190	**3 (0-5.9)**	260	**0.59 (0-1.2)**	<0.001	**110 (110-110)**	4500	**89 (56-120)**	2400	**150 (81-230)**
BDE-99	460	**98 (69-130)**	790	**8.5 (0-17)**	390	**88 (77-100)**	8700	**250 (200-310)**	12000	**470 (290-650)**
BDE-85	<0.003	**<0.003**	<0.003	**0.48 (0-1)**	<0.003	**31 (9.7-52)**	790	**1.2 (0-2.4)**	680	**0.53 (0-1.1)**
BDE-154	110	**6.4 (0-13)**	110	**11 (0-21)**	420	**39 (3.4-74)**	1200	**52 (0-100)**	1200	**30 (28-33)**
BDE-153	<0.004	**<0.004**	<0.004	**<0.004**	<0.004	**45 (0-89)**	1700	**83 (0-170)**	1800	**33 (31-36)**
BDE-183	<0.006	**<0.006**	<0.006	**<0.006**	<0.006	**20 (0-39)**	470	**23 (0-47)**	510	**<0.006**
BDE-209	350	**180 (140-220)**	32	**120 (67-180)**	11	**18 (13-24)**	16000	**290 (58-530)**	15000	**85 (12-160)**
$\sum$PBDEs$_{17:183}$	1700	**230 (140-315)**	1700	**96 (42-150)**	2600	**600 (410-760)**	27000	**970 (540-1400)**	29000	**1300 (910-1600)**
$\sum$PBDEs	2100	**410 (360-460)**	1700	**220 (220-220)**	2700	**610 (440-780)**	43000	**1300 (1100-1500)**	44000	**1400 (1100-1600)**

a – NB all values are to 2 significant figures so $\sum$PBDE values may not correspond to exact totals of above congeners

Table 4.2 PBDE concentrations (ng/kg) in RSM inputs and outputs in each SP experiment

4.4 PBDD/Fs in SP Experiment

4.4.1 Formation of PBDD/Fs

PBDD/Fs were detected in all SP emission samples (Figure 4.2) implying that PBDD/F formation does occur during the sintering process (assuming that they are not present in the RSM), with similar PBDF:PBDD ratios as in Chapter 3 (mean = 25:1).

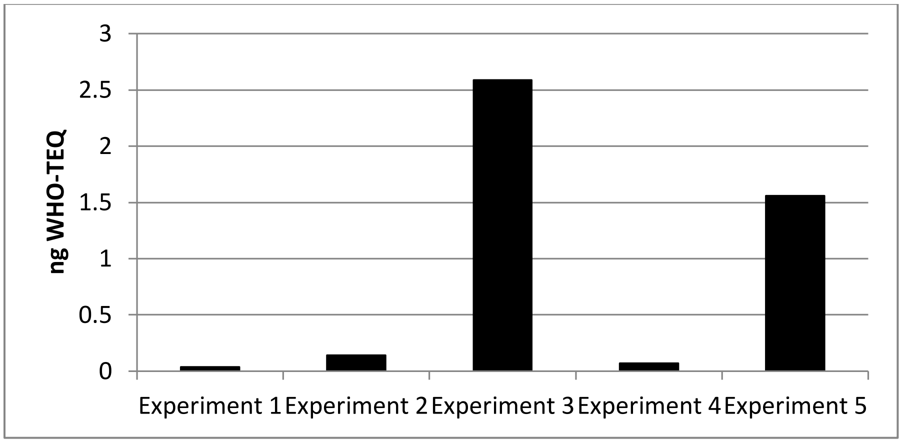
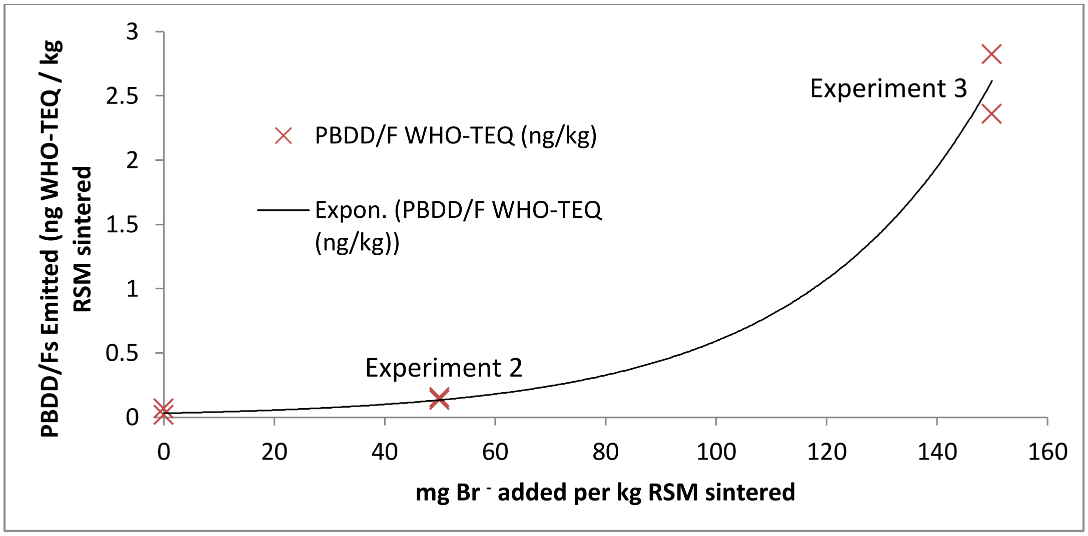


Figure 4.2 – Mass (ng-WHO-TEQ) of PBDD/F formed per kg of RSM in each SP experiment.

The results from Experiments 2 and 3 further reinforced this theory by showing an increase in PBDD/F output with increasing KBr levels in the RSM (Figure 4.3) that is akin to the increases seen in PCDD/F emissions when KCl is added for "activated sintering" (Nzihou et al., 2005).



[a] only experiments without PBDE addition are used

Figure 4.3 – Amount of PBDD/F formation (ng WHO-TEQ) against bromide addition (mg Br$^-$/kg RSM) in SP Experiments 1-3.

However, the output results from Experiment 1 (which best reflects conditions experienced within production-scale iron ore sintering) demonstrate that PBDD/F formation is less facile than PCDD/F formation.

4.4.2 PBDEs as precursors of PBDD/Fs

As mentioned above, PBDEs were added to the RSM in Experiment 4 at a notional concentration of 100 µg PBDE per kg RSM (measured concentration = 43 µg/kg). This was designed to investigate whether increased PBDE input would enhance PBDD/F formation. A marginal increase was seen in PBDD/F formation (mean concentration 0.09 ng WHO-TEQ / kg) in Experiment 4, but this was not proportional to the amount of PBDEs added to the RSM and therefore suggests that the presence of PBDEs in the sintering process does not enhance formation of PBDD/Fs. Moreover, the similar PBDD/F concentrations found in Experiment 5 (where 100 µg PBDEs and 224 mg KBr were added per kg RSM) and Experiment 3 (where 224 mg KBr was added per kg RSM) (i.e. 1.6 and 2.6 ng WHO-TEQ /kg respectively), provide further evidence that PBDD/F formation is not driven by the presence of PBDEs within the sintering process. Finally, given that up to 96% of PBDEs are destroyed within the sintering process, the evidence from this chapter and Chapter 3 suggests that it is plausible that the sintering process causes the destruction of PBDEs without substantial conversion to PBDD/Fs.

4.4.3 Congener Profiles of PBDD/F output in SP

In all cases, PBDFs made up the majority of PBDD/F content. An average of 89 % (range: 55-98%) of ∑PBDD/Fs were PBDFs with 2,3,7,8-TBDF the dominant congener in 7 out of 10 SP runs. In the first of the two runs of Experiment 4 (where PBDE commercial formulations were added without any bromide addition) 1,2,3,7,8-PeBDF was dominant comprising 28% of the total measured ∑PBDD/F content, whilst in the second was dominated by 1,2,3,4,7,8-HxBDF (40%). Interestingly, Experiment 1 saw much higher proportions of 2,3,7,8-TBDD detected (30 and 26.5 %) than all other experiments (range: 1.1-4%), although the average concentration of 0.38 ng PBDD/F is the lowest of all experiments, suggesting that this is reflective of a lower rate of formation of PBDFs, rather than an increase in that of PBDDs.

The congener profile of PBDD/Fs found in the SP study is similar to the emission profile seen in the full scale process in Chapter 3. The average PBDF content in commercial scale emission samples was very similar to the SP at 93%, whilst an average of 39% of PBDD/F content in the SP came from 2,3,7,8-TBDF, compared to 35% in the full-scale study.

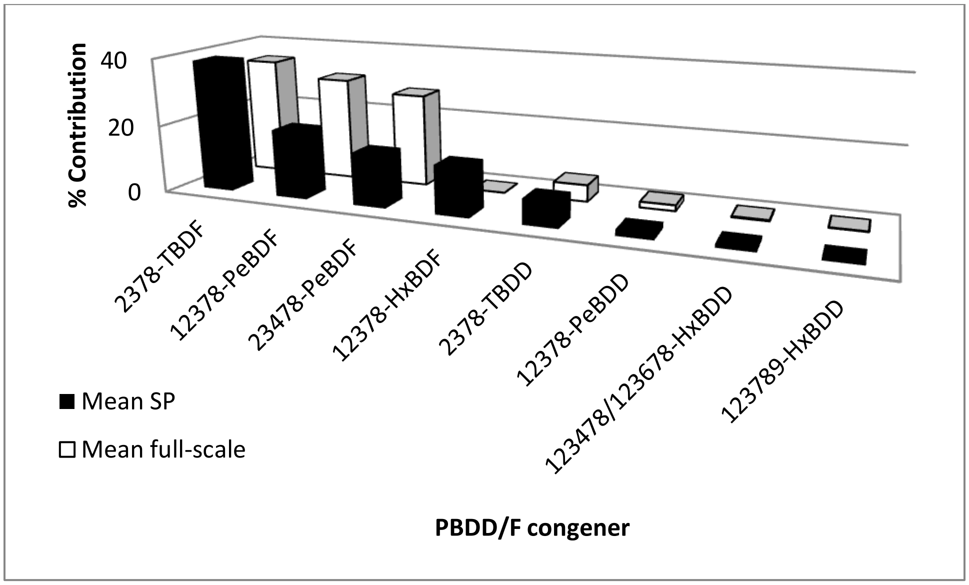


Figure 4.4 – Mean PBDD/F profile in SP and stack emission samples

One difference between the SP study and the full-scale study was that 1,2,3,4,7,8-HxBDF was detected in all measured SP samples with an average contribution of 14% to the total PBDD/F content, but was not detected in any samples in the full-scale study. However, Du et al. (2010a) detected 1,2,3,4,7,8-HxBDF in a stack emission sample from a sinter plant in China, suggesting that its detection in the SP may not be inconsistent with the full-scale sintering process.

The similarities in congener profiles indicate the reliability of the SP as a tool to investigate total PBDE and PBDD/F inputs and outputs in the full-scale sintering process.

4.5 Comparison with previous studies

A key reason for conducting the above experiments was the clear absence of information relating to the formation of both PBDEs and PBDD/Fs within the sintering process. However, there are a small number of previous studies on this subject. Wang et al. (2010b) attempted to characterise emissions of both sets of compounds in (amongst many other metallurgical processes) iron ore sintering. They found PBDEs and PBDD/Fs in stack emission samples from sinter plants and as a result calculated emission factors of 79 µg/tonne produced and 0.0094 µg TEQ/tonne produced of steel respectively. However, these calculations were based on the premise that as no recycled BFR-containing wastes are used in the process, the only input is from the raw materials that the authors assumed did not contain PBDEs. However, the raw materials were not analysed for PBDEs, which have been shown by this study to contain concentrations that exceed those determined in soils. Furthermore, the mass balance equations in both chapters show there is an overall reduction in PBDEs, even with the addition of KBr in Experiments 2 and 3 from the SP study. This suggests that PBDEs are not formed by *de novo* synthesis within the iron ore sintering process.

Whilst there are other studies that have examined PBDEs and PBDD/Fs in various outputs from iron ore sintering, such as stack flue gas and fly ash (Wang et al., 2010a, Wang et al., 2010b) as well as ambient air concentrations within the vicinity of integrated steel works (Li et al., 2011, Choi et al., 2008); this study appears to be the first of its kind as it investigates the formation of these compounds under controlled conditions, and conducts complete mass balances for PBDEs.

Weaknesses of this study are as follows: whilst it was found that PBDD/Fs were present in much lower concentrations than PCDD/Fs, their concentrations were not measured in an experiment where equimolar amounts of KCl and KBr were added. As a result it is unknown as to which group of compound would be preferentially formed under these conditions. Furthermore, Du et al. (2010a) have shown that mixed polybrominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans (PXDD/Fs) are formed in many thermal processes including iron ore sintering. These were not measured in this study due to the difficulty and expense of the analytical procedures involved, and therefore it cannot be ruled out that PXDD/Fs may be formed. Moreover, PBDD/Fs were not measured in the RSM nor in the residual sinter mix at the end of each experiment, thereby precluding full mass balance calculations. Therefore, improvements to future studies on this subject with the SP would be to measure all inputs and outputs for PBDD/Fs as well as PCDD/Fs and PXDD/Fs, along with investigations into the impact of equimolar additions of KCl and KBr across various conditions to try to obtain a more complete mass balance, and therefore understanding of their behaviour within the iron ore sintering process.

Chapter V

Concentrations of PBDEs in air and soil across an urban rural transect and in soil from various UK locations in 2004-05

5.1 Synopsis

This chapter reports the concentrations of PBDEs in ambient air and soil from an urban rural transect across the West Midlands, UK between June 2012 and January 2013. Over this period, passive air samples (PAS) were taken every month from 8 sites along with a single soil sample from each site. PBDEs were also measured in archived soil samples taken in 2004-5 from a number of UK locations. All samples were measured for tri-hepta PBDEs via GC/MS and BDE-209 via LC-APPI-MS/MS.

5.2 Sampling Strategy

5.2.1 West Midlands Samples

Ambient air samples were taken using PAS (as outlined in Section 2.1.4) between June 2012 and January 2013 from 8 locations along a 39 mile transect along the prevailing wind direction from the south-west to the north-east of the West Midlands (Table 5.1; Figure 5.1) with a varying degree of urbanisation. A soil sample was taken for each site in January 2013 from either the same location or from open spaces in very close proximity.

5.2.2 Other UK Samples

Archived soil samples taken from 17 towns and cities across the UK (Table 5.3; Figure 5.2) were analysed to determine the background environmental levels of PBDEs. These samples were taken in 2004-05, shortly after the 2004 EU bans on the Penta- and Octa- formulations but 3 years prior to significant EU restriction of the Deca- formulation. With this in mind these archived soil samples were taken shortly after the peak of PBDE usage and are expected to reflect that in their concentrations. However, due to the persistence of PBDEs and the very slow mixing time of soils (Gouin and Harner, 2003), the concentrations of the soils taken in 2013 are not expected to be significantly lower.

Figure 5.1 – PAS and soil sampling locations for urban-rural transect (Google Maps

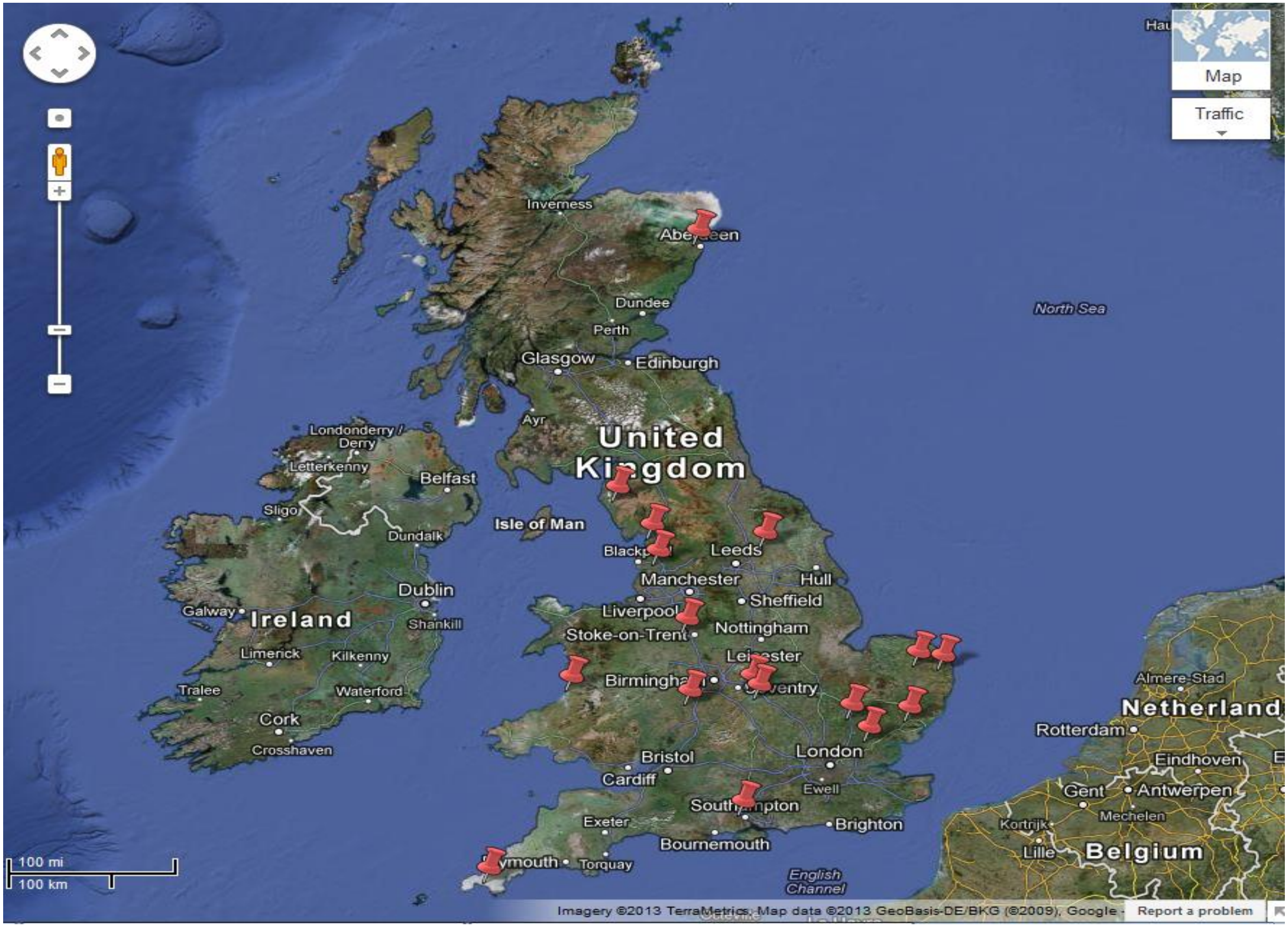


Figure 5.2 – 2005 UK soil sampling locations (Google Maps)

5.3 Concentrations of PBDEs across an urban-rural transect in the West Midlands

5.3.1 Ambient Air Concentrations

BDE-209 was detected in measurable concentrations in the majority of samples (39 out of 48), highlighting its extensive use in the UK. At each site BDE-209 made up an average of 61-92% of total PBDE content. Surprisingly, the highest PBDE concentrations were found in Bromsgrove (a suburban site 20 km southwest of Birmingham city centre) with an average of 490 pg/m^3 (92% BDE-209), at more than double that of the most urban sites of Digbeth and Edgbaston (180 and 210 pg/m^3 respectively). However, the average concentration is skewed by one sample (June-July which contained 1500 pg BDE-209/m^3). There are no known sources of PBDEs close to the Bromsgrove sampling site, such as chemical companies or industries using thermal processes such as steel manufacturing or waste incineration. However, the site is located between two major UK motorways (approximately 1 mile south of the M5 and 1 mile North of the M42) as well as in close proximity to the M5-M42 junction, meaning an extremely high throughput of traffic close to the sampling site. This could explain the elevated PBDE levels, when taking into account the extremely high levels of PBDEs detected in dust from UK cars (average 360,000 ng/g) (Harrad et al., 2008a). After Bromsgrove, the highest concentrations found were close to Birmingham city centre in Digbeth, Edgbaston and Bournville (219, 180 and 180 pg/m^3) which are approximately 0, 6 and 8 km from the city centre respectively. The concentrations of all congeners were highly variable from month to month (Appendix 3), whilst BDE-209 was not sampled at Edgbaston during the third sampling period (August-October 2012) due to the loss of the glass fibre filter required to sample the particulate phase.

Figure 5.3 indicates that (with Bromsgrove excluded) concentrations of BDE-209 and $\sum$PBDEs$_{17:183}$ are more elevated close to the city centre than they are further away. However, a Pearson product-moment correlation shows that this is not statistically significant for BDE-209 (R = -0.073p =0.412) and only moderately significant for $\sum$PBDEs (R = -0.136, p = 0.078) and $\sum$PBDEs$_{17:183}$ (R = -0.265, p = 0.069). This is likely due to the wide month-to-month variation seen (see section 5.3.1.2 on seasonal variation). When the concentrations for each sampling period are summed (excluding Bromsgrove and August-October) a Pearson product-moment correlation shows a significant negative correlation between PBDE concentration and distance from Birmingham city centre (R= -0.93, -0.84, -0.69; p = 0.001, 0.01 and 0.04 for ∑PBDEs, $BDE_{17:183}$ and BDE-209 respectively).

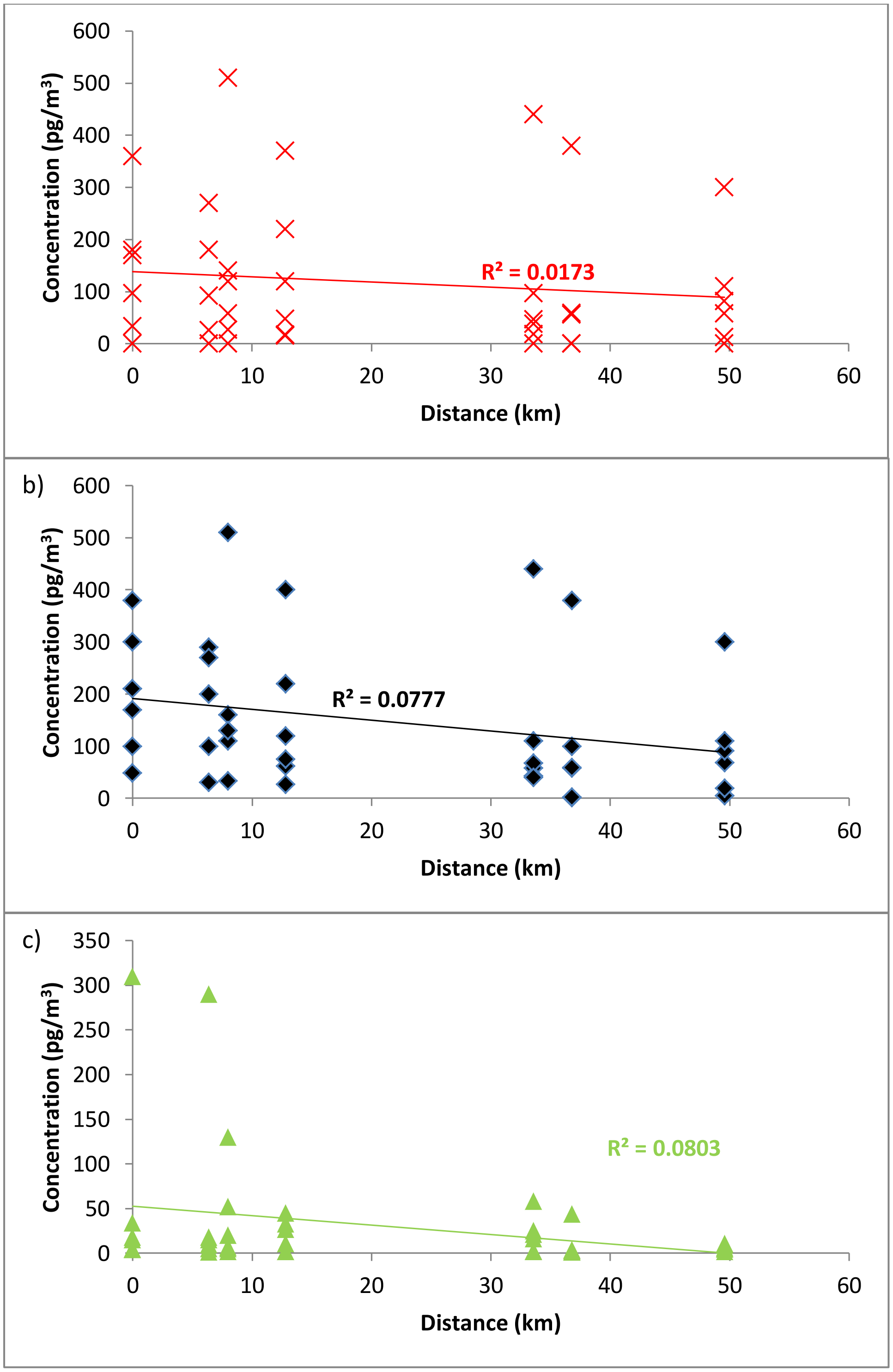


Figure 5.3 Concentrations of a) BDE-209 b) ∑PBDEs and c) ∑PBDEs$_{28:154}$ in ambient air according to distance from Birmingham City Centre (Bromsgrove excluded)

	Sampling Location			
Congener	**WOR**	**DRO**	**BRO**	**BOU**
Sample Size (n)	6	6	6	6
BDE 17	0.47 (<0.2-1.5)	0.68 (<0.2-2.4)	1.7 (<0.2-7.9)	1.9 (0.4-6.4)
BDE 28	1.2 (<0.2-4.2)	2 (0.5-6.3)	3.6 (1.3-9.4)	3.7 (1.4-6.8)
BDE 47	1.9 (0.8-4.5)	1.6 (0.6-6.2)	4.9 (<0.3-3.6)	5.2 (0.5-11)
BDE 66	<0.08	<0.04	1.1 (<0.4-4.4)	2.6 (<0.4-6.6)
BDE 100	0.53 (<0.4-2.2)	<0.4	2.5 (<0.4-15)	1.9 (<0.4-10)
BDE 99	0.62 (<0.5-3.5)	0.22 (<0.5-1.3)	6 (<0.5-36)	3.5 (<0.5-13)
BDE 85	<0.7	<0.7	1.1 (<0.7-6.7)	2.5 (<0.7-11)
BDE 154	0.92 (<0.9-2.6)	1.5 (<0.9-8.7)	4.1 (<0.9-20)	3.8 (<0.9-18)
BDE 153	0.67 (<1-2.3)	1.6 (<1-9.5)	6.5 (<1-31)	5.9 (<1-26)
BDE 183	<1.4	1.8 (<1.4-11)	4.8 (<1.4-29)	4.9 (<1.4-21)
BDE 209	94 (<2.2-300)	92 (<2.2-380)	370 (63-1500)	140 (<2.2-510)
∑PBDEs	100 (6.3-300)	100 (1.8-380)	410 (6.2-1700)	180 (34-510)
∑PBDE$_{17:183}$	6.8 (2.4-12)	11 (1.8-46)	37 (1.2-180)	38 (2-130)
Average 47:99 ratio (N) ^{3}	0.68 (1)	0.46 (1)	0.5 (1)	0.99 (3)
Congener	**EDG**	**DIG**	**SUT**	**TAM**
n	6	6	6	6
BDE 17	7.3 (<0.2-42)	4.8 (<0.2-25)	0.93 (<0.2-3.7)	3 (<0.2-15)
BDE 28	5.4 (<0.2-26)	5.9 (0.5-26)	1.7 (<0.2-3.9)	2.8 (<0.2-9.9)
BDE 47	7.5 (0.4-31)	7.9 (1.3-27)	3.1 (0.6-8.3)	5.1 (0.5-14)
BDE 66	0.9 (<0.4-4.5)	3.2 (<0.4-16)	0.35 (<0.4-2.1)	0.35 (<0.4-1.9)
BDE 100	5.2 (<0.4-30)	2.4 (<0.4-14)	0.53 (<0.4-1.9)	2 (<0.4-8.1)
BDE 99	7.5 (<0.5-43)	6 (<0.5-27)	3 (<0.5-11)	3.9 (<0.5-11)
BDE 85	<0.7	<0.7	0.75 (<0.7-4.5)	<0.7
BDE 154	12 (<0.9-57)	8.4 (<0.9-42)	4.5 (<0.9-11)	0.37 (<0.9-2.2)
BDE 153	11 (<1-62)	14 (<1-70)	2.5 (<1-11)	3 (<1-14)
BDE 183	<1.4	11 (<1.4-57)	2.8 (<1.4-17)	<1.4
BDE 209	110 (<2.2-270)	140 (<2.2-360)	130 (16-370)	110 (<2.2-440)
∑PBDEs	170 (31-300)	210 (50-380)	150 (29-410)	130 (40-440)
∑PBDE$_{17:183}$	60 (1.9-300)	66 (4.5-300)	21 (1.7-63)	21 (1.8-58)
Average 47:99 ratio (N) ^{3}	0.92 (2)	1.8 (4)	0.89 (3)	1.2 (4)

[1] WOR = Worcester; DRO = Droitwich; BRO = Bromsgrove; BOU = Bournville; EDG = Edgbaston; DIG = Digbeth; SUT = Sutton Coldfield; TAM = Tamworth. [2] <0.1 = below detection limit; [3] Average 47:99 ratios calculated only for samples from that location where both congeners were detected. Number of samples used for calculation in parentheses

Table 5.1 Mean (range) PBDE Concentration (pg/m^3) in ambient air along a rural-urban transect across the West Midlands of the UK

This provides strong evidence that cities are sources of PBDEs to the environment creating an urban pulse of high concentrations in Birmingham city centre, decreasing with distance away from the city centre. The strength of this pulse, calculated in a similar way as Harrad and Hunter (2006b) (by the ratio of the sum of concentrations in Birmingham City Centre to the average sum of concentration of all sites), was 1.1 for ∑PBDEs, 0.87 for BDE-209 and 2.2 for $\text{BDEs}_{17:183}$. With Bromsgrove excluded, the urban pulse is stronger still (1.4, 1.2 and 2.1) for ∑PBDEs, BDE-209 and $\text{BDEs}_{17:183}$ respectively. Using the same congeners as Harrad and Hunter (2006b) a value of 2.0 was found for $\sum\text{PBDEs}_{28:154}$. This was similar to the value of 2.2 calculated in an earlier study along a similar (but not identical) transect (Harrad and Hunter, 2006b). The strength of the pulse for BDE-209 (along with the above R and p values) was lower than it was for the lower brominated congeners. This is likely to be due to the more widespread use of Deca-BDE within the UK to meet its fire-regulations in upholstered furniture (Harrad et al., 2008b, The Furniture Industry Research Association (FIRA), 2011). Taking this into account along with the fact that all PAS other than DIG and EDG were taken from gardens in domestic homes, it is likely that BDE-209 represents a larger proportion of PBDE content outside of the city, whilst lower brominated congeners are likely to contribute more substantially to the overall PBDE concentrations inside the city (where there is a more diverse range of sources), thus meaning a lower “urban pulse” for BDE-209 than for $\text{BDEs}_{47:183}$.

5.3.1.2 Seasonal Variation of PBDEs

Whilst only one sample was measured for PDBEs in each sampling month, Worcester, Droitwich, Bournville, Edgbaston, Digbeth, and Tamworth appear to show a negative association for BDE-209 levels in air and average daily high temperatures supplied by the Met Office for the specific sampling months – i.e. concentrations of BDE-209 are lower in warmer periods. This pattern was also observed recently in Beijing by Shi et al. (2013) who found BDE-209 concentrations in outdoor air to be more variable and overall lower in the spring and summer than autumn and winter. A potential explanation for this could be the photolytic debromination of BDE-209 as shown by Da Rosa et al. (2003) under laboratory conditions, although the degradation products of BDE-209 (nona- and octa- congeners) were not measured in this study to confirm whether this is the case. Furthermore, Pearson product moment correlation calculations suggest that this trend is only statistically significant for Digbeth ($p = 0.013$), whilst the opposite appears to have occurred at Bromsgrove. This suggests that further investigation into the seasonal variation of BDE-209, along with its potential photolytic degradation is required. This could be achieved by measuring monthly samples at a range of sites, over the course of a full year or more, monitoring temperature as well as measuring BDE-209 and its known degradation products – i.e. octa- and nona- brominated BDE congeners (such as BDEs -202, 203, -205, -206, -207 and -208 (Eriksson et al., 2004, Söderström et al., 2003).

At all sampling sites, there appears to be a positive trend with respect to $\sum PBDE_{17:183}$ and average temperature with the highest concentrations appearing in the summer samples, and the lowest towards the end of the sampling campaign in November 2012-January 2013. This statement contradicts the previous findings in the West Midlands of Harrad and Hunter (2006b) who observed this pattern at only 2 out of 10 sampling sites monitored. However, again likely due to the low number of samples, these trends are not statistically significant. As with the potential seasonal variation of BDE-209, it would be recommended to measure $BDEs_{17:183}$ in multiple monthly samples along with average temperature data from each site. This would go some distance to confirming or rejecting the hypothesis that $PBDEs_{17::183}$ concentrations are higher in the spring and summer. These elevated levels are expected due to increases in volatilisation of PBDEs from indoor sources combined with increased ventilation as a result of the higher temperatures (Harrad and Hunter, 2006b).

5.3.1.3 Comparison with previous studies from available literature

The concentrations detected in this study are higher than previous measurements by Wilford et al. (2004) who found mean $\sum PBDEs_{47:209}$ (BDEs -47; -99; -100; -153; -154; -183; -209) of 27 pg/m^3 in Hazelrigg (a semi-rural site in north-west England) compared with 99 pg/m^3 for the same congeners in DRO (a rural sampling site in this study). This difference in PBDE concentration is accounted for by increased BDE-209 levels in DRO (92 pg/m^3) compared to that detected at Hazelrigg (20 pg/m^3).

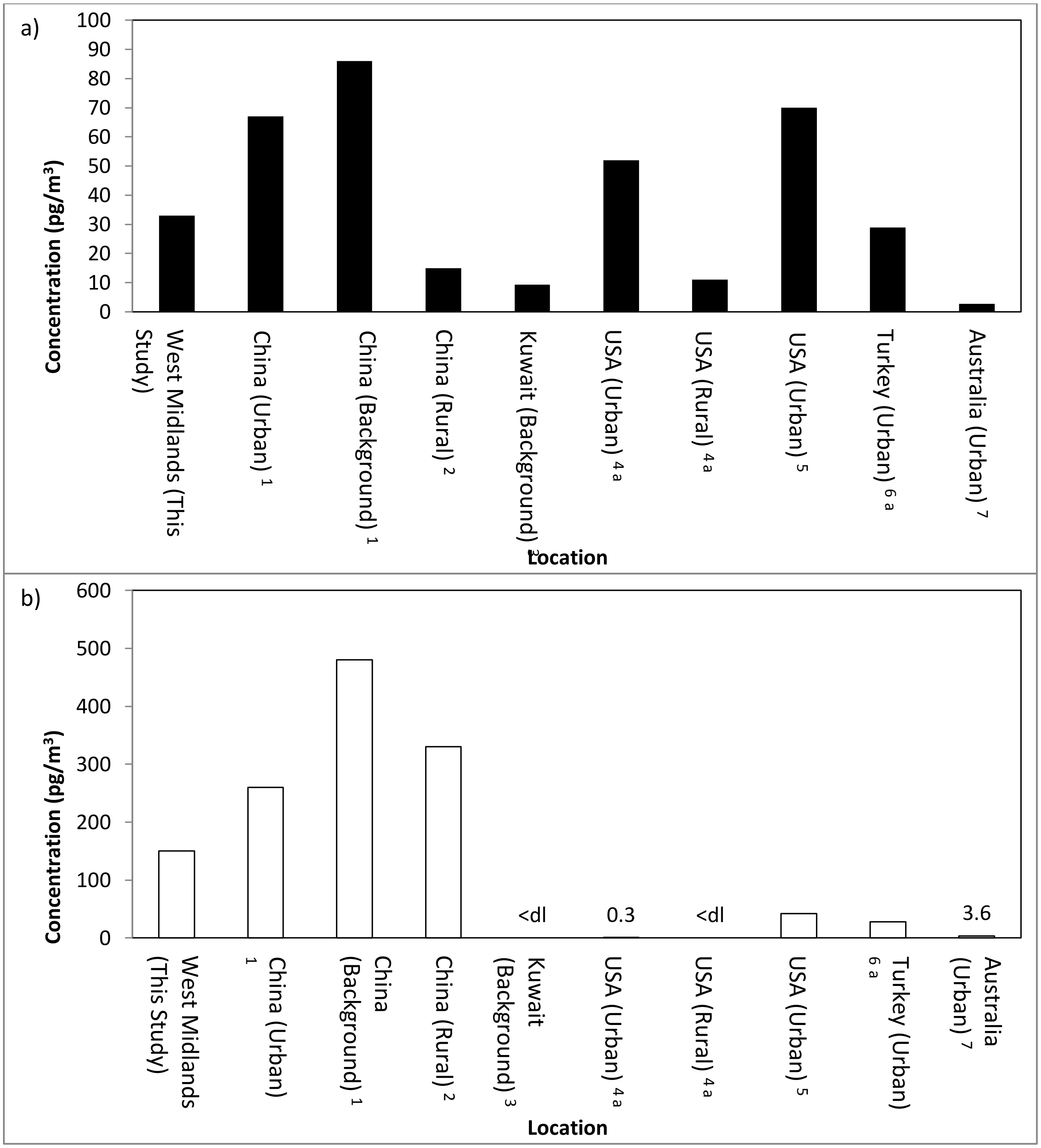
Using the congeners consistent between both studies (BDEs -47; -99; -100; -153; -154 and -183) it would appear that PBDE concentrations detected in this study were similar to peak concentrations from between 2000-2003 by Birgul et al. (2012). For example, PBDE concentrations peaked in Manchester (a highly urban city) in 2002-03 at 48 pg/m^3, which is comparable to the two most urban sites in this study (54 and 50 pg/m^3 for Edgbaston and Digbeth respectively). Concentrations in Europe were of a similar magnitude in 2002 when average levels of $\sum$PBDE$_{47:154}$ were reported – urban = 38 pg/m^3; rural = 23 pg/m^3 (Jaward et al., 2003). Moreover, a study conducted in 2003-04 at 10 sites on a rural-urban sampling transect across the West Midlands (with all sampling sites except for Edgbaston different to this study) measured PBDEs (BDEs -28, -47, -99, -100, -153, -154), finding average concentrations of $\sum$PBDE$_{28:154}$ of 5.4 pg/m^3 in rural areas and 15 pg/m^3 in urban/suburban areas (Harrad and Hunter, 2006b). In the current study, average concentrations of the same congeners a decade later were 14, 12 and 43 pg/m^3 for rural, suburban and urban areas respectively. Whilst these levels appear to suggest there has been no decline in PBDE concentrations over the last decade, it must be taken into account that only the vapour phase was measured in the previous study. By comparison, in this study both vapour and particle phases were measured, rendering objective comparison between the two studies difficult.

Despite this, comparison of the July-January samples from Harrad and Hunter (2006b) with those from July-January from Edgbaston in the current study (the same location in both studies) shows the average concentrations of $\sum$PBDE$_{28:154}$ to be 17 and 8.5 pg/m^3 in 2004-05 and 2012-13 respectively. A paired t-test shows the concentrations in 2012-13 to be significantly lower ($p<0.05$), despite the fact that the current study monitored both phases. This suggests that there has been a significant decrease in atmospheric PBDE concentrations at the EDG site over the last decade. This finding is consistent with the findings of Birgul et al. (2012) who reported a fall in PBDE concentrations in outdoor air at four sites across the UK between 2000 and 2010, with the most recent (2010) concentrations 8.2, 1.3, 1.9 and 2.7 pg/m^3 in Manchester, London, Hazelrigg and High Muffles respectively for $\sum$PBDE$_{47:183}$ being lower than averages of 26, 8.5, 2.5 and 17 pg/m^3 recorded in the same sites in 2000-04. The combination of data from these three studies suggests that whilst PBDE concentrations remain of vital concern with a wide amount of spatial variation both within and between towns and cities, concentrations of Penta- and OctaBDE based congeners measured at the same sites, appear to have decreased significantly in the UK since their bans.

On a global scale, the concentrations of PBDEs in ambient air in this study appear to be approximately in the middle of the range of those measured in various different countries, based on studies that have measured BDE-209 (Figure 5.4). The highest concentrations have been reported in China (Chen et al., 2006, Zhang et al., 2009a), whilst concentrations reported for the UK exceed marginally those reported for urban sites from the USA (Strandberg et al., 2001, Hoh and Hites, 2005, Schecter et al., 2010).

Whilst the concentrations of tri-hexa PBDEs in this study appear to be similar to mainland Europe, there is no comparative data available for BDE-209 concentrations in other European countries, which are expected to be much higher in the UK due to the greater UK usage of the DecaBDE formulation comply with more stringent flame retardancy standards in UK furniture (BSEF, 2010).

Although the overall concentrations of tri- through hexa-PBDEs in the West Midlands do not appear to have decreased since the bans of Penta- and OctaBDE formulations in 2004, concentrations in Edgbaston have halved since their measurement in 2003-04 at the same location (Harrad and Hunter, 2006b), whilst they remain of a similar magnitude in the rest of the West Midlands despite the additional measurement of the particle phase since the previous study (Harrad and Hunter, 2006b). This reduction in PBDEs in UK ambient air is in line with a previously larger study by Birgul et al. (2012) who found concentrations to have fallen by more than half in three of four sites across the UK.



[1]Chen et al. (2006); [2]Zhang et al. (2009a); [3]Gevao et al. (2006); [4]Strandberg et al. (2001); [5]Schecter et al. (2010); [6]Cetin and Odabasi (2008); [7]Toms et al. (2009a) [a] BDE-183 not measured

Figure 5.4 Average Concentration of a) $\sum_6$PBDEs (-47; -99; -100; -153; -154; -183) and b) BDE-209 in ambient air from this study, compared with non-European countries in similar location types

5.3.2 Concentrations of PBDEs in soils

The concentrations of PBDEs in soils appear to follow a similar, but not identical, pattern to those in ambient air. The lowest ∑PBDE concentrations are found in the site furthest from Birmingham city centre (Worcester (3600 pg/g OC) and Droitwich (2300 pg/g OC)), however, the highest (except for Bromsgrove) was found in Digbeth (21000 pg/g – in the centre of Birmingham).

The elevated ∑PBDE concentration found in soil from Bromsgrove (49000 pg/g OC) is consistent with the ambient air concentrations from the same location presented above, with a similar proportion coming from BDE-209, with a slight increase in the contribution of BDE-47 and BDE-99 towards total PBDE content. This increase in key PentaBDE congeners appears to be consistent across all samples (Figure 5.5)

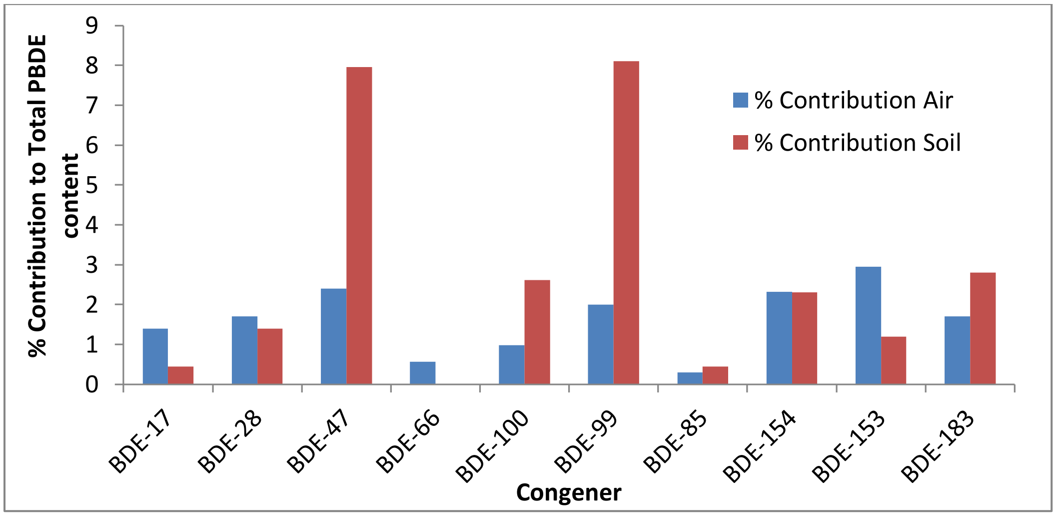


Figure 5.5 Average PBDE congener profile of Soil and Air along the rural-urban transect in the West Midlands

Andrade et al. (2009) estimated half-lives ($t_{1/2}$) in soil of 12.7 years for BDEs -47 and 99; and 22.8 years for BDE-209. Furthermore, Wong et al. (2012) estimated a $t_{1/2}$ of 5.1 years for BDE-17, whilst they stated that they could not estimate $t_{1/2}$ of BDEs -28, -47 and -99 as there wa no significant degradation over a 1 year period in soil. Palm et al. (2002), demonstrated(using estimation software) that $t_{1/2}$ in air are considerably shorter forlower brominated congeners(10.7 and 19.5 days for BDEs -47 and -99 respectively)than for the higher brominated congeners

(BDE-209 $t_{1/2}$ = 318 days). This is reflected by air concentrations from this study where BDE-209 contributed an average of 77% to total PBDE content, with only 2.4 and 2 % coming from BDE-47 and BDE-99 respectively. In soil, the BDE-209 contribution is lower at 72%, whilst BDEs -47 and -99 contribute 7.9 and 8.1% respectively, indicating a legacy contamination of the PentaBDE formulation since its ban. This is likely to be due to the longer mixing time of soil compared to air meaning that the soil concentrations are reflective of an exposure to PBDEs over a longer time period – i.e. congeners from the PentaBDE formulation, such as BDEs -47 and -99 are likely to be found in soil for a longer time period in soil as a result of this longer mixing time when compared with air (Palm et al., 2002, Andrade et al. 2010).

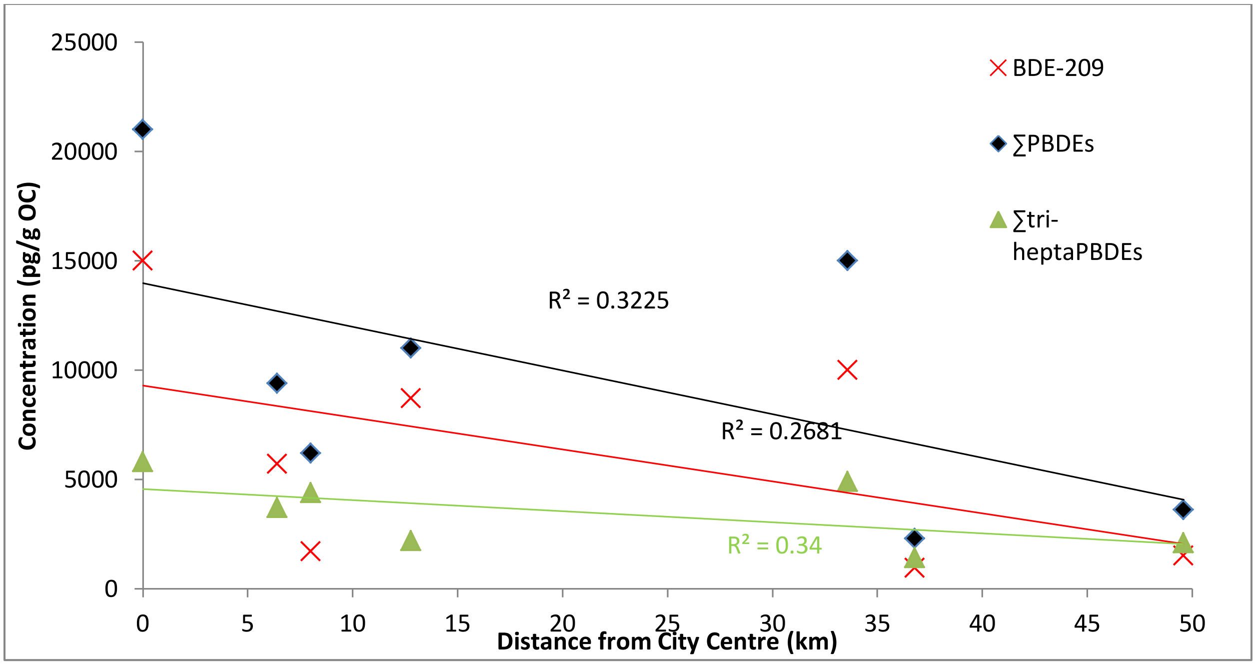


Figure 5.6 PBDEs in soil samples (pg/g OC) according to their distance from Birmingham city centre (Bromsgrove excluded)

Furthermore the overall data expressed on an organic carbon-normalised basis gives a similar result of a negative association between PBDE concentration in soil and distance from Birmingham City Centre (Figure 5.6) as observed for air, although, likely due to the small sample set (n=1 for each site), R coefficient values were only moderately significant (p = 0.09).

	WOR	**DRO**	**BRO**	**BOU**
BDE 17	13 (130)	12 (62)	<1.5	19 (150)
BDE 28	18 (180)	16 (85)	<1.5	120 (260)
BDE 47	33 (680)	76 (580)	230 (2100)	190 (950)
BDE 66	<2.5	<2.5	<2.5	<2.5
BDE 100	19 (190)	22 (120)	56 (450)	61 (260)
BDE 99	57 (580)	110 (550)	200 (1600)	180 (770)
BDE 85	<4.5	<4.5	<4.5	<4.5
BDE 154	<5	<5	<5	360 (1600)
BDE 153	<7	<7	<7	69 (300)
BDE 183	<9	<9	<9	<9
BDE 209	140 (1500)	170 (940)	4100 (45000)	370 (1700)
∑PBDEs	280 (3600)	410 (2300)	4600 (49000)	1400 (6200)
∑ PBDEs$_{17:183}$	140 (2100)	240 (1400)	490 (4200)	1000 (4400)
47:99 ratio	0.57	0.69	1.15	1.1
	EDG	**DIG**	**SUT**	**TAM**
BDE 17	29 (150)	22 (120)	<1.5	<1.5
BDE 28	50 (260)	56 (310)	<1.5	35 (140)
BDE 47	130 (840)	240 (1400)	340 (760)	440 (1900)
BDE 66	<2.5	<2.5	<2.5	<2.5
BDE 100	60 (310)	56 (310)	240 (510)	37 (150)
BDE 99	180 (950)	190 (1100)	420 (880)	370 (1500)
BDE 85	<4.5	96 (520)	<4.5	<4.5
BDE 154	52 (280)	<5	<5	68 (280)
BDE 153	53 (280)	80 (440)	<7	43 (180)
BDE 183	120 (620)	280 (1600)	<9	190 (760)
BDE 209	1100 (5700)	2700 (15000)	4100 (8700)	2500 (10000)
∑PBDEs	1800 (9400)	3700 (21000)	5100 (11000)	3700 (15000)
∑ PBDEs$_{17:183}$	670 (3700)	1000 (5800)	1000 (2200)	1200 (4900)
47:99 ratio	0.72	1.26	0.8	1.2

Table 5.2 PBDE concentrations in pg/g dry wt (pg/g OC) in West Midlands soils (to 2 significant figures)

However, this trend combined with the ambient air concentrations from the previous section are consistent with earlier observations that there is an “urban pulse” of PBDEs with higher concentrations in cities than in rural and suburban areas (Harrad and Hunter, 2006b, Harner et al., 2006). The strength of this urban pulse, based on organic carbon concentrations (calculated in the same way as for air) was 1.6 for ∑PBDEs$_{17:183}$ and 1.4 for BDE-209, which was similar to those calculated for air. Interestingly, using the same congeners as studied in 2003-04

($PBDEs_{28:154}$) a figure of 1.2 was calculated which is a quarter of that calculated by Harrad and Hunter (2006). Soil taken from Edgbaston was also more than five times less contaminated in this study than soil taken from the same location in 2004 (Harrad and Hunter, 2006b). Whilst the sample set in the present study was comparatively small, these figures suggest that soils in urban areas are less exposed to PBDE congeners from the PentaBDE formulation than they were 10 years ago. This is consistent with the theory that since the ban of PBDEs in the UK there has been a gradual removal of PBDE-containing items from indoor environments (of which there would have been a far greater density in city centres) and their replacement with newer items that do not contain PBDEs. However, as previously stated, the present study is based on a very small sample set (1 soil sample per location). Moreover, given the heterogeneous nature of soil, more data is required to draw firm conclusions.

5.3.2.1 BDE 47:99 ratios in air and soil

In the study conducted by Harrad and Hunter (2006) the average BDE 47:99 ratios in air for each site ranged from 2.95 to 3.62 (mean = 3.3), with the highest found in the centre of Birmingham, whilst the lowest were at upwind sites. In this study, the same spatial trend was found, however, average 47:99 ratios ranged from 0.46-1.8 (mean = 0.93) (calculated using only samples that detected both congeners). This is likely due to the difference in PAS used. In the previous study only the gaseous phase was measured for PBDEs. However, in this study glass fibre filters were also used to measure the particulate phase. Due to the higher octanol-air coefficient (K_{OA}) of BDE-99 with respect to BDE-47 (Harner and Shoeib, 2002) it is likely that there would be a greater partitioning to the particulate phase for BDE-99 than BDE-47, meaning that by measuring the concentration of both gas and airborne particulate matter, the BDE 47:99 ratio in this study is likely to be lower than if only the vapour phase is monitored.

The 47:99 ratios in soil were similar in this study as previously reported for the West Midlands with a mean of 0.94 (range 0.57-1.26) compared to an average of 0.6 (range 0.51-0.88) in 2004 (Harrad and Hunter, 2006). The 47:99 ratios in both air and soil are similar to that found in both PentaBDE commercial mixtures, DE-71 and Bromkal 70-5DE (0.79 and 0.96). This suggests that, whilst there is evidence to show that there has been a decrease of PentaBDE based congeners in UK air and soil since the introduction of preventative legislation in the UK in 2004, there is still a legacy of PentaBDE commercial formulations in the environment as their principal congeners are detected in both air and soil in rural and urban samples in the West Midlands.

5.4 Concentrations of PBDEs in UK soil samples archived from 2004-05

A wide range of concentrations (130-8100 pg/g dry wt) of PBDEs was found in UK samples taken in 2004-5 (Table 5.4) with the majority coming from BDE-209 which made up an average of 73% (range: 24-99 %) of the total PBDE content in each sample. The lowest levels were found in Helston, Cornwall which contained 120 pg/g dry wt BDE-209 and 4.5 pg/g BDE-47 The only other congener detected in this sample was BDE-99 but this was below the limits of quantification (5.9 pg/g dry wt).

Usage of the DecaBDE formulation would be expected to be high at the time of sampling, which would explain the high proportion of BDE-209 in the majority of samples. Use of PentaBDE was very much evident also with BDE-47 and BDE-99 found in all samples in measurable concentrations (except for Helston as mentioned above).

5.4.1 Comparison of PBDEs in 2004-5 with 2013 samples

PBDE levels in UK soil samples taken in 2004-5 (Table 5.4) are similar to those taken in 2013 with mean ∑PBDE concentrations of 2400 and 2600 pg/g dry weight in 2004-05 and 2013 respectively suggesting that PBDEs in soils have not decreased since 2005 despite the restrictions on PBDE manufacture and use that have occurred in the interim). However due to a varying amount of organic carbon (OC) in each soil sample as well as the spatial differences between the sample sets, it is more appropriate to compare sample sets normalised to pg/g OC content. This comparison reveals a significant difference in PBDE levels in UK soil between 2004 and 2013 (Figure 5.7) with mean ∑PBDE concentrations of 103000 and 15000 pg/g OC respectively (Man-Whitney U Test, $p < 0.01$). A Man-Whitney U Test also confirms that these significant differences apply when treating BDE-209 ($p = 0.001$) and $\text{PBDEs}_{28:183}$ ($p = 0.00$) separately. This suggests that since restrictions on PBDE usage were put in place, there has been a significant decrease in concentrations of PBDEs to UK soils.

As with the 2013 soil samples, the urban and suburban samples have a higher 47:99 ratio than those from rural areas. Whilst this is the opposite to what is seen by Harrad and Hunter (2006b) it is not statistically significant. The average 47:99 ratios of 0.78 and 0.94 for 2004-05 and 2013 respectively were not found to be significantly different (t-test, p = 0.265). This suggests that BDE-47 and BDE-99 have changed concentrations at a similar rate, suggesting that they are of very similar persistence to one another.

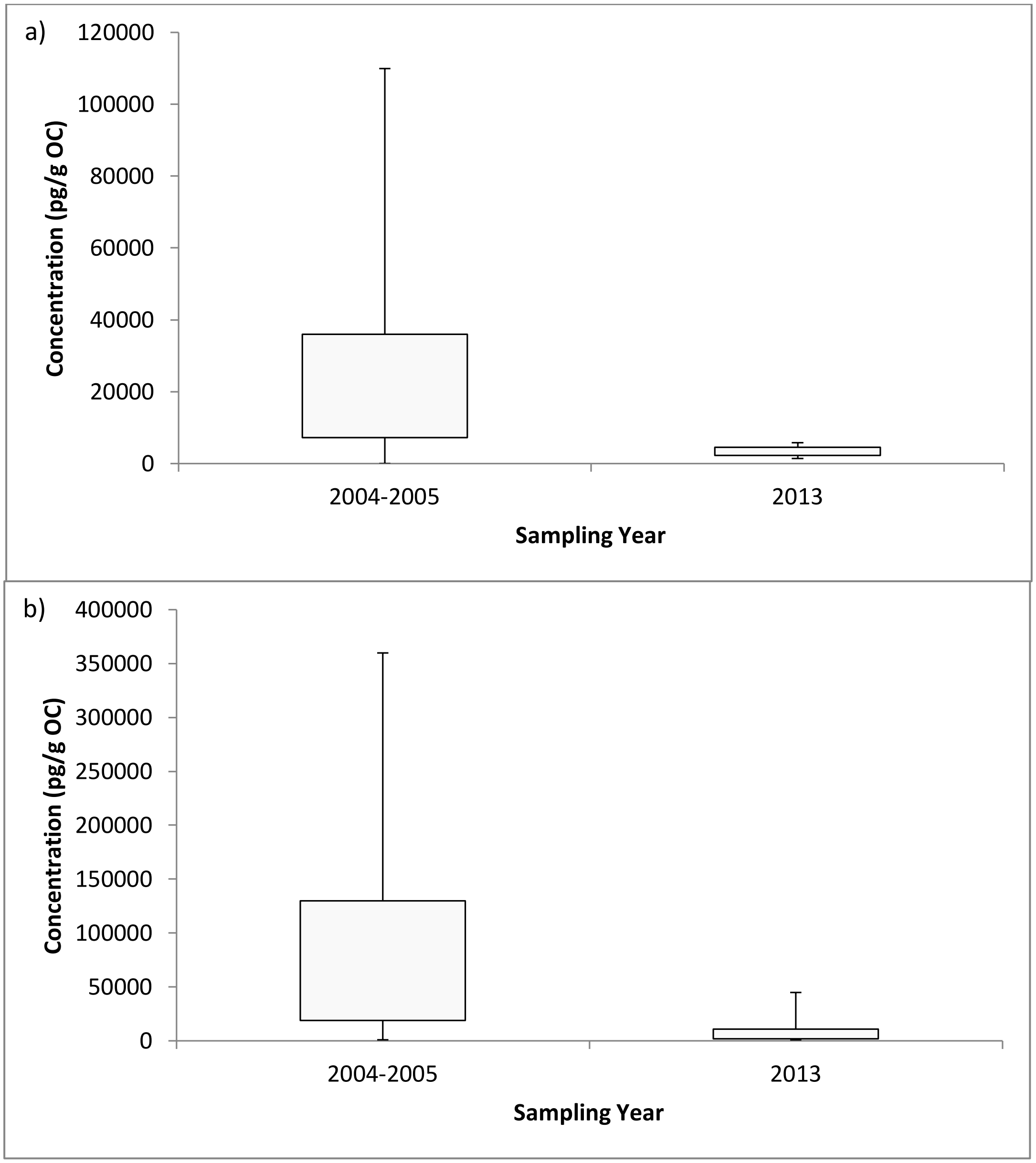


Figure 5.7 Boxplot diagrams showing minimum, maximum and interquartile ranges of a) PBDEs$_{17:183}$ and b) BDE-209 in soils (pg/g OC) taken in 2004-05 and 2013 in the UK.

This section of the study has its limitations, which mean that absolute conclusions regarding temporal changes in PBDE levels in soils cannot be drawn. Both sample sets are small (2004-05 n = 17; 2013 n = 8) and soil samples were not taken from the same locations.

	Norfolk	**Rugby**	**York**	**Keele**	**Suffolk**	**Helston**	**Worcester**	**Saffron Walden**
BDE 17	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
BDE 28	<1.4	<1.4	<1.4	<1.4	190 (29)	<1.4	<1.4	<1.4
BDE 47	51 (3.4)	86 (3.4)	79 (2.8)	150 (5.4)	100 (15)	4.5 (0.03)	88 (4)	25 (2)
BDE-85	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5
BDE-99	53 (3.5)	180 (7.2)	130 (4.6)	300 (11)	240 (37)	<2.7	71 (3.2)	23 (1.9)
BDE-100	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<4.7
BDE-153	<7	<7	<7	<7	<7	<7	<7	<7
BDE-154	<5	<5	<5	<5	<5	<5	<5	<5
BDE-183	<6	<6	<6	<6	<6	<6	<6	<6
BDE-209	1900 (130)	1800 (72)	2500 (89)	5300 (190)	190 (29)	120 (0.8)	3600 (160)	200 (16)
$\sum$PBDEs	2000 (133)	1900 (78)	2600 (94)	5600 (200)	720 (110)	130 (0.81)	3800 (170)	250 (20)
$\sum$PBDEs$_{17:183}$	96 (7)	170 (10)	140 (7.2)	280 (16)	530 (71)	7.2 (0.03)	160 (7.2)	53 (3.9)
47:99 ratio	0.96	0.48	0.61	0.5	0.42	N/A	1.2	1.1

	Wales	**Essex**	**Norwich**	**Lancaster**	**Scoat Tarn**	**Aberdeen**	**Preston**	**Southampton**	**Daventry**
BDE 17	23 (1.4)	<1.3	<1.3	<1.3	<1.3	<1.3	14 (0.7)	47 (3.4)	49 (2.7)
BDE 28	41 (2.6)	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	68 (4.9)	62 (3.4)
BDE-47	120 (7.5)	140 (14)	25 (1)	120 (11)	38 (4)	400 (31)	86 (4.3)	140 (10)	130 (7.2)
BDE-85	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5
BDE-99	120 (7.5)	180 (18)	47 (1.9)	160 (15)	54 (5.7)	680 (52)	190 (9.5)	190 (14)	220 (12)
BDE-100	53 (3.3)	52 (5.2)	<2.7	<2.7	14 (1.5)	300 (23)	51 (2.6)	58 (4.1)	68 (3.8)
BDE-153	<7	100 (10)	<7	<7	<7	<7	<7	<7	44 (2.4)
BDE-154	<5	100 (10)	<5	68 (6.2)	<5	<5	<5	<5	70 (3.9)
BDE-183	<6	<6	<6	690 (62)	<6	<6	<6	<6	<6
BDE-209	5800 (360)	500 (50)	8100 (324)	310 (28)	150 (16)	1500 (120)	380 (19)	1700 (120)	290 (16)
$\sum$PBDEs	6200 (380)	1100 (110)	8200 (330)	1300 (120)	260 (27)	2900 (220)	820 (36)	2200 (160)	930 (52)
$\sum$PBDEs$_{17:183}$	360 (28)	580 (69)	72 (2.9)	1000 (90)	110 (20)	1400 (110)	440 (17)	500 (35)	640 (36)
47:99 ratio	1	0.78	0.53	0.75	0.70	0.59	0.45	0.74	0.59

Table 5.3 PBDE Concentrations in pg/g dry wt (ng/g OC) in 2005 UK soil sample (to 2 significant figures).

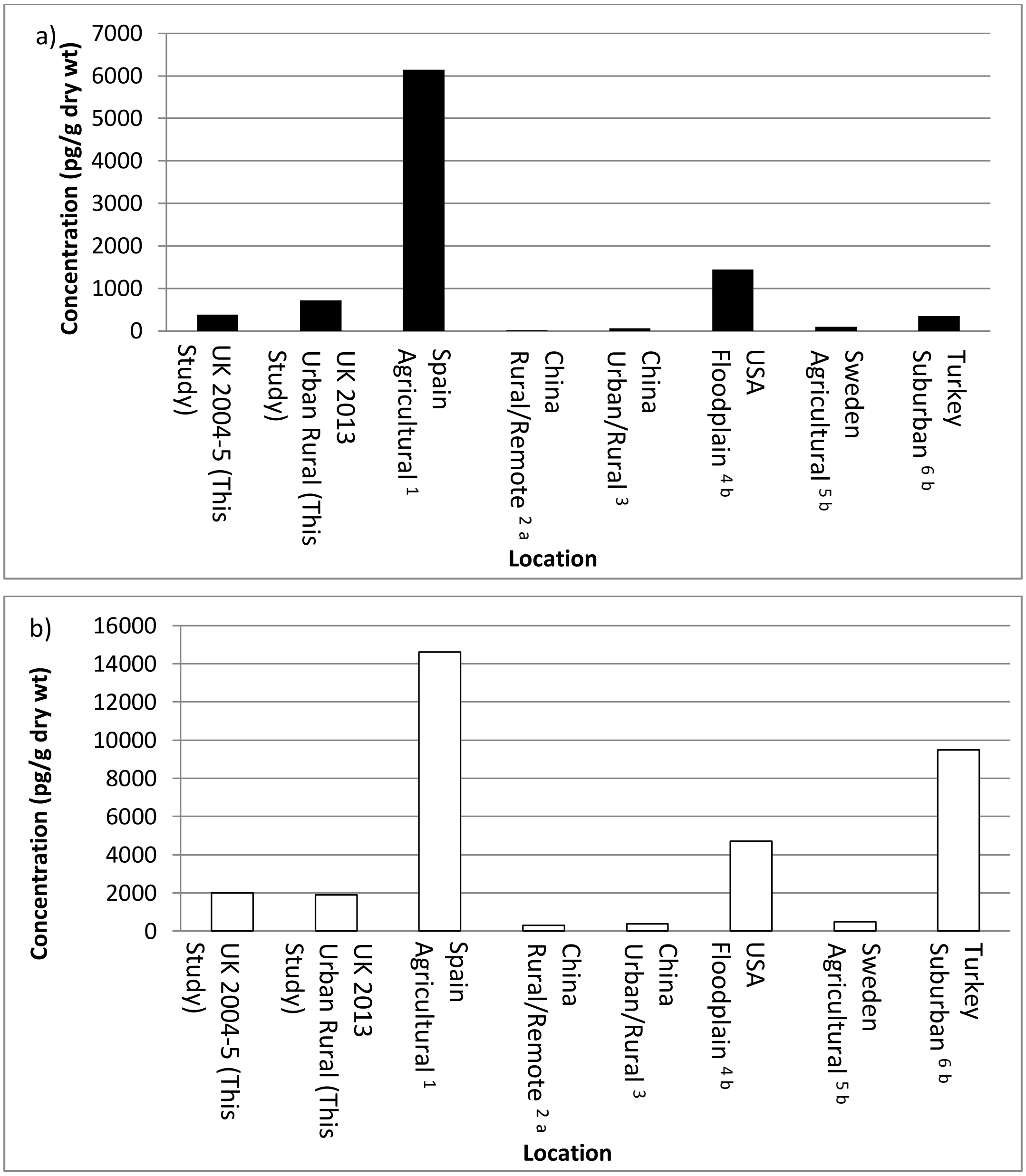
Despite this, although the archived 2004-05 soils were from a range of locations across the whole of the UK (in contrast to the West Midlands rural-urban soils), the ratio of urban/suburban to rural sites are similar in both (2.4 in 2004-05 and 3 in 2013) suggesting that the overall land-use classification distribution in each sample set is similar. A second limitation is that samples were not taken or measured between 2005 and 2013, so the overall temporal trend of PBDEs cannot be determined due to a lack of data in between these dates. Ideally, samples would have been taken in the same locations, annually between the two actual sampling years to get a more detailed account of PBDE levels in UK soil since the bans of commercial PBDE formulations.

5.4.2 Comparison with previous studies

As with ambient air, mean PBDE concentrations in soil from the UK are in the middle of those found in a range of studies from other countries (Figure 5.8 – only those that measured BDE-209 were included). Soil in Spain (Eljarrat et al., 2008), USA (Ma et al., 2009) and Turkey (Odabasi et al., 2010) had higher mean concentrations (21000; 6100; 9900 pg/g dry wt respectively) than those in the current study; whilst a mixture of rural/remote and urban/rural soils from China and agricultural soils from Sweden were 5-10 times lower than those reported here for the UK (Chen et al., 2012, Ma et al., 2009, Sellstrom et al., 2005). More appropriate comparisons would be on an OC-normalised basis, however OC data was not available for many (4 of 6) of the studies.

To the knowledge of the author this is the first study to measure BDE-209 in soil from the UK meaning that no comparisons can be made from within the country. With regards to other countries, the mean levels reported here are not the highest for similar land-use types, with suburban BDE-209 concentrations in Turkish soils at a mean concentration of 9500 pg/g dry wt (Odabasi et al., 2010) whilst both 2004-5 and 2013 samples have higher mean concentrations than in Chinese soils from a mixture of urban and rural environments (380 pg/g dry wt (Ma et al., 2009)).

Whilst it is apparent that urban areas behave as sources of PBDEs to the environment, the evidence suggests that they are by no means the only sources. Much higher concentrations were detected in soils taken from the vicinity of sources such as: informal e-waste treatment (Labunska et al., 2013), industrial sites (Odabasi et al., 2010)) and sewage sludge treatment (Eljarrat et al., 2008)).



[1]Eljarrat et al. (2008); [2]Chen et al. (2012); [3]Ma et al. (2009); [4]Yun et al. (2008); [5]Sellstrom et al. (2005); [6]Odabasi et al. (2010). [a] Median

Figure 5.8 Concentrations (pg/g dry wt) of a) $\sum_6$PBDEs (BDEs -47; -99; -100; -153; -154;-183) and b) BDE-209 in soils from this study and other countries from available literature

5.5 Conclusion

The concentrations of PBDEs detected in both the air and soil samples taken on the West Midlands urban-rural transect have highlighted the city of Birmingham as a source of PBDEs to the environment, with an urban pulse of elevated concentrations in sites closest to the city centre.

The strength of the urban pulse found in this study appears to be similar in ambient air as it was almost 10 years ago, whilst there appears to have been a decrease in the same ratio in soil (Harrad and Hunter, 2006). The overall $\sum PBDE_{28:154}$ concentrations in both soil and ambient air appeared to have decreased significantly in Edgbaston since they were previously measured in 2003-04 (Harrad and Hunter, 2006).

Although, not proven to be statistically significant (likely due to a small sample set), there are indications of two seasonal trends in PBDEs, with $PBDEs_{17:183}$ appearing to be higher in the summer months and lower in the winter, whilst the reverse is seen for BDE-209, likely due to its photolytic degradation in the summer due to increased exposure to higher temperatures and UV light.

Whilst there are no available comparisons on a site-by-site basis for total PBDE content in air and soil in the UK, the concentrations of both BDE-209 and $\sum PBDEs_{28:183}$ in the archived 2004-05 soil samples are significantly higher than those from 2013, which is not inconsistent with an overall decrease in environmental levels of PBDEs in the UK (as seen in air by Birgul et al. (2012)). However, congeners from the Penta- formulation are still being detected in the environment 10 years post-restriction, highlighting their persistence in the environment and the legacy left by their previous intensive use.

Chapter VI

Concentrations of PBDEs in Australian Soils and Sediments

6.1 Synopsis

This chapter reports the concentrations of PBDEs in soils and sediments in Australia. PBDEs were measured in 64 soil samples taken throughout Australia from a mixture of land-type classifications (urban; industrial; remote; agricultural). Concentrations of PBDEs were also measured in radiometrically-dated slices from 4 sediment cores taken in 1999 from various locations in Sydney Harbour, NSW. These data were interpreted in the context of temporal trends in PBDE contamination up to the end of the 20th century. BDE-47 was measured using HRGC/HRMS whilst penta-hepta PBDEs and BDE-209 were measured via LC-APCI-MS/MS.

6.2 Sampling Strategy

6.2.1 Australian Soil Samples

Soil samples in Australia were taken in 2003 by volunteers in accordance with the full protocol outlined in section 2.1.5.1 as part of the Australian National Dioxin Program. Areas were selected based on their land-use category as mentioned above and samples were taken from public open spaces within the area specified. Figure 6.1 outlines the large proportion of the country sampled, whilst Table 6.1 lists all the sampling locations, along with their land-use category.

Urban	**Industrial**	**Agricultural**	**Remote**
Darwin 1, NT	Darwin 2, NT	Katherine, NT	Alice Springs, NT
Brisbane 1, QLD	Brisbane 2, QLD	Gympie, QLD	Cooloola National Park, QLD
Gold Coast, QLD	Brisbane 3, QLD	Emerald, QLD	Carnarvon Gorge National Park, QLD
Cairns, QLD	Gladstone, QLD	Eastern ACT, ACT	Namadgi National Park, ACT
Canberra, ACT	Sydney 4, NSW	Lismore, NSW	Royal National Park, NSW
Newcastle, NSW	Sydney 5, NSW	Bombala, NSW	Sturt National Park, NSW
Sydney 1, NSW	Wollongong 2, NSW	Wagga Wagga, NSW	Hay Plains, NSW
Sydney 2, NSW	Adelaide 2, SA	Kuitpo Peninsula, SA	Cape Grim, TAS
Sydney 3, NSW	Whyalla, SA	Yorke Peninsula, SA	Central Tasmania, TAS
Wollongong 1, NSW	Port Pirie, SA	Flinders Ranges, SA	Canarvon, WA
Adelaide 1, SA	Hobart, TAS	Murray, SA	Mt Buller, VIC
Launceston, TAS	Melbourne 3, VIC	Lower Derwent, TAS	
Melbourne 1, VIC	Melbourne 4, VIC	Elliott, TAS	
Melbourne 2, VIC	Latrobe, VIC	Huon Valley, TAS	
Geelong, VIC	Geelong, VIC	Dandenong, VIC	
Bendigo, VIC	Perth 3, WA	Warracknabeal, VIC	
Perth 1, WA	Perth 4, WA	Bunbury, WA	
Perth 2, WA		Northam, WA	

Table 6.1 Soil sampling locations across Australia categorised by land-use type

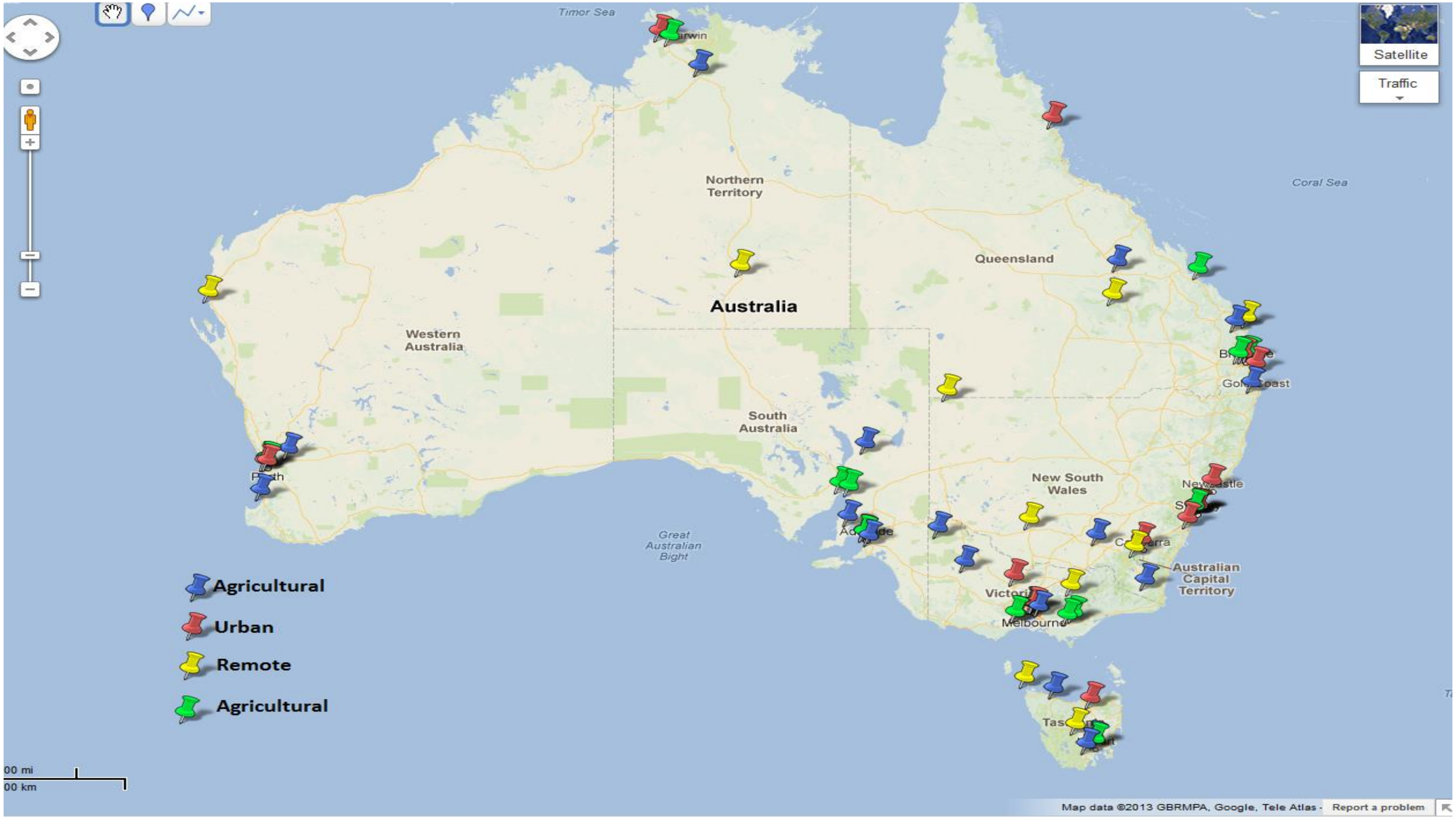


Figure 6.1 – Locations of sampling sites for Australian soil samples (n=64).

6.2.2 Sediment Core Samples

Sediment core samples were taken in 1999 from Port Jackson, Sydney, New South Wales (Figure 6.2) at sites close to storm water drains in Iron Cove (cores IC3 and IC5), Burns Bay (core BB) and North Harbour (core NH) as part of a study looking at temporal changes of trace metals and organochlorine pesticides in sediments from around the area, in line with its historical records of industrialisation and urbanisation (Taylor et al., 2004). Freeze dried samples were stored in sealed glass jars and kept in a dark area until clean-up and analysis.

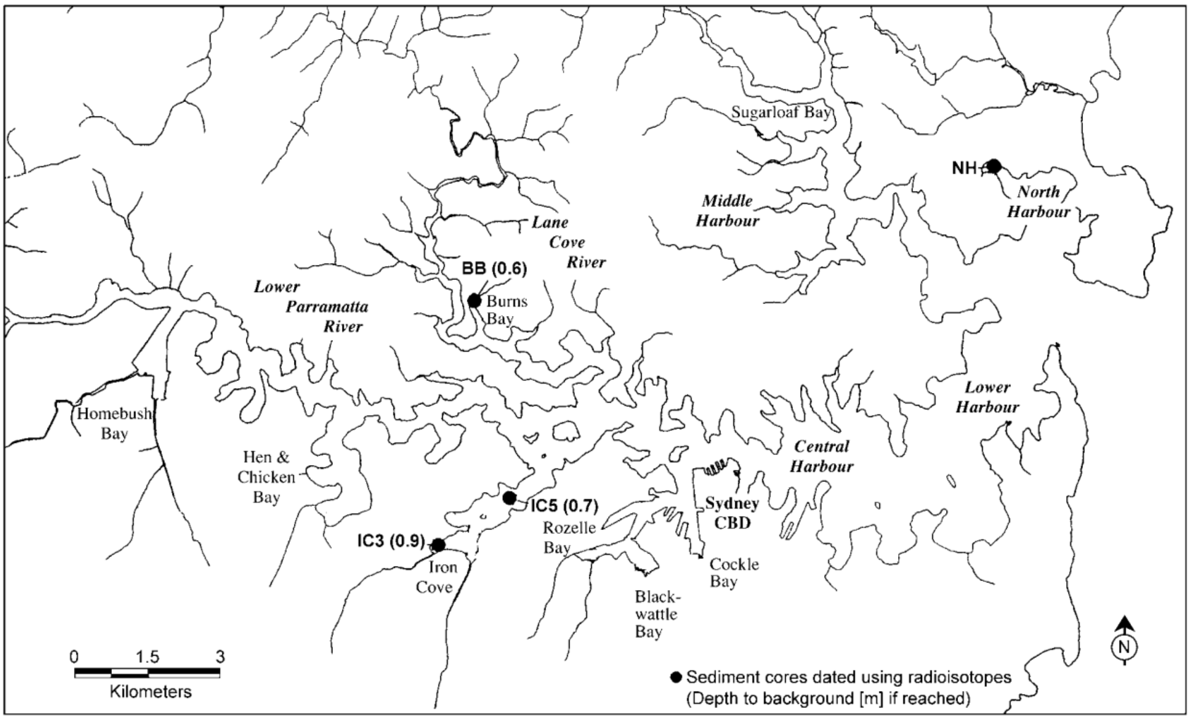


Figure 6.2 – Port Jackson Sediment Core sample names and locations – adapted from (Taylor et al., 2004)

6.3 Concentrations of PBDEs in Australian Soils

A wide range of PBDEs were detected across Australian soil samples with a mean ∑PBDE concentration of 320 (range = 10-3000) pg/g dry wt, with the highest concentrations coming from urban and industrial locations in the South and East of Australia (3000 pg/g (Whyalla, SA), 2800 pg/g (Wollongong, NSW) and 2400 pg/g (Melbourne, VIC)). Table 6.2 shows the concentrations of individual congeners for each sample, organized by land-use.

PBDE Congener →	**-47**	**-85**	**-99**	**-100**	**-153**	**-154**	**-183**	**-191**	**-196**	**-197**	**-206**	**-207**	**-209**	**∑PBDE$_{47:183}$**	**∑PBDEs**
Location	**Urban**														
Darwin 1, NT	15	<2.6	9.5	5.4	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	43	30	73
Brisbane 1, QLD	15	<2.6	7.8	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	33	23	56
Gold Coast, QLD	14	<2.6	11.7	3.8	<1.6	<2.1	<1	<1.5	<1.5	<1.5	5.2	3.2	74	30	110
Cairns, QLD	8.1	<2.6	4.3	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	2.7	5.8	91	15	110
Canberra, ACT	12	<2.6	11	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	50	23	73
Newcastle, NSW	51	<2.60	54	7.1	3.5	<2.1	<1	<1.5	<1.5	2.4	2.9	6.7	77	120	200
Sydney 1, NSW	39	<2.6	41	7.9	3.2	2.1	2.6	2.3	2	3.1	6.4	7.2	180	96	300
Sydney 2, NSW	52	<2.6	47	33	8.9	6.7	8.1	<1.5	3.2	7.5	24	28	480	160	700
Sydney 3, NSW	27	<2.6	24	6.9	<1.6	<2.1	2.2	<1.5	<1.5	<1.5	<2.6	4.3	81	60	150
Wollongong 1, NSW	110	<2.6	120	30	22	18	26	2.8	33	32	77	84	2200	330	2800
Adelaide 1, SA	24	<2.6	17	4.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	6.7	8.4	80	46	140
Launceston, TAS	28	<2.6	39	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	47	69	120
Melbourne 1, VIC	91	<2.6	92	<2.6	<1.6	5.2	66	<1.5	5.9	16	2.7	35	87	260	400
Melbourne 2, VIC	<1.4	<2.6	46	6.5	4.2	3	12	<1.5	<1.5	4.3	5.1	7.5	170	72	260
Geelong, VIC	41	<2.6	40	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	38	82	120
Bendigo, VIC	8.5	<2.6	8.3	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	26	17	43
Perth 1, WA	12	<2.6	13	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	34	25	59
Perth 2, WA	11	<2.6	10	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	53	7.3	21	82

[a]All concentrations given to 2 significant figures so totals may not equal sums of individual congeners; [b] <0.1 = not detected or below detection limit of 0.1 pg/g

Table 6.2 Concentrations of PBDEs (pg/g dry wt) in Australian Soils

PBDE Congener →	**-47**	**-85**	**-99**	**-100**	**-153**	**-154**	**-183**	**-191**	**-196**	**-197**	**-206**	**-207**	**-209**	**$\sum$PBDE$_{47:183}$**	**$\sum$PBDEs**
Location	**Industrial**														
Darwin 2, NT	7.7	<2.6	6.3	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	13	8.1	14	35
Brisbane 2, QLD	78	<2.6	71.4	8.8	6.5	3.2	12	<1.5	<1.5	7.6	10.4	12	530	180	740
Brisbane 3, QLD	66	<2.6	61	3.9	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	18	130	150
Gladstone, QLD	12	<2.6	12	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	31	25	56
Sydney 4, NSW	740	<2.6	590	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	99	1300	1400
Sydney 5, NSW	13	<2.6	12	4.1	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	88	29	120
Wollongong 2, NSW	30	3	50	7.3	3.8	<2.1	<1	<1.5	<1.5	<1.5	6.5	4.1	95	94	200
Adelaide 2, SA	20	<2.6	7.6	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	3.8	24	30	57
Whyalla, SA	1000	59	1400	260	98	94	2.1	<1.5	<1.5	<1.5	<2.6	<2.6	37	2900	3000
Port Pirie, SA	57	<2.6	20	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	53	78	130
Hobart, TAS	12	<2.6	13	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	68	26	94
Melbourne 3, VIC	30	<2.6	33	<2.6	<1.6	<2.1	2.8	<1.5	<1.5	<1.5	44	19	2300	66	2400
Melbourne 4, VIC	26	<2.6	60	<2.6	9	5	37	<1.5	8.1	15.6	11	20	300	140	500
Latrobe, VIC	11	<2.6	8.8	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	2.7	<2.6	40	21	65
Geelong, VIC	12	<2.6	12	<2.6	<1.6	<2.1	2.2	<1.5	<1.5	<1.5	<2.6	<2.6	61	27	88
Perth 3, WA	9.4	<2.6	11	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	67	22	89
Perth 4, WA	6.8	<2.6	7	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	16	14	30

[a] All concentrations given to 2 significant figures so totals may not equal sums of individual congeners; [b] <0.1 = not detected or below detection limit of 0.1 pg/g

Table 6.2 Concentrations of PBDEs (pg/g dry wt) in Australian Soils

PBDE Congener →	**-47**	**-85**	**-99**	**-100**	**-153**	**-154**	**-183**	**-191**	**-196**	**-197**	**-206**	**-207**	**-209**	**$\sum$PBDE $_{47:183}$**	**$\sum$PBDEs**
Location	**Agricultural**														
Katherine, NT	6	<2.6	9	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	10	15	25
Gympie, QLD	5	<2.6	10	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	8.7	8.8	190	15	220
Emerald Region, QLD	11	<2.6	11	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	9.3	23	32
Eastern, ACT	8.5	<2.6	6	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	<5	15	15
Lismore, NSW	39	<2.6	57	3.4	120	27	420	9.6	34	130	3.5	56	17	670	920
Bombala, NSW	15	<2.6	5.6	<2.6	<1.6	<2.1	3.3	<1.5	<1.5	<1.5	<2.6	<2.6	46	25	71
Wagga Wagga, NSW	7.1	<2.6	3	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	<5	10	10
Kuitpo Peninsula, SA	12	<2.6	4.5	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	200	17	220
York Peninsula, SA	<1.3	<2.6	<2.1	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	54	0.28	54
Flinders Ranges, SA	9.5	<2.6	9.7	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	10	19	29
Murray, SA	<1.3	<2.6	<2.1	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	4.6	79	0	84
Lower Derwent, TAS	11	<2.6	9.4	<2.6	<1.6	<2.1	2.3	<1.5	<1.5	3.9	<2.6	<2.6	31	23	58
Elliott, TAS	<1.3	<2.6	<2.1	<2.6	3.2	<2.1	15	<1.5	<1.5	4.8	<2.6	<2.6	48	18	71
Huon Valley, TAS	8.9	<2.6	17	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	18	26	44
Dandenongs, VIC	18	<2.6	22	<2.6	<1.6	<2.1	11	<1.5	<1.5	3	<2.6	<2.6	87	51	140
Warracknabeal, VIC	<1.3	<2.6	<2.1	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	5.8	5.1	180	0	190
Bunbury, WA	<1.3	<2.6	<2.1	9.7	<1.6	<2.1	<1	<1.5	<1.5	<1.5	5.9	5	280	9.7	300
Northam Region, WA	<1.3	<2.6	<2.1	<2.6	<1.6	<2.1	3.8	<1.5	<1.5	<1.5	4.9	5.1	170	3.8	180

[a]All concentrations given to 2 significant figures so totals may not equal sums of individual congeners; [b] <0.1 = not detected or below detection limit of 0.1 pg/g

Table 6.2 Concentrations of PBDEs (pg/g dry wt) in Australian Soils

PBDE Congener →	**-47**	**-85**	**-99**	**-100**	**-153**	**-154**	**-183**	**-191**	**-196**	**-197**	**-206**	**-207**	**-209**	**$\sum$PBDE $_{47:183}$**	**$\sum$PBDEs**
Location	**Remote**														
Alice Springs, NT	5.2	<2.6	3.2	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	12	3.5	600	8.4	620
Cooloola National Park, QLD	<1.3	<2.6	<2.1	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	3.2	2.9	170	0	180
Carnarvon Gorge, QLD	10	4.5	92	9	11	4.9	<1	<1.5	<1.5	<1.5	9.2	8.8	230	130	380
Namadgi National Park, ACT	<1.3	<2.6	<2.1	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	13	4.2	710	0	730
Royal National Park, NSW	7.2	<2.6	13	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	80	20	100
Stuart National Park, NSW	6.7	<2.6	4.1	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	15	11	26
Hay Plains, NSW	<1.3	<2.6	<2.1	14	4.4	3.2	<1	<1.5	<1.5	<1.5	<2.6	<2.6	15	22	37
Cape Grim, TAS	8.7	8.2	44	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	90	61	150
Central Tasmania, TAS	4.6	<2.6	36	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	79	41	120
Canarvon, WA	21	<2.6	34	<2.6	<1.6	<2.1	2.9	<1.5	<1.5	<1.5	<2.6	4.4	52	58	110
Mt Buller, VIC	14	<2.6	22	<2.6	<1.6	<2.1	<1	<1.5	<1.5	<1.5	<2.6	<2.6	<5	36	36

[a] All concentrations given to 2 significant figures so totals may not equal sums of individual congeners; [b] <0.1 = not detected or below detection limit of 0.1 pg/g

Table 6.2 Concentrations of PBDEs (pg/g dry wt) in Australian Soils

Overall, PBDEs are present in Australian soil in comparatively low concentrations with a median ∑PBDE concentration of 120 pg/g dry wt. On a dry weight basis, the mean ∑PBDE concentrations in soils from industrial and urban areas (430 and 290 pg/g dry wt respectively) are more than double that from soils in a remote area (130 pg/g dry wt), however a Mann-Whitney U test shows that these differences are insignificant (p=0.210 and 0.605 respectively). Figure 6.3 demonstrates that when soils are normalised to organic carbon content (pg/g OC), soils from industrial areas are the most contaminated with a mean concentration of 27000 pg/g OC.

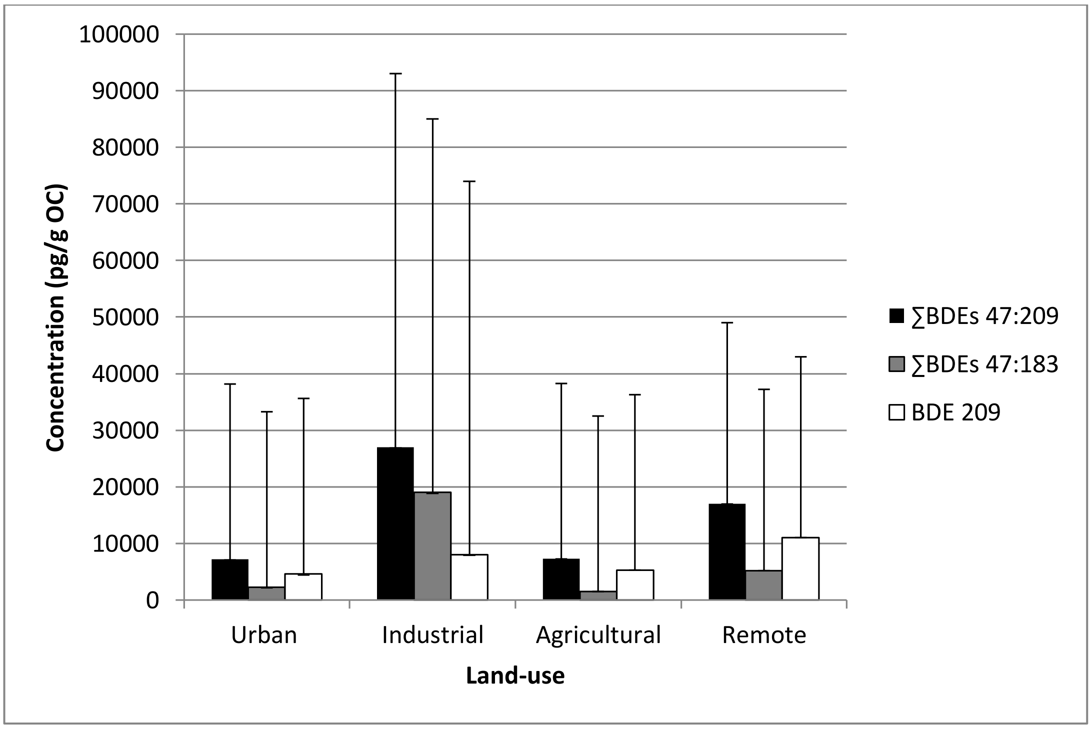


Figure 6.3 Mean concentrations of PBDEs in Australian soils (pg/g OC) according to different land-uses

Whilst it appears that industrial areas are more contaminated with PBDEs, such is the variability of concentrations within each category that an ANOVA test shows that there is no significant statistical difference between the mean concentrations between each group for ∑PBDEs and $\sum$PBDEs$_{47:183}$ (p = 0.194 and 0.434) as well individual BDE congeners -47, -99 and -209 (p = 0.194, -0.277 and 0.257).

Whilst there is no statistical difference between the average concentrations of soil samples in areas of different land-use, the ranges for each group indicate that there is an increased likelihood of elevated PBDE concentrations in areas close to industrial activity. The minimum ∑PBDE concentrations are of similar magnitude across all categories (urban = 1000 pg/g OC; industrial = 540 pg/g OC, agricultural = 710 pg/g OC, remote = 430 pg/g OC), however the maximum concentrations were much higher in industrial areas (230000 pg/g OC) than in urban, agricultural and remote areas (39000, 33000 and 58000 pg/g dry wt respectively).

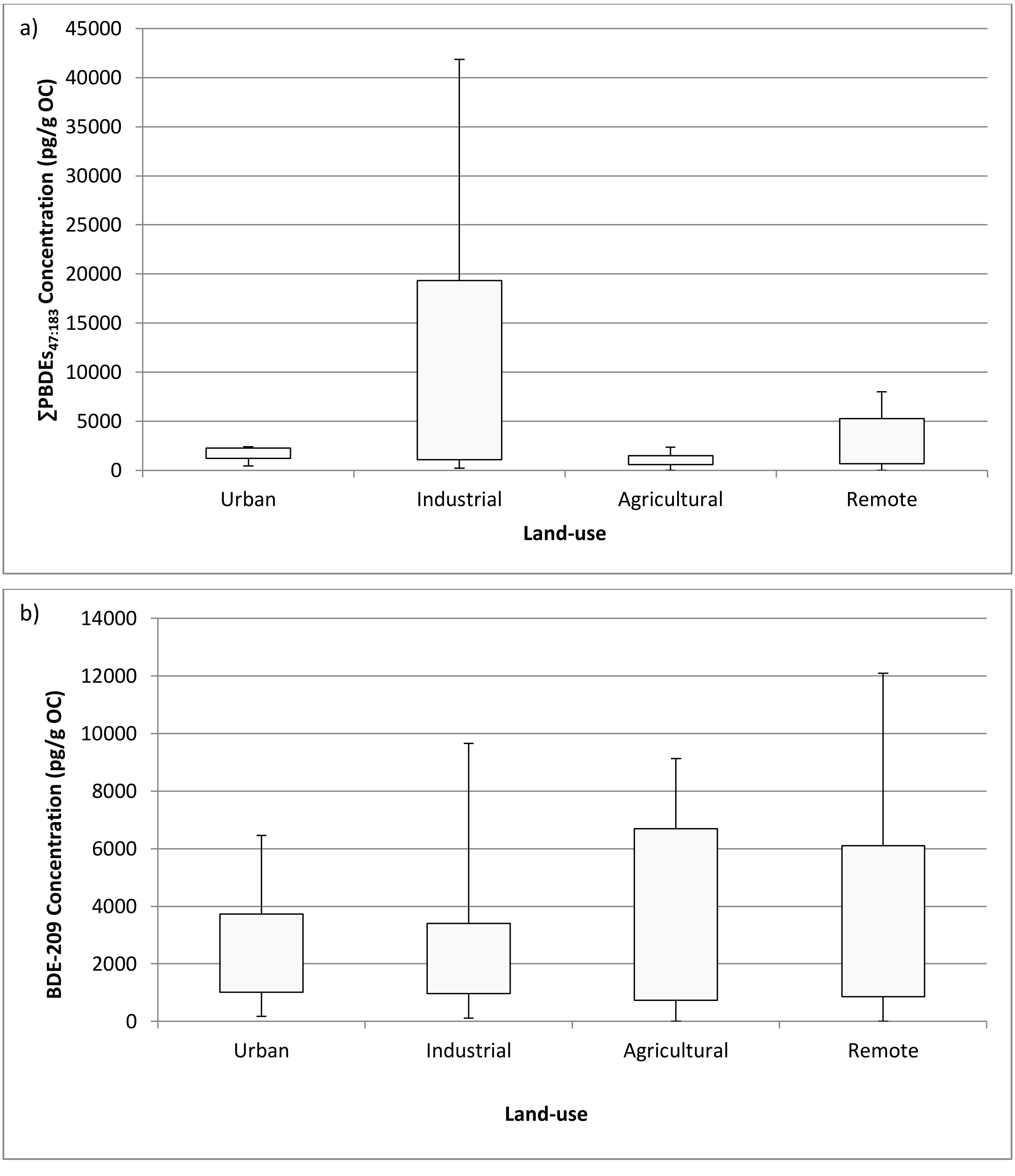


Figure 6.4 – Boxplot diagram for a) ∑PBDEs$_{47:183}$ and b) BDE-209 in different land-uses showing inter-quartile range, minimum and maximum (÷10) concentrations in soil (pg/g OC).

Figure 6.4 suggests that this increased contamination is sourced from lower-brominated PBDE congeners with a much wider range of $\sum PBDE_{47:183}$ concentrations in soils from industrial locations than in those from other land-use categories (discussed further in the next section), whilst BDE-209 concentrations appear to be similar across all categories.

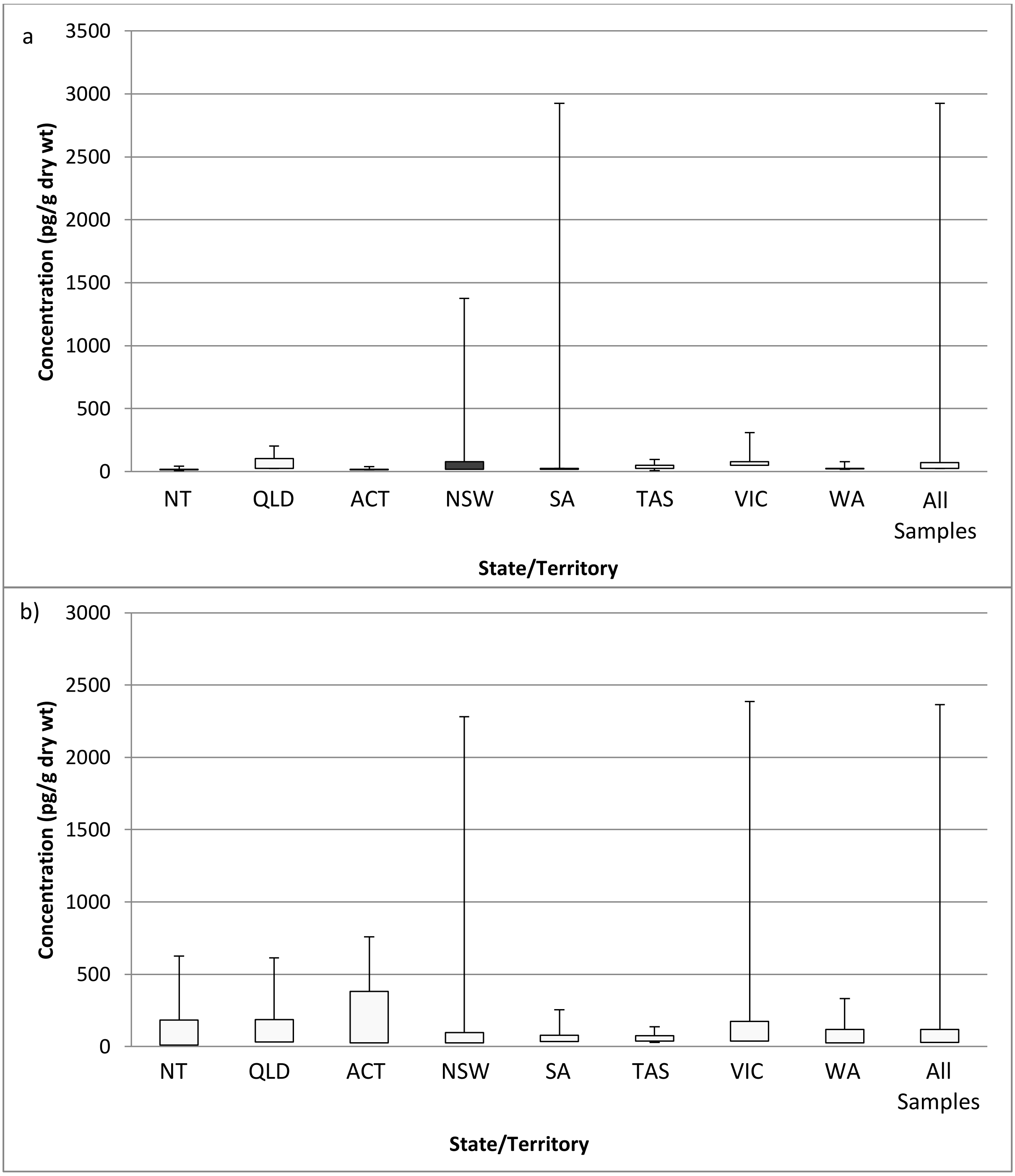


Figure 6.5 Boxplot diagram of a) $\sum PBDE_{47:183}$ and b)BDE-209 concentrations in Australian soils, from different states showing the interquartile range, minimum and maximum values for each region (pg/g dry wt)

As with their concentrations according to land-use, ∑PBDE levels in soils do not appear to show any particular trends (Figure 6.5). Overall, in all states the concentrations are low; 85% of soils across all regions are <350 pg/g dry wt), with the 3 soil samples that display elevated concentrations originating from urban and industrial environments.

6.3.1 Congener Profiles

BDE-209 is the dominant congener of the mean PBDE profile in soils across all land-use categories, (urban = 66%, industrial = 42%, agricultural = 54%, remote = 82%) implying that the primary commercial formulation used would have been Deca-BDE – although the higher K_{OA} of BDE-209 meaning that it should have higher affinity for accumulation in soil than lower brominated congeners will also be a factor. Whilst this dominance of BDE-209 exists, there are a few samples which indicate that some areas have been exposed to other commercial formulations. Specific examples are the samples from: (a) an industrial site in Whyalla, SA which shows a congener profile similar to that of a commercial PentaBDE mixture, and (b) an agricultural site in Lismore, NSW that displays a very similar profile to that of OctaBDE, suggesting that different formulations have influenced these locations (Figure 6.4).

The average congener profiles found in soils from each land-use category (Figure 6.5) suggest that industrial soils contain a greater proportion of congeners from the PentaBDE formulation than soils from other land-use categories. Whilst BDE-209 still contributes 42% to the average total PBDE content in industrial soils, BDEs -47 and -99 contribute a combined total of 49% (23% and 26% respectively) suggesting that industrial soils have been equally influenced by both the Penta-BDE and Deca-BDE commercial mixtures. The profile for urban soil also suggests an influence (to a lesser extent) of the Penta-BDE formulation with 20% of the average congener profile attributed to BDEs -47 and -99.

Whilst Penta-BDE based congeners are prominent in urban and industrial soils and those from Deca-BDE prominent in all soils, soils from an agricultural background appear to have been more influenced by congeners indicative of Octa-BDE formulations (BDEs -153 = 5%, -183 = 17%, -197 = 5.3%). Studies from other countries such as Spain (Eljarrat et al., 2008) and Sweden (Sellstrom et al., 2005) have shown how agricultural soils are contaminated with PBDEs, although they have not necessarily been attributed to the Octa-BDE formulations.

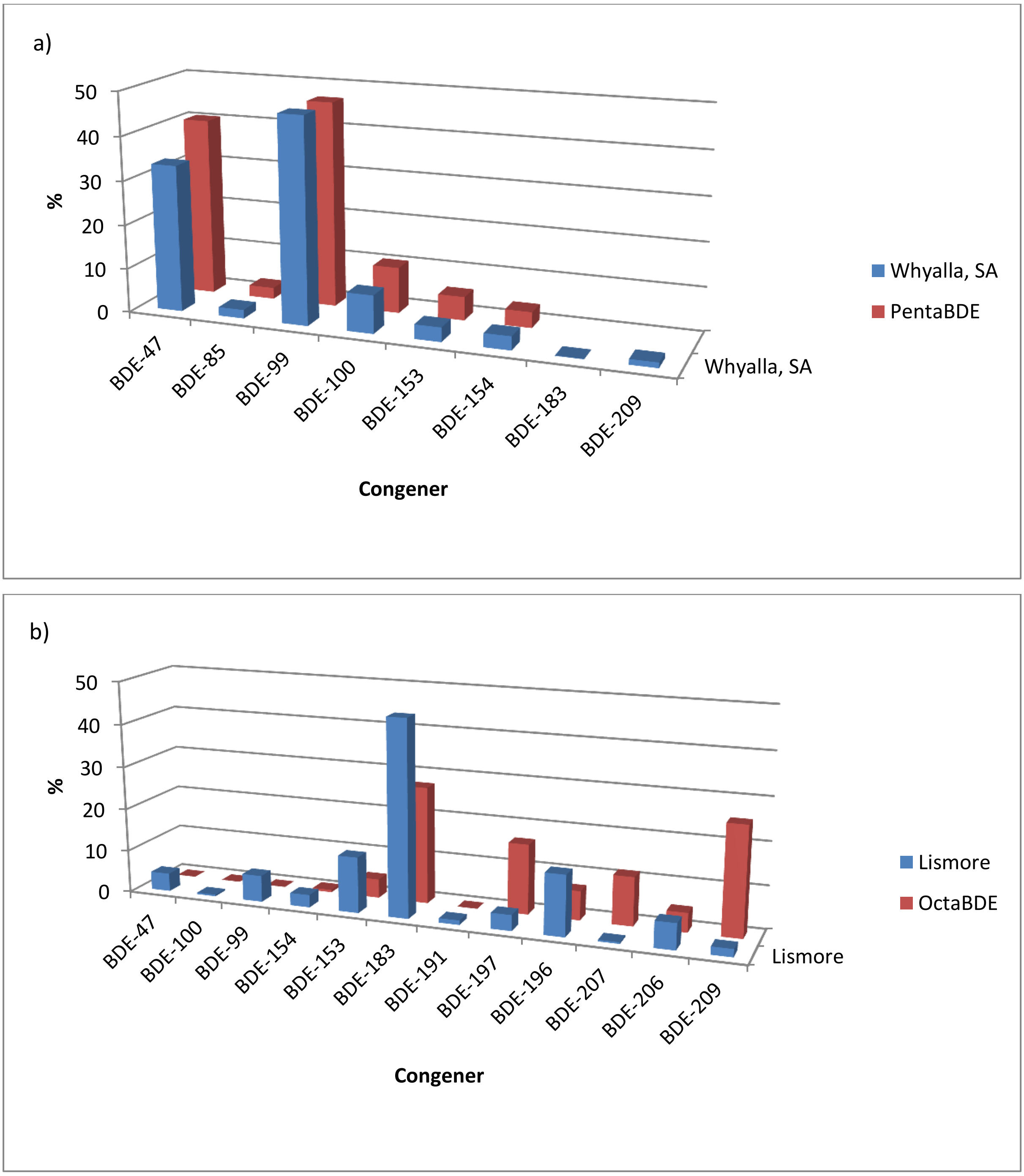


Figure 6.4 A Comparison of the PBDE congener profile in soil from a) Whyalla, SA (industrial site) from this study, compared with the proportions in the commercial PentaBDE mixture and b) Lismore, NSW (Agricultural site) compared with those from commercial OctaBDE (La Guardia et al., 2006)

The abundance of key congeners from both formulations such as BDEs -47, -99 and -100 for PentaBDE and BDEs -183; -197, -196, -207 and -206 for OctaBDE (based on technical mixtures analysed by La Guardia et al. (2006), along with the aforementioned overall dominance of BDE-209 suggests that all three commercial formulations have been used fairly heavily within Australia.

Whilst the statistical evidence (ANOVA) suggests that there are no significant differences in the concentrations of PBDEs in different land-use categories, there is evidence from the above data to suggest that whilst DecaBDE has been the principal PBDE formulation used, the different commercial PBDE formulations have all been used widely in Australia. Industrial and, to a lesser extent, urban soils appear more heavily contaminated with lower brominated PBDEs indicative of the PentaBDE formulation, whilst agricultural soils are the only samples to show raised levels of congeners typical of OctaBDE, while the congener profiles of remote sites are dominated by BDE-209 (82%).

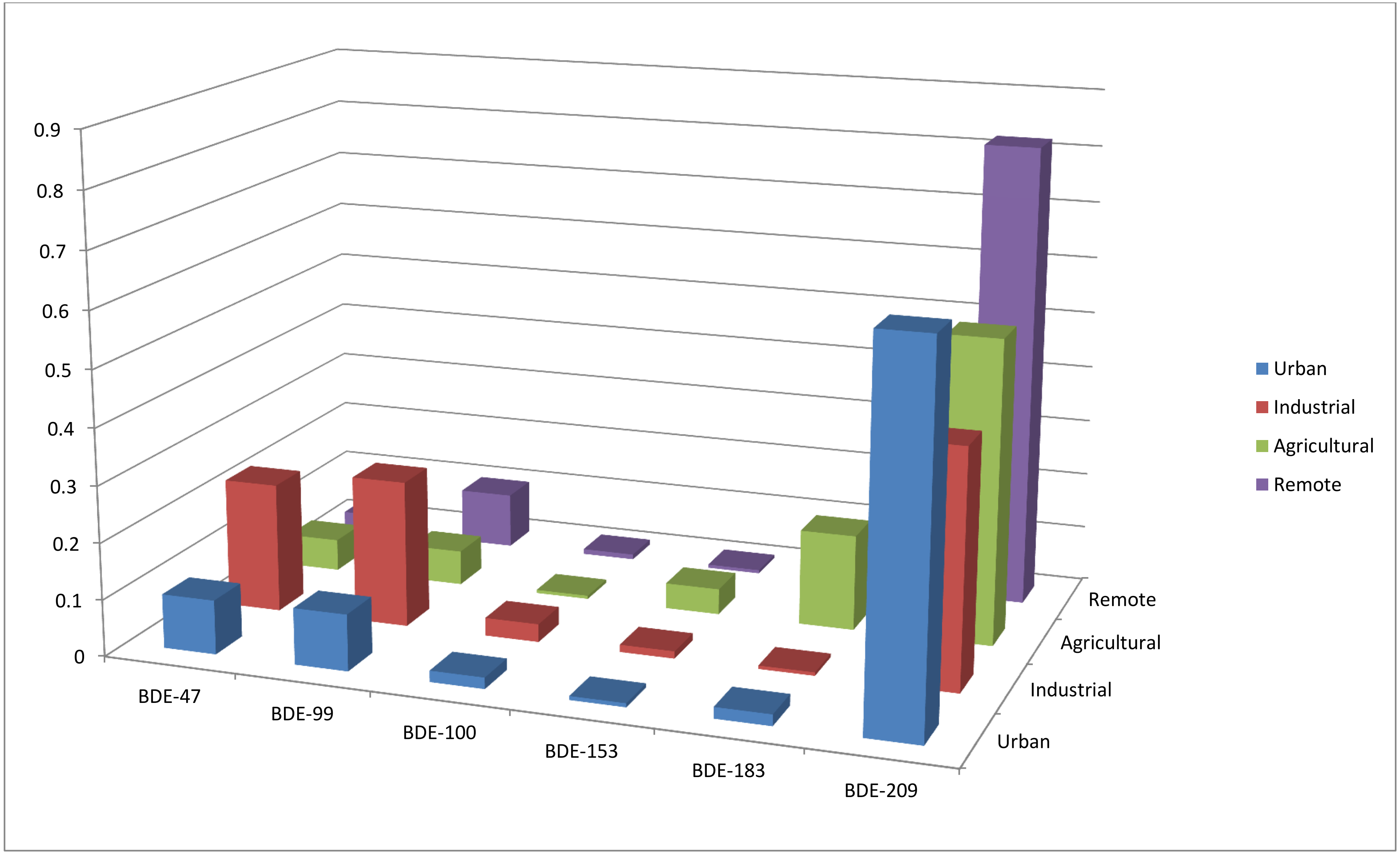


Figure 6.5 Mean congener profile of soils from different land-uses

6.3.2 Comparisons with PBDEs in Australian soil and those from other countries

The soil concentrations presented in this paper are at the lower end of the range of soils found in other literature presented and UK data from Chapter V of this study (Table 6.5) with the concentrations from all land-use categories lower than in other countries. The most similar concentrations found were those in rural/remote areas in China (Chen et al., 2012, Ma et al., 2009) and agricultural soils in Sweden (Sellstrom et al., 2005). It should be noted that measurements from known sources, such as e-waste sites, landfill or treated soils were not used for comparison, whilst studies that did not measure BDE-209 were also not used.

When comparing Australian samples with UK samples based on organic carbon (OC) content it would appear that soils from the UK sampled at a similar time (2004-05) contain at least 20 times the amount of PBDEs as Australian soils, while urban and remote samples from Australia display similar average concentrations to those detected in the UK 2013 rural-urban transect samples. Similarly, the concentrations in these Australian soils are approximately 5-10 times lower than in those taken at a similar time in both the USA (Yun et al., 2008) and from Spain (Eljarrat et al., 2008). This indicates that concentrations of PBDEs in soil from Australia during the peak period for PBDE usage were 5-20 times lower than North America, UK (both on an OC basis), and continental Europe (on a dry weight basis). Furthermore, what are expected to be the peak concentrations in Australia are at a similar level to those in UK soils measured in 2013, which were considered to be significantly lower than previously (several years after restrictions on the various PBDE commercial formulations). This would suggest that PBDE levels in Australia are relatively low in comparison to other countries.

	n	**Land-use**	**BDE 47**	**BDE 99**	**BDE 100**	**BDE 153**	**BDE 154**	**BDE 183**	**BDE 209**	**$\sum_7$PBDE**
Australia (this study)	18	Urban	31 (870)	12 (8900)	6.3 (1300)	2.3 (47)	1.8 (35)	6.9 (130)	210 (4300)	270 (16000)
Australia (this study)	17	Industrial	130 (7500)	39 (8900)	17 (1300)	6.9 (520)	6 (460)	3.3 (150)	230 (7900)	430 (27000)
Australia (this study)	18	Agricultural	8.4 (440)	234 (440)	0.86 (23)	1.4 (120)	0.74 (23)	0.26 (470)	190 (5200)	120 (6800)
Australia (this study)	11	Remote	7 (2400)	6.2 (3200)	2.1 (210)	1.4 (170)	0.74 (85)	2.9 (140)	190 (11000)	210 (17000)
UK 2013 Soil (this study)	8	Urban/Rural	210 (1200)	210 (990)	69 (290)	31 (150)	60 (270)	74 (370)	1900 (11000)	2600 (14000)
UK 2004 Soil (this study)	17	Urban/Rural	100 (7400)	170 (11000)	33 (12000)	8 (2500)	13 (690)	36 (3400)	1700 (100000)	2100 (140000)
China Chen et al. (2012)[a]	20	Rural/Remote	2.1	3.4	3.3	2.6	1.6	4.3	300	320
Sweden Sellstrom et al. (2005)	11	Agricultural	86 (1900)	120 (2700)	25 (620)	11 (200)	9.7 (230)	<6	560 (16000)	810 (21000)
China Ma et al. (2009)	5	Urban/Rural	30	90	10	50	<dl	not measured	380	560
China Ma et al. (2009)	12	Industrial (Chemical complex)	70	90	10	50	<dl	not measured	40000	40000
Turkey Odabasi et al. (2010)	10	Suburban	90	120	30	50	60	not measured	9500	9900
Turkey Odabasi et al. (2010)	7	Industrial	220	400	70	150	110	not measured	36000	37000
Spain Eljarrat et al. (2008)[a]	6	Agricultural	690	630	1,080	940	930	1870	14600	20740
USA Yun et al. (2008)	55	Floodplain	400 (11000)	350 (9400)	80 (2200)	45 (1400)	38 (1000)	not measured	3900 (130000)	4800 (150000)

[1]Only studies that measured BDE-209 are included in this table. [a] median (mean not given or available in supplementary data)

Table 6.3 Comparisons of average PBDE concentrations (dry wt and OC-normalised where available) in soils from Australia and other countries (pg/g dry wt (pg/g OC))

6.4 Concentrations of PBDEs in Archived Sediment Cores from Port Jackson

Using the sedimentation rates measured in the initial study, dates were estimated for each layer in each sediment core Taylor et al. (2004). The total PBDE concentrations for each layer along with their estimated dates are presented in Table 6.7. Doubling times were also calculated if an increase in concentrations occurred in 3 or more consecutive layers. This was calculated using Equation 6.1. In this section BDE-209 is reported separately from tetra-hepta PBDEs as it contributes an average of 82% of total PBDE content across all 4 sediment cores. Other than in 2 samples (NH 9-11 cm = 29%; IC5 40 cm = not detected) BDE-209 was the dominant congener in sediment. This is in line with other countries, such as Switzerland (Kohler et al., 2008), UK (Vane et al., 2010, Webster et al., 2008), Japan (Choi et al., 2003a) as well as others.

$$Doubling\ time = \frac{Ln(2)}{k} \qquad \text{Equation 6.1}$$

where k = the 1st order rate constant for the increase in concentration

With the exception of the upper-most layers, sediment concentrations from Port Jackson, Australia appear to contain much lower levels of PBDEs than the majority of other countries. The upper-most layers suggest that PBDEs (in particular DecaBDE) were used most intensively during the mid-late 1990s, with average ∑PBDE concentrations from the 1990s of 3400 pg/g dry wt (range: 560-14000 pg/g dry wt). The concentrations were highest in the top layer of all cores except for IC3, suggesting that PBDE usage levels were still rising at the end of the 1990s. The mean 1990s concentrations are similar to those detected in 46 surface sediments from around Australia in 2002-03, which had a mean value of 4200 pg/g dry wt (range: <dl-41000 pg/g dry wt) for the same congeners (Toms et al., 2006). From the same study, two surface sediment samples were measured from Port Jackson, with concentrations in the west at 23000 pg/g dry wt and 850 pg/g in the east. Such spatial variation is consistent with the current study, in which concentrations from the top layer of sediment cores gave mean values of 6600 pg/g dry wt for sites on the west of Port Jackson (IC3, IC5 and BB), whilst NH on the east of Port Jackson had a concentration of 650 pg/g dry wt. Interestingly, whilst organochlorine data is not available for the same cores, the sharp rise in PBDE levels coincides with the decline in PCB levels in 2 cores taken at the same time in very close proximity to IC3 and IC5 in Iron Cove. In these two cores, PCBs peak in the early 1970s at

approximately 150 ng/g dry wt each before a sharp decline in the 1980-1990s – the opposite that is found for PBDEs. This is unsurprising given that PCBs were phased out following their ban in the USA in 1977, and PBDEs were introduced around a similar time (Usenko et al., 2007). The concentrations from Port Jackson are of a similar magnitude in the two studies but slightly higher in 2002-3 than in this study, suggesting that PBDE concentrations were still increasing between 1999 and 2003, although given the known spatial variations in PBDE concentrations in sediments, this conclusion is not absolute without measurement from the exact locations for both studies. Ideally, comparisons would have been made based on OC content, however, there was insufficient sample remaining for measurement of OC in this study.

The historical changes of PBDE concentrations in sediment from Port Jackson (Figure 6.6) appear to be of a similar pattern to those seen elsewhere, with concentrations being minimal before the 1970s, with sharp increases (primarily in BDE-209) between 1980 and 1999. This pattern has also been seen in Switzerland where PBDEs were found in sediments from 1975-1980 rising sharply to 8.8 ng/g dry wt in 2000 (Kohler et al., 2008); UK and Europe (Vane et al., 2010, Zegers et al., 2003), China (Chen et al., 2007) and North America (Song et al., 2005a) as well as the Arctic (Evenset et al., 2007) and others.

Port Jackson is primarily an industrial area, particularly to the west in Iron Cove (IC3, IC5) and Burns Bay (BB), whilst towards the east the land is a mixture of industrial and urban use, whilst sampling sites were chosen in the original study due to their known proximity to sources of industrial contamination (Taylor et al., 2004). It is therefore surprising that the PBDE concentrations are lower than those of sites elsewhere in the world located away from point sources, such as Lake Superior, North America where the top 2 cm measured 6.5-21 ng/g dry wt (Song et al., 2004) compared with 0.65-14.1 ng/g dry wt from samples in this study. Furthermore, the top layer of NH, representative of sediment from around 1996 (0.65 ng/g dry wt) is of a similar concentration to Ellasjøen surface sediment from 2001 (0.73 ng/g dry wt) – a remote freshwater lake in the Norwegian Arctic (Evenset et al., 2007). The concentrations found in this study appear to be substantially lower than those found in urban and industrialised areas such as the Scheldt river in Antwerp where Covaci et al. (2005) found that even the lower layers of sediment cores have concentrations around 20 times higher (320 ng/g dry wt) than the highest levels in Port Jackson (14 ng/g dry wt), whilst the highest concentrations found in the Scheldt were more than 500 times the highest found in this study.

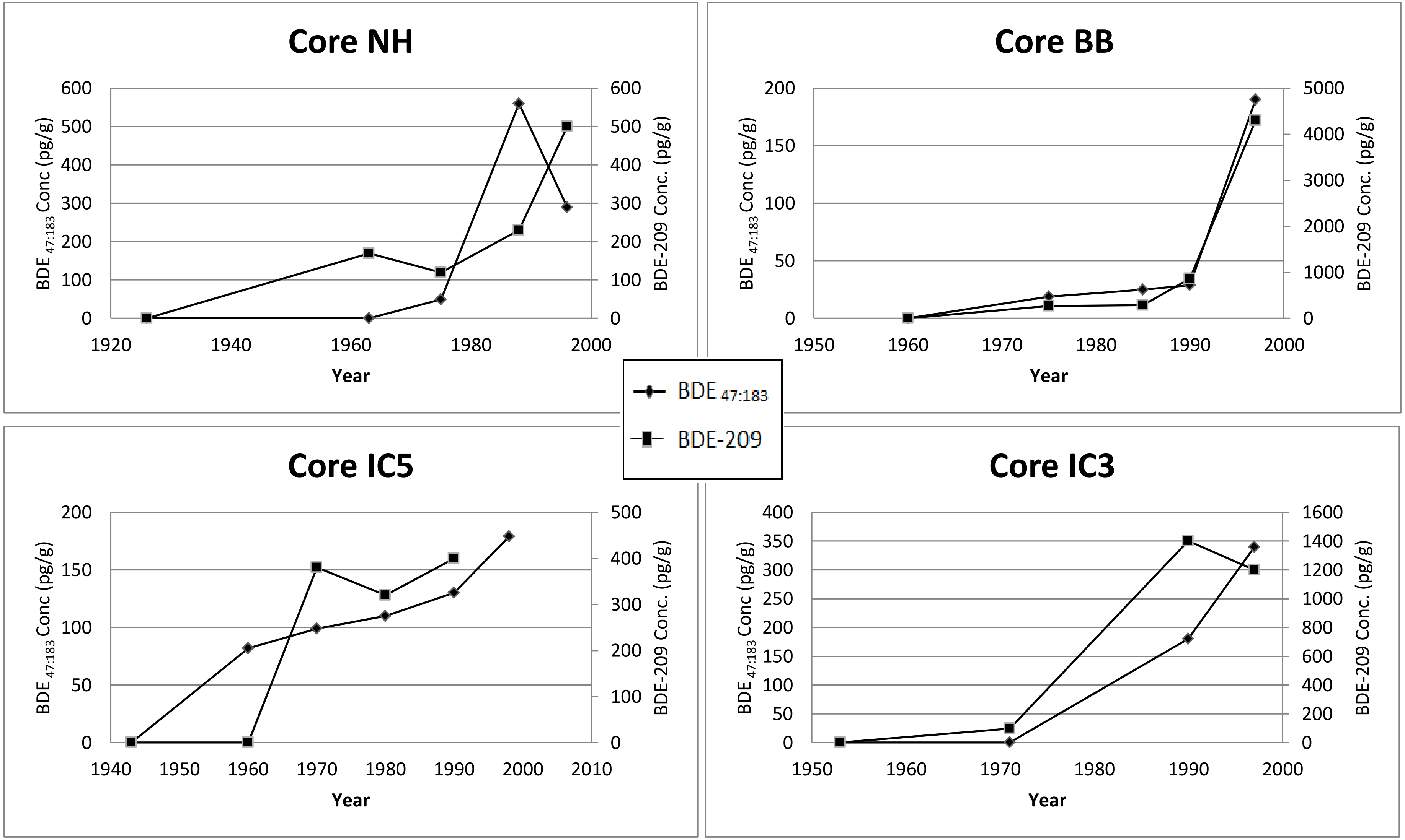


Figure 6.6 – Historical trends of PBDEs sediment cores from Port Jackson, Sydney, NSW (pg/g dry wt)

Core	Depth (cm)	Year	BDE-47	BDE-99	BDE-100	BDE-153	BDE-183	BDE-191	BDE-196	BDE-197	BDE-207	BDE-206	BDE-209	PBDE$_{47:183}$	∑PBDEs
IC3	**2**	**1997**	154	160	<2.6	14.5	11	7.8	<2	<2	22	28	1200	340	1600
	10	**1990**	78	91	<2.6	<1.6	16	<2	<2	<2	95	50	1400	180	1700
	30	**1971**	<25	<13	<2.6	<1.6	<1	<2	<2	<2	<5	<5	97	0	97
	50	**1953**	<25	<11	<2.6	<1.6	<1	<2	<2	<2	<2	<2	<5	0	0
	70	**1935**	<25	<15	<2.6	<1.6	<1	<2	<2	<2	<2	<2	<5	0	0
IC5	**1**	**1998**	100	79	<2.6	<1.6	<1	<2	<2	29	81	155	14000	179	14000
	9	**1990**	73	59	<2.6	<1.6	<1	<2	7.5	5.5	10	10	400	130	560
	20	**1980**	54	51	<2.6	<1.6	<1	<2	<2	3.8	5.4	9	320	110	450
	30	**1970**	50	49	<2.6	<1.6	<1	<2	<2	12	13	8.6	380	99	510
	40	**1960**	30	52	<2.6	<1.6	<1	<2	<2	18	18	<4	<5	82	82
	60	**1943**	<25	<4.4	<2.6	<1.6	<1	<2	<2	7.52	<4	<4	<5	0	0
	80	**1925**	<25	<2.5	<2.6	<1.6	<1	<2	<2	<2	<5	<5	<5	0	0
	99	**1910**	<25	<2.5	<2.6	<1.6	<1	<2	<2	<2	<5	<5	<5	0	0
BB	**4-6**	**1997**	120	67	<2.6	<1.6	<1	<2	<2	<2	15	130	4300	190	4600
	9.5-10.5	**1990**	4	25	<2.6	<1.6	<1	<2	<2	<2	28	17	860	29	930
	19.5-20.5	**1985**	5	20	<2.6	<1.6	<1	<2	<2	<2	<5	<5	290	25	320
	38.5-40.5	**1975**	<25	19	<2.6	<1.6	<1	<2	<2	<2	<5	<5	270	19	290
	58-60	**1960**	<25	<10	<2.6	<1.6	<1	<2	<2	<2	<5	<5	<50	0	0
	88-90	**1950**	<20	<20	<2.6	<1.6	<1	<2	<2	<2	<5	<5	<90	0	0
NH	**2-4**	**1996**	65	180	19	9.2	21	<2	<2	<2	25	27	500	290	850
	9-11	**1988**	260	270	26	<1.6	7.7	<2	<2	<2	16	<5	230	560	810
	19-21	**1975**	25	24	<2.6	<1.6	<1	<2	<2	<2	11	<5	120	49	180
	29-31	**1963**	<35	<24	<2.6	<1.6	<1	<2	<2	<2	12	<5	170	0	180
	59-61	**1926**	<20	<40	<6	<1.6	<20	<2	<2	<2	<5	<5	<50	0	0
	89-91	**1901**	<20	<40	<2.6	<1.6	<1	<2	<2	<2	<5	<5	<98	0	0
	115-118	**1859**	<20	<30	<2.6	<1.6	<1	<2	<2	<2	<5	<5	<120	0	0

Table 6.4 Concentrations (pg/g dry wt) of PBDEs in 4 sediment cores from Port Jackson, Sydney, Australia (values to 2 significant figures)

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Of the congeners measured, only 10 congeners were detected in measurable quantities (BDEs -47; -99; 100; -153; -183; -191; -197; -206; -207; -209). As already mentioned, BDE-209 was the most common BDE congener present. In 13 of the 15 samples containing BDE-209 the BDEs -206 and 207 were also detected at 2-10% of the concentration of BDE-209 (a very similar ratio to the commercial DecaBDE formulations, (the average congener proportions of Saytex 102E and Bromkal 82-0DE are approximately 94% BDE-209, 5.8% BDEs 206 + 207 (La Guardia et al., 2006)). The dominance of BDE-209 in the majority of samples suggests that primarily the DecaBDE technical mix was used in the area surrounding Port Jackson. The short BDE-209 doubling times (Table 6.8) between 1970-75 and 1996-98 (mean = 6.5 years; range = 3.1-10.2 years), particularly on the western side of Port Jackson show the rapid increase in BDE-209, with a further indication that the concentrations were still rising at the end of the 20th Century and into the 21st Century.

		Doubling time (years)	
Core	**Timeframe**	**PBDE$_{47:183}$**	**BDE-209**
IC3	1971-1997	-	6.5
IC5	1970-1998	34	6.2
BB	1985-1997	4	3.1
NH	1975-1996	-	10

Table 6.5 Doubling times for PBDE$_{47:183}$ and BDE-209

The proportions of BDEs -47, -99, -100 and to a lesser extent -153 and -183 were higher in layers corresponding to the 1980s and 1990s in cores IC3 (10 cm (1990) = 7.7% 2 cm (1997) = 15% BDE$_{47:183}$) and NH (9-11 cm (1988) = 62%, 2-4 cm (1996) = 23% BDE$_{47:183}$) suggesting that there was also modest usage of the PentaBDE formulation in the 1980s and 1990s. However, the concentrations, for the most part, are substantially lower than BDE-209, whilst it was only possible to calculate a doubling time for BDE$_{47:183}$ for IC5 between 1970 and 1998 (34 years) and BB from 1985-1997 (4 years) as levels did not increase by depth/year in any other sediment core as they did for BDE-209, suggesting that any use of either the PentaBDE and OctaBDE formulations was not extensive.

Overall, the pattern in Port Jackson observed over time with respect to PBDEs, particularly BDE-209, is very similar to that seen across the world, with sharp increases between the 1970s and 2000s and similar doubling times to elsewhere, such as in the Great Lakes (Zhu and Hites, 2005). Furthermore, the peak levels were found in the top layers of sediment cores, whilst surface sediments from 2002-3 in similar areas of Port Jackson were higher still (Toms et al., 2006) strongly suggesting that PBDE levels were still increasing past 2000, assuming little spatial variation between sampling locations in this study and the later study of Toms et al. (2006). However, in order to assert this theory with more confidence, it would be ideal to take new sediment cores to measure PBDE levels in layers from later dates with any spatial variation eliminated. However, considering the land-use in the vicinity of Port Jackson the levels are comparatively low in comparison with other countries in areas of similar land-use such as in China, Japan and the UK. This, coupled with the overall low PBDE levels in soils from 2002-3 suggests that the usage of PBDEs in Australia has been considerably lower than in other areas of the globe.

Chapter 7

Summary & Conclusions

PBDEs were used extensively across the world towards the end of the 20th century and very early 21st century to flame retard a wide range of products, such as upholstered furniture, electrical goods (circuit boards, and products casings), polyurethane foam in furniture, pipes and sealants (D'Silva et al., 2004, BSEF, 2003, BSEF, 2007) .

There has been extensive scientific study to show that the additive nature of the incorporation of PBDEs into these products means that they can easily migrate from their products into a wide range of environmental compartments, such as dust (Stapleton et al., 2005, Harrad et al., 2006), indoor (Fromme et al., 2009, Toms et al., 2009b) and outdoor air (Harrad and Hunter, 2006, Birgul et al., 2012, Hoh and Hites, 2005), soil (Harrad and Hunter, 2006, Hassanin et al., 2003, Chen et al., 2012) and sediment (Nylund et al., 1992, Liu et al., 2005, Webster et al., 2008). This contamination along with their hydrophobicity and resistance to metabolism has led to bioaccumulation in biota and their biomagnification along the food chain (Lim and Lastoskie, 2011), with the result that they have been detected in humans (Hearn et al., 2013, Toms et al., 2009b) with exponential increases found in breast milk concentrations between 1972-1999 (Meironyte et al., 1999).

PBDD/Fs are unintentionally produced, with their main form of release believed to be as by-products from the manufacture, use and recycling of BFR-containing products, such as PBDEs (Hayakawa et al., 2004). A limited number of studies have investigated the presence of PBDD/Fs in the environment, which show their presence in dust (Suzuki et al. 2007, Tue et al. 2013) and from inside consumer products (Takigami et al. 2008) as well as in air (Wang et al. 2008) and soil surrounding industrial areas (Ma et al. 2009). PBDD/Fs have also been found in human adipose tissue since the 1970s (Choi et al. 2003b).

Concerns over this environmental and human exposure to PBDEs and PBDD/Fs has led to an increased knowledge of their toxicology with evidence to suggest that both can cause a wide range of health problems in humans and animals such as inhibition of neurodevelopment, endocrine disruption, estrogenic toxicity, immune system disruption as well as various cancers (D'Silva et al., 2004)

This evidence led to legislative action where Penta- and Octa-BDE were banned within the EU in 2004 (Birnbaum and Staskal, 2004), and Australia in 2005 (Toms et al., 2009b) with voluntary bans in the U.S (Lagalante et al., 2009) to prevent the new use and manufacture of these commercial formulations as well as being named as persistent organic pollutants (POPs) under the Stockholm Convention (Stockholm Convention, 2009). Restrictions were also placed on Deca-BDE in the EU in 2008 (Deffree, 2008).

Due to their addition to so many consumer goods, PBDE-containing products are more densely populated in urban areas, leading to evidence to suggest that cities themselves are sources to the environment (Wilford et al., 2004, Harrad and Hunter, 2006b). Studies have also shown that various chemical and thermal industrial processes are sources of their release into the environment (Cetin and Odabasi, 2008, Chen et al., 2006), whilst there is also much evidence to suggest that PBDEs can be converted to PBDD/Fs during these thermal processes (Weber and Kuch, 2003, Duan et al., 2011). The recent legislative restrictions of PBDEs mean their use and application as flame retardants is likely to diminish. This suggests that the significance of combustion process as sources of PBDD/Fs is likely to increase as a result.

In light of the above evidence, the principal aim of this thesis was to gain a greater understanding of the behaviour of PBDEs and PBDD/Fs within the integrated steel-making process – specifically the iron ore sintering process – as well as investigating the spatial and temporal distribution of PBDEs in the environment.

The aims and objectives of this thesis were achieved as summarised below:

- Measurement of PBDEs in a stack gas emission sample along with electrostatic precipitator (ESP) dust samples from the iron ore sintering process revealed high levels of PBDE emissions. The stack emission gas sample contained 140 ng/m^3 of $\sum$PBDEs$_{17:154}$ whilst ESP dust contained an average of 32000 ng/kg $\sum$PBDEs$_{17:154}$ (range 8200-110000 ng/kg). Further analysis of the raw sinter mix (RSM) and its individual components revealed substantial contamination of the raw materials used within the sintering process with average $\sum$PBDEs$_{17:154}$ concentrations in RSM of 11000 ng/kg. Analysis of the individual components, combined with calculations based on tonnages provided by Tata Steel demonstrated that PBDE contamination in the RSM came from one or more of the following: iron ores, reverts and fuels. This demonstrated a substantial PBDE input in from the raw materials that had previously been assumed to be negligible (Wang et al., 2010b).

- Mass balance calculations of the total PBDE input and output into various sinter beds revealed that PBDE outputs were up to 96% lower than inputs, suggesting that PBDEs were destroyed in the sintering process. However, the measurement of PBDD/Fs in 15 stack gas emission samples confirmed the sintering process in the UK as a source to the environment, with an average concentration of 0.14 ng WHO-TEQ/m^3 meaning that conversion of PBDEs to PBDD/Fs during the sintering process was a possibility. PBDD/F concentrations in all samples were lower than those found by Du et al. (2010a), although the congener profiles were very similar with PBDFs predominating over PBDDs.
- Experiments were conducted using a sinter pot (SP) apparatus designed to mimic the sintering process on a laboratory scale basis. These revealed that formation of PBDEs within the sintering process is unlikely as the increase of availability of bromine produced no noticeable increase in PBDE concentrations, and moreover mass balance calculations revealed similar reductions in overall PBDE content for experiments 1, 2 (50 mg Br^- /kg RSM), 3 and 5 (both 150 mg Br^- /kg RSM) at 81%, 87%, 77% and 97% respectively. Furthermore, addition of a 100 µg mixture of Penta- and Deca-BDE commercial formulations to the RSM (experiment 4) produced no significant increases in PBDD/F output indicating that PBDEs are not precursors of PBDD/Fs in the sintering process.
- However, the exponential increase of PBDD/F output through experiments 1, 2 and 3 (0.04, 0.14, 2.6 ng WHO-TEQ/kg RSM sintered) as a result of increasing levels of Br^- suggests strongly that *de novo* synthesis of PBDD/Fs occurs in the sintering process, most likely through the same “trace chemistry of fire” pathway as is hypothesised for PCDD/Fs (Bumb et al., 1980). This also offers a likely explanation for the consistently lower PBDD/F concentrations in comparison to PCDD/Fs in the production-scale process, where KCl is added in “activated sintering” (Nzihou et al., 2005) whilst only natural levels of Br^- are present.
- Using passive air samplers (PAS), measurements of PBDEs were made in ambient air at 5 locations surrounding Scunthorpe Sinter Plant (SSP). The resulting data highlighted a source of PBDEs to the atmosphere within the integrated steel works. The concentrations of PBDEs in air downwind from SSP indicated a significantly

higher occupational exposure through inhalation of air (1.9 ng/hour) than in the upwind and control sites (0.47 ng/hour) as well as ambient air from the West Midlands (0.17 ng/hour). Principal component analysis of all samples in this section of the study showed that ambient air concentrations in the site directly downwind from SSP were dominated by congeners indicative of the Penta-BDE formulation. This, combined with the elevated concentrations at all sites downwind from various integrated steel-making processes, highlighted (in spite of the overall PBDE reduction seen in the sintering process) the steel-making process to be a source of PBDEs to the atmosphere.

- The deployment of six monthly PAS at 8 sites along a transect through Birmingham city centre, UK showed that there is an "urban pulse" with concentrations generally higher in the city centre than in the more rural locations. This pulse was of a similar strength to that measured by Harrad and Hunter (2006) approximately 10 years earlier for PBDEs$_{28:154}$. Whilst atmospheric BDE-209 concentrations were elevated in the city centre, the "urban pulse" was less pronounced than for the lower brominated congeners. This may to be due to the greater proportion of domestic sources of BDE-209 in suburban as opposed to city centre sites (where industrial/commercial buildings are more prevalent), as BDE-209 was used widely in upholstered furniture. Moreover cities contain a wider range of consumer products likely to have been flame retarded by a variety of options. The measurement of PBDEs in a soil sample from each site also demonstrated the role of cities as a source of PBDEs with Digbeth containing 21000 pg ∑PBDEs/g OC whilst levels at sites further away were 3600 pg/g OC (Worcester) and 2300 pg/g OC (Droitwich).
- Temporal trends in ambient air concentrations since the ban of the Penta-BDE formulation were investigated at an urban monitoring site in Edgbaston, Birmingham. Average concentrations in this study were found to be significantly lower than those detected by Harrad and Hunter (2006) at the same site. This suggested that at this location, Penta-BDE based congener levels have decreased since their ban in the UK. These findings were in agreement with those of Birgul et al. (2012) who found a similar trend in other urban (but not rural) locations around the UK.
- The evidence for an overall decrease in UK concentrations of PBDEs associated with the Penta-BDE formulation was even more pronounced in a comparison of concentrations between soil samples taken in 2013 (average: 3600 pg ∑PBDEs$_{17:183}$/g

OC) and archived soil samples from 2004-05 (average: 31000 pg ∑PBDE/g OC). This was true for BDE-209 also whose average levels were 100000 pg/g OC in 2004-05 and 11000 pg/g OC in 2013. Although samples were taken from different UK locations in both studies, the relative proportion of urban and rural locations in each sample set was similar. Combined, these data add to the weight of evidence that points to a decline in environmental levels of PBDEs since recent restrictions in the UK for all congeners measured.

- Measurement of PBDEs in both soil and sediment cores from Australia revealed that PBDE levels in the Australian environment are much lower than other countries. Soil samples taken in 2003 were more comparable to those 2013 UK samples than those from 2004-05. Measurement of radiometrically dated sediment cores from Port Jackson, Sydney suggested that PBDE levels were still rising at the end of the 20th century (supported by measurements of surface sediments from similar locations in 2003 which were found to be higher (Toms et al., 2006)). This meant that Australian soils were expected to have been taken around the time of peak environmental contamination with PBDEs, indicating that PBDE usage (and therefore its presence in the environment) is less pronounced than in the UK, Europe, Asia and North America.
- Concentrations in Australian soil revealed elevated levels in urban and industrial areas. Urban, industrial, agricultural and remote soils appeared to be influenced by different congener profiles. In soils from industrial locations, BDEs -47 and -99 contributed 49% of ∑PBDE concentrations on average, with a further 42% contributed by BDE-209, showing an equal influence of Penta- and Deca-BDE at such locations. Urban soils demonstrated a similar pattern, although with a greater influence of BDE-209. Remote soils were almost completely dominated by BDE-209. This pattern was also seen in the UK, with urban samples influenced by both Penta- and Deca-BDE, whilst samples away from the city were dominated by BDE-209. Agricultural soils from Australia were the only samples to show an influence of the Octa-BDE formulation perhaps as a result of sludge-treatent or some alternative unknown source activity.

7.2 Research gaps and future perspectives

Whilst understanding of the environmental sources, fate, and behaviour of PBDD/Fs and (in particular) PBDEs has improved over the last fifteen years, there remain significant research gaps. With this in mind, further research is required to:

a) Attempt to locate the source(s) of PBDE contamination within the iron ore sintering process. There remains substantial uncertainty about where the contamination of raw materials originates. Each individual RSM component should be traced back to its point of origin to attempt to determine at what stage(s) the contamination occurs.

b) Gain a fuller understanding of the source of PBDD/F emissions within the sintering process as well as investigating emissions of mixed bromo- chloro- dioxins and furans (PXDD/Fs). The SP should be utilised for further experiments whereby different levels of both Br^- and Cl^- are added to the inputs to examine the relative formation of PCDD/Fs, PBDD/Fs and PXDD/Fs.

c) Elucidate if urban and suburban areas closest to the steel works are affected by PBDE emissions from the SSP. Ambient air in the proximity of the SSP displays elevated concentrations of PBDEs when compared to the West Midlands. However no work has been done to determine whether this is true of towns closer to SSP, and thus ambient air and soils from populated areas close to SSP should also be monitored.

d) Gain an understanding on the impact of PBDD/F emissions on the exposure of both workers and the public. PBDD/Fs should be monitored both within the vicinity of the steel-works and in populated areas in close proximity. This would be more difficult to do than for PBDEs and would require high volume samplers in order to provide sufficient sample volumes for analysis.

e) Improve understanding of temporal trends in concentrations of PBDEs in ambient air and soil within the UK. Regular, on-going monitoring of PBDE concentrations in ambient air should be made at urban and rural locations to evaluate whether PBDEs are continuing to decrease in response to legislative restrictions. Such monitoring should also study seasonal variations in atmospheric concentrations of PBDEs. Of particular interest is the potential photolytic degradation of BDE-209 in spring and summer, as well as increased concentrations of lower brominated congeners in warmer periods as a result of volatilisation from products/environmental surfaces.. Regular monitoring of soils from the same locations would provide additional evidence of temporal trends.

f) Determine whether PBDE levels in Port Jackson, Sydney are still increasing. Fresh sediment cores should be taken in a variety of locations to determine recent temporal trends in response to legislative restrictions.

g) Determine whether PBDE levels in Australian soils have decreased in the same manner as in the UK. A sampling campaign of a similar nature should be undertaken to determine how PBDE levels have changed since the Australian soils were taken – one year before the ban of Penta- and Octa-BDE.

References

Abdallah, M. A.-E. & Harrad, S. 2010. Modification and Calibration of a Passive Air Sampler for Monitoring Vapor and Particulate Phase Brominated Flame Retardants in Indoor Air: Application to Car Interiors. *Environmental Science & Technology,* 44**,** 3059-3065.

Abdallah, M. A., Harrad, S. & Covaci, A. 2009. Isotope Dilution Method for Determination of Polybrominated Diphenyl Ethers Using liquid Chromatography Coupled to Negative Ionization Atmospheric Pressure Photoionization Tandem Mass Spectrometry: Validation and Application to House Dust. *Analytical Chemistry,* 81**,** 7460-7467.

Agrell, C., Ter Schure, A. F. H., Sveder, J., Bokenstrand, A., Larsson, P. & Zegers, B. N. 2004. Polybrominated diphenyl ethers (PBDES) at a solid waste incineration plant I: Atmospheric concentrations. *Atmospheric Environment,* 38**,** 5139-5148.

Allchin, C. R., law, R. J. & Morris, S. 1999. Polybrominated diphenylethers in sediments and biota downstream of potential sources in the UK. *Environmental Pollution,* 105**,** 197-207.

Anderson, D. R. & Fisher, R. 2002. Sources of dioxins in the United Kingdom: the steel industry and other sources. *Chemosphere,* 46**,** 371-381.

Andrade, N.A., McConnell, L.L., Torrents, A., Ramirez, M., 2010, Persistence of Polybrominated Diphenyl Ethers in Agricultural Soils after Biosolids Applications.. *Journal of Agricultural and Food Chemistry*, 58, 3077-3084.

Aries, E., Anderson, D. R. & Fisher, R. 2008. Exposure assessment of workers to airborne PCDD/Fs, PCBs and PAHs at an electric arc furnace steelmaking plant in the UK. *Annals of Occupational Hygiene,* 52**,** 213-225.

Arnoldsson, K., Andersson, P. L. & Haglund, P. 2012. Formation of Environmentally Relevant Brominated Dioxins from 2,4,6,-Tribromophenol via Bromoperoxidase-Catalyzed Dimerization. *Environmental Science & Technology,* 46**,** 7239-7244.

Bahn, A. K., Mills, J. L., Synder, P. J., Gann, P. H., Houten, L., Bialik, O., Hollmann, L. & Utiger, R. D. 1980. Hypothyroidism in workers exposed to polybrominated biphenyls. *The New England Journal of Medicine,* 302**,** 31-33.

Bastos, P. M., Eriksson, J., Vidarson, J., Bergman, A., 2008, Oxidative transformation of polybrominated diphenyl ether congeners (PBDEs) and of hydroxylated PBDEs (OH-PBDEs), *Environmental Science and Pollution Research,* 15, 606-613

Bakker, M. I., De Winter-Sorkina, R., De Mul, A., Boon, P. E., Van Donkersgoed, G., Van Klaveren, J. D., Baumann, B. A., Hijman, W. C., Van Leeuwen, S. P. J., De Boer, J. & Zeilmaker, M. J. 2008. Dietary intake and risk evaluation of polybrominated diphenyl ethers in The Netherlands. *Molecular Nutrition & Food Research,* 52**,** 204-216.

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

Bi, X., Qu, W., Sheng, G., Zhang, W., Mai, B., Chen, D., Yu, L. & Fu, J. 2006. Polybrominated diphenyl ethers in South China maternal and fetal blood and breast milk. *Environmental Pollution,* 144**,** 1024-1030.

Binelli, A., Sarkar, S. K., Chatterjee, M., Riva, C., Parolini, M., Bhattacharya, B. D., Bhattacharya, A. K. & Satpathy, K. K. 2007. Concentration of polybrominated diphenyl ethers (PBDEs) in sediment cores of Sundarban mangrove wetland, northeastern part of Bay of Bengal (India). *Marine Pollution Bulletin,* 54**,** 1220-1229.

Birgul, A., Katsoyiannis, A., Gioia, R., Crosse, J., Earnshaw, M., Ratola, N., Jones, K. C. & Sweetman, A. J. 2012. Atmospheric polybrominated diphenyl ethers (PBDEs) in the United Kingdom. *Environmental Pollution,* 169**,** 105-111.

Birnbaum, L. S. & Staskal, D. F. 2004. Brominated flame retardants: Cause for concern? *Environmental Health Perspectives,* 112**,** 9-17.

Birnbaum, L. S., Staskal, D. F. & Diliberto, J. J. 2003. Health effects of polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs). *Environment International,* 29**,** 855-860.

Bogdal, C., Schmid, P., Kohler, M., Müller, C. E., Iozza, S., Bucheli, T. D., Scheringer, M. & Hungerbühler, K. 2008. Sediment Record and Atmospheric Deposition of Brominated Flame Retardants and Organochlorine Compounds in Lake Thun, Switzerland: Lessons from the Past and Evaluation of the Present. *Environmental Science & Technology,* 42**,** 6817-6822.

Borghesi, N., Corsolini, S., Leonards, P., Brandsma, S., De Boer, J. & Focardi, S. 2009. Polybrominated diphenyl ether contamination levels in fish from the Antarctic and the Mediterranean Sea. *Chemosphere,* 77**,** 693-698.

Boswell, K. A., Wang, X., Shah, M. V. & Aapro, M. S. 2012. Disease burden and treatment outcomes in second-line therapy of patients with estrogen receptor-positive (ER+) advanced breast cancer: a review of the literature. *Breast,* 21**,** 701-6.

Bradner, J. M., Suragh, T. A., Wilson, W. W., Lazo, C. R., Stout, K. A., Kim, H. M., Wang, M. Z., Walker, D. I., Pennell, K. D., Richardson, J. R., Miller, G. W. & Caudle, W. M. 2013. Exposure to the polybrominated diphenyl ether mixture DE-71 damages the nigrostriatal dopamine system: Role of dopamine handling in neurotoxicity. *Experimental Neurology,* 241**,** 138-147.

Bromine Science and Environmental Forum (BSEF). 2003. *Major Brominated Flame Retardants Volume Estimates: Total Market Demand By Region in 2001* [Online]. Available: www.bsef.com.

Bromine Science Environmental Forum (BSEF) 2007. *Brominated Flame Retardant, Deca-BDE, Brominated Science and Environmental Forum Fact Sheet*.

http://www.bsef.org/china/uploads/library/BSEF_factsheet_Deca-BDE_160108.pdf accessed on 03/08/2012

Bromine Science Environmental Forum (BSEF). 2010. *Brominated Flame Retardant Deca-BDE Decabromodiphenyl Ether. Brominated Science and Environmental Forum Fact Sheet* [Online]. http://www.bsef.com/uploads/Documents/documents/BSEF_Deca-BDE_08-10f.pdf accessed on 09/05/2013.

Buckland, S. T., Magurran, A. E., Green, R. E. & Fewster, R. M. 2005. Monitoring Change in Biodiversity through Composite Indices. *Philosophical Transactions: Biological Sciences*, 360**,** 243-254.

Buekens, A., Stieglitz, L., Hell, K., Huang, H. & Segers, P. 2001. Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry. *Chemosphere*, 42**,** 729-735.

Bumb, R. R., Crummett, W. B., Cutie, S. S., Gledhill, J. R., Hummel, R. H., Kagel, R. O., Lamparski, L. L., Luoma, E. V., Miller, D. L., Nestrick, T. J., Shadoff, L. A., Stehl, R. H. & Woods, J. S. 1980. Trace chemistries of fire: a source of chlorinated dioxins. *Science*, 210**,** 385-90.

Buser, H.-R. 1988. Rapid photolytic decomposition of brominated and brominated/chlorinated dibenzodioxins and dibenzofurans. *Chemosphere*, 17**,** 889-903.

Buser, H. R. 1986. Polybrominated Dibenzofurans And Dibenzo-Para-Dioxins - Thermal-Reaction Products Of Polybrominated Diphenyl Ether Flame Retardants. *Environmental Science & Technology*, 20**,** 404-408.

Butt, C. M., Diamond, M. L., Truong, J., Ikonomou, M. G. & Ter Schure, A. F. H. 2003. Spatial Distribution of Polybrominated Diphenyl Ethers in Southern Ontario As Measured in Indoor and Outdoor Window Organic Films. *Environmental Science & Technology*, 38**,** 724-731.

Castro-Jiménez, J., Mariani, G., Vives, I., Skejo, H., Umlauf, G., Zaldívar, J. M., Dueri, S., Messiaen, G. & Laugier, T. 2011. Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France). *Environmental Pollution*, 159**,** 1948-1956.

Cetin, B. & Odabasi, M. 2007. Particle-phase dry deposition and air-soil gas-exchange of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Environmental Science & Technology*, 41**,** 4986-4992.

Cetin, B. & Odabasi, M. 2008. Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Chemosphere*, 71**,** 1067-1078.

Chao, H.-R., Wang, S.-L., Lee, W.-J., Wang, Y.-F. & Päpke, O. 2007. Levels of polybrominated diphenyl ethers (PBDEs) in breast milk from central Taiwan and their relation to infant birth outcome and maternal menstruation effects. *Environment International,* 33**,** 239-245.

Chen, C. E., Zhao, H., Chen, J., Qiao, X., Xie, Q. & Zhang, Y. 2012. Polybrominated diphenyl ethers in soils of the modern Yellow River Delta, China: Occurrence, distribution and inventory. *Chemosphere,* 88**,** 791-797.

Chen, E. C. M., Albyn, K., Dussack, L. & Wentworth, W. E. 1989. Determination of bond dissociation energies from dissociative thermal electron attachment. *The Journal of Physical Chemistry,* 93**,** 6827-6832.

Chen, L.-G., Mai, B.-X., BI, X.-H., Chen, S.-J., Wang, X.-M., Ran, Y., Luo, X.-J., Sheng, G.-Y., Fu, J.-M. & Zeng, E. Y. 2006. Concentration Levels, Compositional Profiles, and Gas-Particle Partitioning of Polybrominated Diphenyl Ethers in the Atmosphere of an Urban City in South China. *Environmental Science & Technology,* 40**,** 1190-1196.

Chen, S.-J., Luo, X.-J., Lin, Z., Luo, Y., Li, K.-C., Peng, X.-Z., Mai, B.-X., Ran, Y. & Zeng, E. Y. 2007. Time Trends of Polybrominated Diphenyl Ethers in Sediment Cores from the Pearl River Estuary, South China. *Environmental Science & Technology,* 41**,** 5595-5600.

Choi, J.-W., Fujimaki, S., Kitamura, K., Hashimoto, S., Ito, H., Sakurai, T., Suzuki, N., Nagasaka, H., Tanabe, K., Sakai, S.-I. & Morita, M. 2003a. Historical Trends of PBDD/Fs, PBDEs, PCDD/Fs and Dioxin-like PCBs in Sediment Cores from Tokyo Bay. *Organohalgen Compounds,* 61**,** 119-122.

Choi, J. W., Fujimaki, T. S., Kitamura, K., Hashimoto, S., Ito, H., Suzuki, N., Sakai, S. & Morita, M. 2003b. Polybrominated dibenzo-p-dioxins, dibenzofurans, and diphenyl ethers in Japanese human adipose tissue. *Environmental Science & Technology,* 37**,** 817-21.

Choi, S.-D., Baek, S.-Y. & Chang, Y.-S. 2008. Atmospheric levels and distribution of dioxin-like polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the vicinity of an iron and steel making plant. *Atmospheric Environment,* 42**,** 2479-2488.

Costa, L. G., Giordano, G., Tagliaferri, S., CaglierI, A., Mutti, A. 2008. Polybrominated diphenyl ether (PBDE) flame retardants: environmental contamination, human body burden and potential adverse health effects. *Acta Bio Medica,* 79**,** 172-183.

Covaci, A., Gheorghe, A., Voorspoels, S., Maervoet, J., Steen redeker, E., Blust, R. & Schepens, P. 2005. Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): analytical aspects and depth profiles. *Environment International,* 31**,** 367-375.

Crosse, J. D., Shore, R. F., Wadsworth, R. A., Jones, K. C. & Pereira, M. G. 2012. Long-Term Trends in PBDEs in Sparrowhawk (Accipiter nisus) Eggs Indicate Sustained Contamination of UK Terrestrial Ecosystems. *Environmental Science & Technology,* 46**,** 13504-13511.

D'Have, H., Covaci, A., Scheirs, J., Schepens, P., Verhagen, R. & De Coen, W. 2005. Hair as an indicator of endogenous tissue levels of brominated flame retardants in mammals. *Environmental Science & Technology,* 39**,** 6016-6020.

D'Silva, K., Fernandes, A. & Rose, M. 2004. Brominated organic micropollutants - Igniting the flame retardant issue. *Critical Reviews in Environmental Science and Technology,* 34**,** 141-207.

Da Rosa, M. B., Krüger, H. U., Thomas, S. & Zetzsch, C. 2003. Photolytic debromination and degradation of decabromodiphenyl ether, an exploratory kinetic study in toluene. *Fresenius Environmental Bulletin,* 12**,** 940-945.

Daniels, J. L., Pan, I. J., Jones, R., Anderson, S., Patterson, D. G., JR., Needham, L. L. & Sjodin, A. 2010. Individual characteristics associated with PBDE levels in U.S. human milk samples. *Environ Health Perspect,* 118**,** 155-60.

Darnerud, P. O. 2003. Toxic effects of brominated flame retardants in man and in wildlife. *Environment international,* 29**,** 841-853.

Darnerud, P. O., Eriksen, G. S., Johannesson, T., Larsen, P. B. & Viluksela, M. 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environmental Health Perspectives,* 109 Suppl 1**,** 49-68.

De La Cal, A., Eljarrat, E. & Barceló, D. 2003. Determination of 39 polybrominated diphenyl ether congeners in sediment samples using fast selective pressurized liquid extraction and purification. *Journal of Chromatography A,* 1021**,** 165-173.

De Wit, C. A., Herzke, D. & Vorkamp, K. 2010. Brominated flame retardants in the Arctic environment - trends and new candidates. *Science of the Total Environment,* 408**,** 2885-2918.

De Wit, C. A. & Muir, D. C. G. 2004. Levels and trends of brominated flame retardants in the Arctic. *BFR 2004.* Toronto.

Deffree, S. 2008. *ROHS DecaBDE exemption ending* [Online]. EDN. Available: http://www.edn.com/electronics-news/4326700/ROHS-DecaBDE-exemption-ending [Accessed 08-02-2013].

Devito, M. J., Ross, D. G., Dupuy JR, A. E., Ferrario, J., McDaniel, D. & Birnbaum, L. S. 1998. Dose–Response Relationships for Disposition and Hepatic Sequestration of Polyhalogenated Dibenzo-p-dioxins, Dibenzofurans, and Biphenyls Following Subchronic Treatment in Mice. *Toxicological Sciences,* 46**,** 223-234.

Dirtu, A. C. & Covaci, A. 2010. Estimation of daily intake of organohalogenated contaminants from food consumption and indoor dust ingestion in Romania. *Environmental Science & Technology,* 44**,** 6297-304.

Domingo, J. L., Martí-Cid, R., Castell, V. & Llobet, J. M. 2008. Human exposure to PBDEs through the diet in Catalonia, Spain: Temporal trend: A review of recent literature on dietary PBDE intake. *Toxicology,* 248**,** 25-32.

Du, B., Zheng, M., Tian, H., Liu, A., Huang, Y., Li, L., Ba, T., Li, N., Ren, Y., Li, Y., Dong, S. & Su, G., 2010a Occurrence and characteristics of polybrominated dibenzo-p-dioxins and dibenzofurans in stack gas emissions from industrial thermal processes. *Chemosphere*, 80, 1227-1233

Du, B., Zheng, M., Huang, Y., Liu, A., Tian, H., Li, L., Li, N., Ba, T., Li, Y., Dong, S., Liu, W. & Su, G. 2010b. Mixed Polybrominated/chlorinated Dibenzo-p-dioxins and Dibenzofurans in Stack Gas Emissions from Industrial Thermal Processes. *Environmental Science & Technology,* 44**,** 5818-5823.

Duan, H., Li, J., Liu, Y., Yamazaki, N. & Jiang, W. 2011. Characterization and inventory of PCDD/Fs and PBDD/Fs emissions from the incineration of waste printed circuit board. *Environmenal Science & Technology,* 45**,** 6322-8.

Dyke, P., Coleman, P. & James, R. 1997. Dioxins in ambient air, bonfire night 1994. *Chemosphere,* 34**,** 1191-1201.

EBFRIP 1990. The European Brominated Flame Retardant Panel. *European Economic Community.* Brussels, Belgium.

Eitzer, B. D. & Hites, R. A. 1998. Vapor Pressures of Chlorinated Dioxins and Dibenzofurans. *Environmental Science & Technology,* 32**,** 2804-2804.

Eljarrat, E., De La Cal, A., Raldua, D., Duran, C. & Barcelo, D. 2004. Occurrence and Bioavailability of Polybrominated Diphenyl Ethers and Hexabromocyclododecane in Sediment and Fish from the Cinca River, a Tributary of the Ebro River (Spain). *Environmental Science & Technology,* 38**,** 2603-2608.

Eljarrat, E., Marsh, G., Labandeira, A. & Barcelo, D. 2008. Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. *Chemosphere,* 71**,** 1079-86.

Environmental Agency Japan 1991. Chemicals in the environment. Report on environmental survey and wildlife monitoring of chemicals in F.Y. 1988 and 1989. Tokyo, Japan.

Ericson Jogsten, I., Hagberg, J., Lindström, G. & Bavel, B. V. 2010. Analysis of POPs in human samples reveal a contribution of brominated dioxin of up to 15% of the total dioxin TEQ. *Chemosphere,* 78**,** 113-120.

Eriksson, J., Green, N., Marsh, G. & Bergman, Å. 2004. Photochemical Decomposition of 15 Polybrominated Diphenyl Ether Congeners in Methanol/Water. *Environmental Science & Technology,* 38**,** 3119-3125.

Erratico, C. A., Szeitz, A. & Bandiera, S. M. 2012. Oxidative Metabolism of BDE-99 by Human Liver Microsomes: Predominant Role of CYP2B6. *Toxicological Sciences,* 129**,** 280-292.

European Commission 2010. Best Available Techniques (BAT) Reference Document for Iron and Steel Production. Luxembourg.

European Food Safety Authority (EFSA) 2011. Scientific Opinion on Polybrominated Diphenyl Ethers (PBDEs) in Food. *EFSA Journal,* 9**,** 2156.

Evans, T. E. 2007. Chiral Analysis as a Novel Tracer of the Environmental Behaviour of Polychlorinated Biphenyls (PCBs), PhD thesis, Univrsity of Birmingham, 2007.

Evenset, A., Christensen, G. N., Carroll, J., Zaborska, A., Berger, U., Herzke, D. & Gregor, D. 2007. Historical trends in persistent organic pollutants and metals recorded in sediment from Lake Ellasjøen, Bjørnøya, Norwegian Arctic. *Environmental Pollution,* 146**,** 196-205.

Fang, M., Choi, S. D., Baek, S. Y., Jin, G. & Chang, Y. S. 2012. Deposition of polychlorinated biphenyls and polybrominated diphenyl ethers in the vicinity of a steel manufacturing plant. *Atmospheric Environment,* 49**,** 206-211.

Fangstrom, B., Athanassiadis, L., Odsjo, T., Noren, K. & Bergman, A. 2008. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in milk from Stockholm mothers, 1980-2004. *Molecular Nutrition & Food Research,* 52**,** 187-193.

Fernandes, A. R., Tlustos, C., Smith, F., Carr, M., Petch, R. & Rose, M. 2009. Polybrominated diphenylethers (PBDEs) and brominated dioxins (PBDD/Fs) in Irish food of animal origin. *Food Additives & Contaminants Part B-Surveillance,* 2**,** 86-94.

Frederiksen, M., Vorkamp, K., Thomsen, M. & Knudsen, L. E. 2009. Human internal and external exposure to PBDEs--a review of levels and sources. *International Journal of Hygeine & Environmental Health,* 212**,** 109-34.

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

Fu, J. & Suuberg, E. M. 2011. Vapor pressure of solid polybrominated diphenyl ethers determined via Knudsen effusion method. *Environmental Toxicology and Chemistry,* 30**,** 2216-2219.

Garí, M. & Grimalt, J. O. 2013. Inverse age-dependent accumulation of decabromodiphenyl ether and other PBDEs in serum from a general adult population. *Environment International,* 54**,** 119-127.

Gascon, M., Fort, M., Martinez, D., Carsin, A.-E., Forns, J., Grimalt, J. O., Santa Marina, L., Lertxundi, N., Sunyer, J. & Vrijheid, M. 2012. Polybrominated Diphenyl Ethers

(PBDEs) in Breast Milk and Neuropsychological Development in Infants. *Environmental Health Perspectives,* 120**,** 1760-1765.

Gevao, B., Al-Omair, A., Sweetman, A., Al-Ali, L., Al-Bahloul, M., Helaleh, M. & Zafar, J. 2006. Passive sampler-derived air concentrations for polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons in Kuwait. *Environmental Toxicology and Chemistry,* 25**,** 1496-1502.

Gevao, B., Ghadban, A. N., Uddin, S., Jaward, F. M., Bahloul, M. & Zafar, J. 2011. Polybrominated diphenyl ethers (PBDEs) in soils along a rural-urban-rural transect: Sources, concentration gradients, and profiles. *Environmental Pollution,* 159**,** 3666-3672.

Gevao, B., Muzaini, S. & Helaleh, M. 2008. Occurrence and concentrations of polybrominated diphenyl ethers in sewage sludge from three wastewater treatment plants in Kuwait. *Chemosphere,* 71**,** 242-247.

Gerecke, A. C., Hartmann, P. C., Heeb, N. V., Kohler, H. E., Giger, W., Schmid, P., Zennegg, M., Kohler, M., 2005, Anaerobic Degradation of Decabrominated Diphenyl Ether, *Environmental Science & Technology*, 39, 1078-1083

Gevao, B., Ghadban, A. N., Porcelli, M., Ali, L., Rashdan, A., Al-Bahloul, M., Matrouk, K., Zafar, J., 2013. Seasonal variations in the atmospheric concentrations of polybrominated diphenyl ethers in Kuwait, *Science of the Total Environment*, 454-455, 534-541

Gioia, R., Steinnes, E., Thomas, G. O., Mejier, S. N. & Jones, K. C. 2006. Persistent organic pollutants in European background air: derivation of temporal and latitudinal trends. *Journal of Environmental Monitoring,* 8**,** 700-710.

Glynn, A., Lignell, S., Darnerud, P. O., Aune, M., Halldin Ankarberg, E., Bergdahl, I. A., Barregard, L. & Bensryd, I. 2011. Regional differences in levels of chlorinated and brominated pollutants in mother's milk from primiparous women in Sweden. *Environment International,* 37**,** 71-9.

Goldberg, E. D. Geochronology with PB-210. Symposium on Radioactive Dating, 1963 Vienna, Austria. International Atomic Energy Agency.

Gorgy, T., Li, L. Y., Grace, J. R., Ikonomou, M. G., 2011, Polybrominated Diphenyl Ethers Mobility in Biosolids-Amended Soils Using Leaching Column Tests, *Water, Air and Soil Pollution*, 222, 77-90

Gouin, T. & Harner, T. 2003. Modelling the environmental fate of the polybrominated diphenyl ethers. *Environment International,* 29**,** 717-724.

Gouin, T., Harner, T., Daly, G. L., Wania, F., Mackay, D. & Jones, K. C. 2005. Variability of concentrations of polybrominated diphenyl ethers and polychlorinated biphenyls in air: implications for monitoring, modeling and control. *Atmospheric Environment,* 39**,** 151-166.

Greenpeace 2003. Consuming Chemicals - Hazardous Chemicals in House Dust as an Indicator of Chemical Exposure in the Home. *In:* Green Peace Research Laboratories (ed.).

Gu, C., Goodarzi, M., Yang, X., Bian, Y., Sun, C. & Jiang, X. 2012. Predictive insight into the relationship between AhR binding property and toxicity of polybrominated diphenyl ethers by PLS-derived QSAR. *Toxicology Letters,* 208**,** 269-274.

Haglund, P., Malmvärn, A., Bergek, S., Bignert, A., Kautsky, L., Nakano, T., Wiberg, K. & Asplund, L. 2007. Brominated Dibenzo-p-Dioxins: A New Class of Marine Toxins? *Environmental Science & Technology,* 41**,** 3069-3074.

Hale, R. C., La Guardia, M. J., Harvey, E., Chen, D., Mainor, T. M., Luellen, D. R. & Hundal, L. S. 2012. Polybrominated Diphenyl Ethers in U.S. Sewage Sludges and Biosolids: Temporal and Geographical Trends and Uptake by Corn Following Land Application. *Environmental Science & Technology,* 46**,** 2055-2063.

Hale, R. C., La Guardia, M. J., Harvey, E. & Matt Mainor, T. 2002. Potential role of fire retardant-treated polyurethane foam as a source of brominated diphenyl ethers to the US environment. *Chemosphere,* 46**,** 729-735.

Harner, T. & Shoeib, M. 2002. Measurements of Octanol−Air Partition Coefficients (KOA) for Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment. *Journal of Chemical & Engineering Data,* 47**,** 228-232.

Harner, T., Shoeib, M., Diamond, M., Ikonomou, M. & Stern, G. 2006. Passive sampler derived air concentrations of PBDEs along an urban–rural transect: Spatial and temporal trends. *Chemosphere,* 64**,** 262-267.

Harrad, S. & Abdallah, M. A.-E. 2011. Brominated flame retardants in dust from UK cars - Within-vehicle spatial variability, evidence for degradation and exposure implications. *Chemosphere,* 82**,** 1240-1245.

Harrad, S., Goosey, E., Desborough, J., Abdallah, M. A.-E., Roosens, L. & Covaci, A. 2010. Dust from U.K. Primary School Classrooms and Daycare Centers: The Significance of Dust As a Pathway of Exposure of Young U.K. Children to Brominated Flame Retardants and Polychlorinated Biphenyls. *Environmental Science & Technology,* 44**,** 4198-4202.

Harrad, S., Hazrati, S. & Ibarra, C. 2006. Concentrations of Polychlorinated Biphenyls in Indoor Air and Polybrominated Diphenyl Ethers in Indoor Air and Dust in Birmingham, United Kingdom: Implications for Human Exposure. *Environmental Science & Technology,* 40**,** 4633-4638.

Harrad, S. & Hunter, S. 2006. Concentrations of polybrominated diphenyl ethers in air and soil on a rural-urban transect across a major UK conurbation. *Environmental Science & Technology,* 40**,** 4548-4553.

Harrad, S., Ibarra, C., Abdallah, M. A.-E., Boon, R., Neels, H. & Covaci, A. 2008a. Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: Causes of variability and implications for human exposure. *Environment International,* 34**,** 1170-1175.

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

Harrad, S. & Porter, L. 2007. Concentrations of polybrominated diphenyl ethers in blood serum from New Zealand. *Chemosphere,* 66**,** 2019-2023.

Harrad, S., Wijesekera, R., Hunter, S., Halliwell, C. & Baker, R. 2004. Preliminary Assessment of U.K. Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers. *Environmental Science & Technology,* 38**,** 2345-2350.

Hassanin, A., Breivik, K., Meijer, S. N., Steinnes, E., Thomas, G. O. & Jones, K. C. 2003. PBDEs in European Background Soils: Levels and Factors Controlling Their Distribution. *Environmental Science & Technology,* 38**,** 738-745.

Hassanin, A., Johnston, A. E., Thomas, G. O. & Jones, K. C. 2005. Time trends of atmospheric PBDEs inferred from archived UK herbage. *Environmental Science & Technology,* 39**,** 2436-2441.

Hayakawa, K., Takatsuki, H., Watanabe, I. & Sakai, S.-I. 2004. Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan. *Chemosphere,* 57**,** 343-356.

Hazrati, S. and Harrad, S., 2007. Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rates, *Chemosphere*, 67, 448-455

He, J., Robrock, K. R., Alvarez-Cohen, L., 2006, Microbial Reductive Debromination of Polybrominated Diphenyl Ethers (PBDEs), *Environmental Science & Technology*, 40, 4429-4434

Hearn, L. K., Hawker, D. W., Toms, L.-M. L. & Mueller, J. F. 2013. Assessing exposure to polybrominated diphenyl ethers (PBDEs) for workers in the vicinity of a large recycling facility. *Ecotoxicology and Environmental Safety,* 92**,** 222-228.

Henny, C., Kaiser, J., Grove, R., Johnson, B. & letcher, R. 2009. Polybrominated diphenyl ether flame retardants in eggs may reduce reproductive success of ospreys in Oregon and Washington, USA. *Ecotoxicology,* 18**,** 802-813.

Hites, R. A. 2004. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environmental Science & Technology,* 38**,** 945-956.

Hoh, E. & Hites, R. A. 2005. Brominated Flame Retardants in the Atmosphere of the East-Central United States. *Environmental Science & Technology,* 39**,** 7794-7802.

Hong, S. H., Kannan, N., Jin, Y., Won, J. H., Han, G. M. & Shim, W. J. 2010. Temporal trend, spatial distribution, and terrestrial sources of PBDEs and PCBs in Masan Bay, Korea. *Marine Pollution Bulletin,* 60**,** 1836-1841.

Hornung, M. W., Zabel, E. W. & Peterson, R. E. 1996. Toxic Equivalency Factors of Polybrominated Dibenzo-p-dioxin, Dibenzofuran, Biphenyl, and Polyhalogenated Diphenyl Ether Congeners Based on Rainbow Trout Early Life Stage Mortality. *Toxicology and Applied Pharmacology,* 140**,** 227-234.

Huang, H., Zhang, S., Christie, P., Wang, S., Xie, M., 2010, Behavior of Decabromodiphenyl Ether (BDE-209) in the Soil-Plant System: Uptake, Translocation, and Metabolism in Plants and Dissipation in Soil, *Environmental Science & Technology*, 44, 663-667

Iacovidou, E., Mandalakis, M. & Stephanou, E. G. 2009. Occurrence and diurnal variation of polychlorinated biphenyls and polybrominated diphenyl ethers in the background atmosphere of Eastern Mediterranean. *Chemosphere,* 77**,** 1161-1167.

Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J. & Jones, K. C. 2003. Passive Air Sampling of PCBs, PBDEs, and Organochlorine Pesticides Across Europe. *Environmental Science & Technology,* 38**,** 34-41.

Ji, K., Choi, K., Giesy, J. P., Musarrat, J. & Takeda, S. 2011. Genotoxicity of Several Polybrominated Diphenyl Ethers (PBDEs) and Hydroxylated PBDEs, and Their Mechanisms of Toxicity. *Environmental Science & Technology,* 45**,** 5003-5008.

Jin, J., Liu, W., Wang, Y. & Yan Tang, X. 2008. Levels and distribution of polybrominated diphenyl ethers in plant, shellfish and sediment samples from Laizhou Bay in China. *Chemosphere,* 71**,** 1043-1050.

Johannessen, S. C., Macdonald, R. W., Wright, C. A., Burd, B., Shaw, D. P. & Van Roodselaar, A. 2008. Joined by geochemistry, divided by history: PCBs and PBDEs in Strait of Georgia sediments. *Marine Environmental Research,* 66, Supplement**,** S112-S120.

Joint FAO/WHO Expert Committee On Food Additives (JECFA) 2006. Evaluation of Polybrominated Diphenyl Ethers. 930 ed. Geneva: World Health Organization (WHO).

Jones-Otazo, H. A., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J. J. & Wilford, B. 2005. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environmental Science & Technology,* 39**,** 5121-5130.

Kalantzi, O. I., Martin, F. L., Thomas, G. O., Alcock, R. E., Tang, H. R., Drury, S. C., Carmichael, P. L., Nicholson, J. K. & Jones, K. C. 2004. Different levels of polybrominated diphenyl ethers (PBDEs) and chlorinated compounds in breast milk from two U.K. Regions. *Environmental Health Perspectives,* 112**,** 1085-91.

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

Klosterhaus, S. L., Stapleton, H. M., LA Guardia, M. J. & Greig, D. J. 2012. Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife. *Environment International,* 47**,** 56-65.

Knutsen, H. K., Kvalem, H. E., Thomsen, C., Frøshaug, M., Haugen, M., Becher, G., Alexander, J. & Meltzer, H. M. 2008. Dietary exposure to brominated flame retardants correlates with male blood levels in a selected group of Norwegians with a wide range of seafood consumption. *Molecular Nutrition & Food Research,* 52**,** 217-227.

Koenig, C. M., Lango, J., Pessah, I. N. & Berman, R. F. 2012. Maternal transfer of BDE-47 to offspring and neurobehavioral development in C57BL/6J mice. *Neurotoxicology and Teratology,* 34**,** 571-580.

Kohler, M., Zennegg, M., Bogdal, C., Gerecke, A. C., Schmid, P., Heeb, N. V., Sturm, M., Vonmont, H., Kohler, H. P. & Giger, W. 2008. Temporal trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss lake sediments. *Environmental Science & Technology,* 42**,** 6378-84.

La Guardia, M. J., Hale, R. C. & Harvey, E. 2006. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures. *Environmental Science & Technology,* 40**,** 6247-6254.

Labunska, I., Harrad, S., Santillo, D., Johnston, P. & Brigden, K. 2013. Levels and distribution of polybrominated diphenyl ethers in soil, sediment and dust samples collected from various electronic waste recycling sites within Guiyu town, southern China. *Environmental Science-Processes & Impacts,* 15**,** 503-511.

Lagalante, A. F., Oswald, T. D. & Calvosa, F. C. 2009. Polybrominated diphenyl ether (PBDE) levels in dust from previously owned automobiles at United States dealerships. *Environment International,* 35**,** 539-544.

Lahl, U. 1994. Sintering Plants Of Steel-Industry – PCDD/F Emission Status And Perspectives. *Chemosphere,* 29**,** 1939-1945.

Lake, I. R., Foxall, C. D., Fernandes, A., Lewis, M., Rose, M., White, O. & Dowding, A. 2013. Seasonal variations in the levels of PCDD/Fs, PCBs and PBDEs in cows' milk. *Chemosphere,* 90**,** 72-79.

Lee, H. J., Kim, G. B. & Lee, R. F. 2012. Genotoxicity and development effects of brominated flame retardant PBDEs and UV-exposed PBDEs on grass shrimp (Palaemonetes pugio) embryo. *Marine pollution bulletin,* 64**,** 2892-5.

Lee, R. G. M., Thomas, G. O. & Jones, K. C. 2003. PBDEs in the Atmosphere of Three Locations in Western Europe. *Environmental Science & Technology,* 38**,** 699-706.

Leung, A. O. W., Luksemburg, W. J., Wong, A. S. & Wong, M. H. 2007. Spatial Distribution of Polybrominated Diphenyl Ethers and Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Soil and Combusted Residue at Guiyu, an Electronic Waste Recycling Site in Southeast China. *Environmental Science & Technology,* 41**,** 2730-2737.

Li, H., Feng, J., Sheng, G., Lü, S., Fu, J., Peng, P. A. & Man, R. 2008. The PCDD/F and PBDD/F pollution in the ambient atmosphere of Shanghai, China. *Chemosphere,* 70**,** 576-583.

Li, H., Yu, L., Sheng, G., Fu, J. & Peng, P. A. 2007. Severe PCDD/F and PBDD/F Pollution in Air around an Electronic Waste Dismantling Area in China. *Environmental Science & Technology,* 41**,** 5641-5646.

Li, K., Fu, S., Yang, Z. Z. & Xu, X. B. 2009. Polybrominated Diphenyl Ethers in the Soil of Typical Industrial City. *Bulletin of Environmental Contamination and Toxicology,* 83**,** 926-930.

Li, X., Li, Y., Zhang, Q., Wang, P., Yang, H., Jiang, G. & Wei, F. 2011. Evaluation of atmospheric sources of PCDD/Fs, PCBs and PBDEs around a steel industrial complex in northeast China using passive air samplers. *Chemosphere,* 84**,** 957-963.

Lim, D.-H. & Lastoskie, C. M. 2011. A dynamic multimedia environmental and bioaccumulation model for brominated flame retardants in Lake Huron and Lake Erie, USA. *Environmental Toxicology and Chemistry,* 30**,** 1018-1025.

Lind, Y., Darnerud, P. O., Atuma, S., Aune, M., Becker, W., Bjerselius, R., Cnattingius, S. & Glynn, A. 2003. Polybrominated diphenyl ethers in breast milk from Uppsala County, Sweden. *Environmental research,* 93**,** 186-194.

Litten, S., Mcchesney, D. J., Hamilton, M. C. & Fowler, B. 2003. Destruction of the World Trade Center and PCBs, PBDEs, PCDD/Fs, PBDD/Fs, and Chlorinated Biphenylenes in Water, Sediment, and Sewage Sludge. *Environmental Science & Technology,* 37**,** 5502-5510.

Liu, Y., Zheng, G. J., Yu, H., Martin, M., Richardson, B. J., Lam, M. H. W. & Lam, P. K. S. 2005. Polybrominated diphenyl ethers (PBDEs) in sediments and mussel tissues from Hong Kong marine waters. *Marine Pollution Bulletin,* 50**,** 1173-1184.

Ma, J., Addink, R., Yun, S., Cheng, J., Wang, W. & Kannan, K. 2009. Polybrominated Dibenzo-p-dioxins/Dibenzofurans and Polybrominated Diphenyl Ethers in Soil, Vegetation, Workshop-Floor Dust, and Electronic Shredder Residue from an Electronic Waste Recycling Facility and in Soils from a Chemical Industrial Complex in Eastern China. *Environmental Science & Technology,* 43**,** 7350-7356.

Ma, J., Qiu, X., Ren, A., Jin, L. & Zhu, T. 2012. Using placenta to evaluate the polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) exposure of fetus in a region with high prevalence of neural tube defects. *Ecotoxicology and Environmental Safety,* 86**,** 141-146.

Mai, Chenchen, Luo, Chenchen, Yang, Sheng, Peng, Fu & zeng, E. Y. 2005. Distribution of Polybrominated Diphenyl Ethers in Sediments of the Pearl River Delta and Adjacent South China Sea. *Environmental Science & Technology,* 39**,** 3521-3527.

Malarvannan, G., Isobe, T., Covaci, A., Prudente, M. & Tanabe, S. 2013. Accumulation of brominated flame retardants and polychlorinated biphenyls in human breast milk and scalp hair from the Philippines: Levels, distribution and profiles. *Science of the total environment,* 442**,** 366-79.

Malarvannan, G., Kunisue, T., Isobe, T., Sudaryanto, A., Takahashi, S., Prudente, M., Subramanian, A. & Tanabe, S. 2009. Organohalogen compounds in human breast milk from mothers living in Payatas and Malate, the Philippines: Levels, accumulation kinetics and infant health risk. *Environmental Pollution,* 157**,** 1924-1932.

Mandalakis, M., Besis, A. & Stephanou, E. G. 2009. Particle-size distribution and gas/particle partitioning of atmospheric polybrominated diphenyl ethers in urban areas of Greece. *Environmental Pollution,* 157**,** 1227-1233.

Mandalakis, M., Stephanou, E. G., Horii, Y. & Kannan, K. 2008. Emerging Contaminants in Car Interiors: Evaluating the Impact of Airborne PBDEs and PBDD/Fs. *Environmental Science & Technology,* 42**,** 6431-6436.

Marvin, C., Williams, D., Kuntz, K., Klawunn, P., Backus, S., Kolic, T., Lucaciu, C., Macpherson, K. & Reiner, E. 2007. Temporal trends in polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like PCBs, and polybrominated diphenyl ethers in Niagara river suspended sediments. *Chemosphere,* 67**,** 1808-1815.

Matsuda, M., Okimoto, M., Takechi, Y., Nakamura, M., Handa, H., Kawano, M., Nose, K., Ebiharia, K. & Morita, M. 2010. Estimation of PBDD/F Toxicity Equivalency Factors from Ah receptor binding affinity and clearance rate in rats. *BFR2010,* Kyoto.

Mazdai, A., Dodder, N. G., Abernathy, M. P., Hites, R. A. & Bigsby, R. M. 2003. Polybrominated diphenyl ethers in maternal and fetal blood samples. *Environmental Health Perspectives,* 111**,** 1249-52.

Meeker, J. D., Johnson, P. I., Camann, D. & Hauser, R. 2009. Polybrominated diphenyl ether (PBDE) concentrations in house dust are related to hormone levels in men. *Science of The Total Environment*, 407**,** 3425-3429.

Meironyte, D., Noren, K. & Bergman, A. 1999. ANALYSIS OF POLYBROMINATED DIPHENYL ETHERS IN SWEDISH HUMAN MILK. A TIME-RELATED TREND STUDY, 1972-1997. *Journal of Toxicology and Environmental Health, Part A*, 58**,** 329-341.

Minh, N. H., Isobe, T., Ueno, D., Matsumoto, K., Mine, M., Kajiwara, N., Takahashi, S. & Tanabe, S. 2007. Spatial distribution and vertical profile of polybrominated diphenyl ethers and hexabromocyclododecanes in sediment core from Tokyo Bay, Japan. *Environmental Pollution,* 148**,** 409-417.

Mitchell, M. M., Woods, R., Chi, L. H., Schmidt, R. J., Pessah, I. N., Kostyniak, P. J. & Lasalle, J. M. 2012. Levels of select PCB and PBDE congeners in human postmortem brain reveal possible environmental involvement in 15q11-q13 duplication autism spectrum disorder. *Environmental and Molecular Mutagenesis,* 53**,** 589-598.

Mo, L., Wu, J.-P., Luo, X.-J., Zou, F.-S. & Mai, B.-X. 2012. Bioaccumulation of polybrominated diphenyl ethers, decabromodiphenyl ethane, and 1,2-bis(2,4,6-tribromophenoxy) ethane flame retardants in kingfishers (Alcedo atthis) from an electronic waste-recycling site in South China. *Environmental Toxicology and Chemistry,* 31**,** 2153-2158.

Moon, H.-B., Kannan, K., Lee, S.-J. & Choi, M. 2007. Polybrominated diphenyl ethers (PBDEs) in sediment and bivalves from Korean coastal waters. *Chemosphere,* 66**,** 243-251.

Muenhor, D., Harrad, S., Ali, N. & Covaci, A. 2010. Brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand. *Environment International,* 36**,** 690-698.

Neupert, M., Grupe, A. & Weis, H. 1988. Stability of polybrominated dibenzo-p-dioxins and dibenzofurans under laboratory handling conditions. *Chemosphere,* 17**,** 1089-1097.

Ni, H. G., Ding, C., Lu, S. Y., Yin, X. L. & Samuel, S. O. 2012. Food as a main route of adult exposure to PBDEs in Shenzhen, China. *Science of the Total Environment,* 437**,** 10-14.

Noren, K. & Meironyte, D. 2000. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20-30 years. *Chemosphere,* 40**,** 1111-1123.

North, K. D. 2004. Tracking Polybrominated Diphenyl Ether Releases in a Wastewater Treatment Plant Effluent, Palo Alto, California. *Environmental Science & Technology,* 38**,** 4484-4488.

Nyholm, J. R., Asamoah, R. K., Van Der Wal, L., Danielsson, C., Andersson, P. L., 2010, Accumulation of Polybrominated Diphenyl Ethers, Hexabromobenzen and 1,2-Dibromo-4-(1,2-dibromoethyl)-cyclohexane in Earthworm (*Eisenia fetida*). Effects of Soil Type and Aging, *Environmental Science & Technology*, 44, 9189-9194

Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzén, K. & Sellström, U. 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. *Chemosphere,* 24**,** 1721-1730.

Nzihou, A., Adhikari, B. & Pfeffer, R. 2005. Effect of Metal Chlorides on the Sintering and Densification of Hydroxyapatite Adsorbent. *Industrial & Engineering Chemistry Research,* 44**,** 1787-1794.

Odabasi, M., Bayram, A., Elbir, T., Seyfioglu, R., Dumanoglu, Y., Bozlaker, A., Demircioglu, H., Altiok, H., Yatkin, S. & Cetin, B. 2009. Electric Arc Furnaces for Steel-Making: Hot Spots for Persistent Organic Pollutants. *Environmental Science & Technology,* 43**,** 5205-5211.

Odabasi, M., Bayram, A., Elbir, T., Seyfioglu, R., Dumanoglu, Y. & ORNEKTEKIN, S. 2010. Investigation of Soil Concentrations of Persistent Organic Pollutants, Trace Elements, and Anions Due to Iron–Steel Plant Emissions in an Industrial Region in Turkey. *Water, Air, & Soil Pollution,* 213**,** 375-388.

Olsman, H., EngwalL, M., Kammann, U., Klempt, M., Otte, J., Bavel, B. & Hollert, H. 2007. Relative differences in aryl hydrocarbon receptor-mediated response for 18 polybrominated and mixed halogenated dibenzo-p-dioxins and -furans in cell lines from four different species. *Environmental Toxicology & Chemistry,* 26**,** 2448-54.

Ooi, T. C., Aries, E., Ewan, B. C. R., Thompson, D., Anderson, D. R., Fisher, R., Fray, T. & Tognarelli, D. 2008. The study of sunflower seed husks as a fuel in the iron ore sintering process. *Minerals Engineering,* 21**,** 167-177.

Palm, A., Cousins, I. T., Mackay, D., Tysklind, M., Metcalfe, C. & Alaee, M. 2002. Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers. *Environmental Pollution,* 117**,** 195-213.

Parolini, M., Guazzoni, N., Comolli, R., Binelli, A. & Tremolada, P. 2013. Background levels of polybrominated diphenyl ethers (PBDEs) in soils from Mount Meru area, Arusha district (Tanzania). *Science of the total environment,* 452-453**,** 253-61.

Puzyn, T., Suzuki, N. & Haranczyk, M. 2008. How Do the Partitioning Properties of Polyhalogenated POPs Change When Chlorine Is Replaced with Bromine? *Environmental Science & Technology,* 42**,** 5189-5195.

Qiu, X., Marvin, C. H. & Hites, R. A. 2007. Dechlorane Plus and Other Flame Retardants in a Sediment Core from Lake Ontario. *Environmental Science & Technology,* 41**,** 6014-6019.

Rappe, C. 1992. Sources Of PCDDs And PCDFs - Introduction - Reactions, Levels, Patterns, Profiles And Trends. *Chemosphere,* 25**,** 41-44.

Regueiro, J., Llompart, M., Garcia-Jares, C. & Cela, R. 2007. Factorial-design optimization of gas chromatographic analysis of tetrabrominated to decabrominated diphenyl ethers. Application to domestic dust. *Analytical and Bioanalytical Chemistry,* 388**,** 1095-107.

Ren, M., Peng, P. A., Chen, D. Y., Chen, P. & Zhou, L. 2009. PBDD/Fs in Surface Sediments from the East River, China. *Bulletin of Environmental Contamination and Toxicology,* 83**,** 440-443.

Ren, X.-M. & Guo, L.-H. 2013. Molecular toxicology of polybrominated diphenyl ethers: nuclear hormone receptor mediated pathways. *Environmental Science: Processes & Impacts,* 15**,** 702-708.

RPA LTD. 2000. *Risk reduction strategy and analysis of advantages and drawbacks for pentabromodiphenyl ether,* Department of the Environment, Transport and the Regions, DEFRA.

Schecter, A. 2012. Dioxins and Health Including other Persistent Organic Pollutants and Endocrine Disruptors. *Dioxins and Health.* New Jersey, USA: John Wiley & Sons, Inc.

Schecter, A., Colacino, J. A., Shah, N., Päpke, O., Opel, M., Patel, K. & Birnbaum, L. S. 2010. Indoor and outdoor air PBDE levels in a Southwestern US city. *Toxicological & Environmental Chemistry,* 92**,** 1053-1063.

Schecter, A., Päpke, O., Harris, T. R., Tung, K. C., Musumba, A., Olson, J. & Birnbaum, L. 2006. Polybrominated Diphenyl Ether (PBDE) Levels in an Expanded Market Basket Survey of U.S. Food and Estimated PBDE Dietary Intake by Age and Sex. *Environmental Health Perspectives,* 114**,** 1515-1520.

Schecter, A., Pavuk, M., Papke, O., Ryan, J. J., Birnbaum, L. & Rosen, R. 2003. Polybrominated diphenyl ethers (PBDEs) in U.S. mothers' milk. *Environmental Health Perspectives,* 111**,** 1723-9.

Schenker, U., Soltermann, F., Scheringer, M. & Hungerbühler, K. 2008. Modeling the Environmental Fate of Polybrominated Diphenyl Ethers (PBDEs): The Importance of Photolysis for the Formation of Lighter PBDEs. *Environmental Science & Technology,* 42**,** 9244-9249.

Schreiber, T., Gassmann, K., Goetz, C., Huebenthal, U., Moors, M., Krause, G., Merk, H. F., Nguyen, N.-H., Scanlan, T. S., Abel, J., Rose, C. R. & Fritsche, E. 2010. Polybrominated Diphenyl Ethers Induce Developmental Neurotoxicity in a Human in Vitro Model: Evidence for Endocrine Disruption. *Environmental Health Perspectives,* 118**,** 572-578.

Schroter-Kermani, C., Helm, D., Hermann, T. & Paepke, O. 2000. The German Environmental Specimen Bank - Application in Trend Monitoring of Polybrominated Diphenyl Ethers in Human Blood. *Organohalgen Compounds,* 47**,** 49-52.

Schuster, J. K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M. & Jones, K. C. 2010. Trends in European Background Air Reflect Reductions in Primary Emissions of PCBs and PBDEs. *Environmental Science & Technology,* 44**,** 6760-6766.

Sellstrom, U., De Wit, C. A., Lundgren, N. & Tysklind, M. 2005. Effect of sewage-sludge application on concentrations of higher-brominated diphenyl ethers in soils and earthworms. *Environmental Science & Technology,* 39**,** 9064-9070.

Sellström, U., Kierkegaard, A., De Wit, C. & Jansson, B. 1998. Polybrominated diphenyl ethers and hexabromocyclododecane in sediment and fish from a Swedish River. *Environmental Toxicology and Chemistry,* 17**,** 1065-1072.

Shi, S., Huang, Y., Wan, K., Dong, L. & Yang, Y. 2013. Levels and Seasonal Variations of Polybrominated Diphenyl Ethers in the Urban Atmosphere of Beijing, China. *Bulletin of Environmental Contamination and Toxicology,* 90**,** 296-301.

Shoeib, M., Harner, T., 2002, Characterization and comparison of three passive air samplers for persistent organic pollutants, *Environmental Science & Technology,* 36, 4142-4151

Siddiqi, M. A., Laessig, R. H. & Reed, K. D. 2003. Polybrominated Diphenyl Ethers (PBDEs): New Pollutants–Old Diseases. *Clinical Medicine & Research,* 1**,** 281-290.

Siddique, S., Xian, Q., Abdelouahab, N., Takser, L., Phillips, S. P., Feng, Y.-L., Wang, B. & Zhu, J. 2012. Levels of dechlorane plus and polybrominated diphenylethers in human milk in two Canadian cities. *Environment International,* 39**,** 50-55.

Sjodin, A., Hagmar, L., Klasson-Wehler, E., Kronholm-Diab, K., Jakobsson, E. & Bergman, A. 1999. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environmental Health Perspectives,* 107**,** 643-8.

Sjodin, A., Papke, O., McGahee, E., Focant, J. F., Jones, R. S., Pless-Mulloli, T., Toms, L. M., Herrmann, T., Muller, J., Needham, L. L. & Patterson, D. G., JR. 2008. Concentration of polybrominated diphenyl ethers (PBDEs) in household dust from various countries. *Chemosphere,* 73**,** S131-6.

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

Sjödin, A., Patterson, D. G. & Bergman, Å. 2001. Brominated Flame Retardants in Serum from U.S. Blood Donors. *Environmental Science & Technology,* 35**,** 3830-3833.

Söderström, G. & Marklund, S. 2002. PBCDD and PBCDF from Incineration of Waste-Containing Brominated Flame Retardants. *Environmental Science & Technology,* 36**,** 1959-1964.

Söderström, G., Sellström, U., De Wit, C. A. & Tysklind, M. 2003. Photolytic Debromination of Decabromodiphenyl Ether (BDE 209). *Environmental Science & Technology,* 38**,** 127-132.

Song, W., Ford, J. C., Li, A., Mills, W. J., Buckley, D. R. & Rockne, K. J. 2004. Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 1. Lake Superior. *Environmental Science & Technology,* 38**,** 3286-3293.

Song, W., Ford, J. C., Li, A., Sturchio, N. C., Rockne, K. J., Buckley, D. R. & Mills, W. J. 2005a. Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 3. Lakes Ontario and Erie. *Environmental Science & Technology,* 39**,** 5600-5605.

Song, W., Li, A., Ford, J. C., Sturchio, N. C., Rockne, K. J., Buckley, D. R. & Mills, W. J. 2005b. Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environmental Science & Technology,* 39**,** 3474-3479.

Stapleton, H. M., Brazil, B., Holbrook, R. D., Mitchelmore, C. L., Benedict, R., Konstantinov, A. & Potter, D. 2006. In Vivo and In Vitro Debromination of Decabromodiphenyl Ether (BDE 209) by Juvenile Rainbow Trout and Common Carp. *Environmental Science & Technology,* 40**,** 4653-4658.

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

Stasinska, A., Reid, A., Hinwood, A., Stevenson, G., Callan, A., Odland, J. Ø. & Heyworth, J. 2013. Concentrations of polybrominated diphenyl ethers (PBDEs) in residential dust samples from Western Australia. *Chemosphere,* 91**,** 187-193.

Stern, G. A., Braekevelt, E., Helm, P. A., Bidleman, T. F., Outridge, P. M., Lockhart, W. L., McNeeley, R., Rosenberg, B., Ikonomou, M. G., Hamilton, P., Tomy, G. T. & Wilkinson, P. 2005. Modern and historical fluxes of halogenated organic contaminants to a lake in the Canadian arctic, as determined from annually laminated sediment cores. *Science of The Total Environment,* 342**,** 223-243.

Stockholm Convention. 2009. *The 9 new POPs* [Online]. Available: http://chm.pops.int/Programmes/NewPOPs/The9newPOPs/tabid/672/language/en-US/Default.aspx [Accessed 11 January 2010].

Stoker, T. E., Cooper, R. L., Lambright, C. S., Wilson, V. S., Furr, J. & Gray, L. E. 2005. In vivo and in vitro anti-androgenic effects of DE-71, a commercial polybrominated diphenyl ether (PBDE) mixture. *Toxicology and Applied Pharmacology,* 207**,** 78-88.

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

Suzuki, G., nose, K., Takigami, H., Takahashi, S. & sakai, S. 2006. PBDEs and PBDD/Fs in House and Office Dust from Japan. *Organohalgen Compounds,* 68**,** 1843-1846.

Suzuki, G., Takigami, H., nose, K., Takahashi, S., asari, M. & Sakai, S.-I. 2007. Dioxin-Like and Transthyretin-Binding Compounds in Indoor Dusts Collected from Japan: Average Daily Dose and Possible Implications for Children. *Environmental Science & Technology,* 41**,** 1487-1493.

Takigami, H., Suzuki, G., hirai, Y. & Sakai, S.-I. 2008. Transfer of brominated flame retardants from components into dust inside television cabinets. *Chemosphere,* 73**,** 161-169.

Takigami, H., Suzuki, G., Hirai, Y. & Sakai, S.-I. 2009. Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. *Chemosphere,* 76**,** 270-277.

Taylor, S. E., Birch, G. F. & Links, F. 2004. Historical catchment changes and temporal impact on sediment of the receiving basin, Port Jackson, New South Wales. *Australian Journal of Earth Sciences,* 51**,** 233-246.

Ter Schure, A. F. H., Larsson, P., Agrell, C. & Boon, J. P. 2004. Atmospheric Transport of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls to the Baltic Sea. *Environmental Science & Technology,* 38**,** 1282-1287.

Terauchi, H., Takahashi, S., Lam, P. K. S., Min, B.-Y. & Tanabe, S. 2009. Polybrominated, polychlorinated and monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans and dioxin-like polychlorinated biphenyls in marine surface sediments from Hong Kong and Korea. *Environmental Pollution,* 157**,** 724-730.

The Furniture Industry Research Association (FIRA). 2011. *Fire safety of furniture and furnishings in the home: A Guide to the UK regulations* [Online]. Available: http://www.fira.co.uk/document/fira-flammability-guide-october-2011pdf.pdf [Accessed 26 June 2013 2013].

Thomas, G. O., Wilkinson, M., Hodson, S. & Jones, K. C. 2006. Organohalogen chemicals in human blood from the United Kingdom. *Environmental Pollution,* 141**,** 30-41.

Thomsen, C., Lundanes, E. & Becher, G. 2002. Brominated Flame Retardants in Archived Serum Samples from Norway: A Study on Temporal Trends and the Role of Age. *Environmental Science & Technology,* 36**,** 1414-1418.

Tittlemier, S. A., Halldorson, T., Stern, G. A. & Tomy, G. T. 2002. Vapor pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants. *Environmental Toxicology and Chemistry,* 21**,** 1804-1810.

Toms, L.-M. L., Bartkow, M. E., Symons, R., Paepke, O. & Mueller, J. F. 2009a. Assessment of polybrominated diphenyl ethers (PBDEs) in samples collected from indoor environments in South East Queensland, Australia. *Chemosphere,* 76**,** 173-178.

Toms, L.-M. L., Harden, F. A., Symons, R. K., Burniston, D., Fürst, P. & Müller, J. F. 2007. Polybrominated diphenyl ethers (PBDEs) in human milk from Australia. *Chemosphere,* 68**,** 797-803.

Toms, L.-M. L., Hearn, L., Kennedy, K., Harden, F., Bartkow, M., Temme, C. & Mueller, J. F. 2009b. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. *Environment International,* 35**,** 864-869.

Toms, L.-M. L., Mortimer, M., Symons, R. K., Paepke, O. & Mueller, J. F. 2008. Polybrominated diphenyl ethers (PBDEs) in sediment by salinity and land-use type from Australia. *Environment International*, 34**,** 58-66.

Toms, L.-M. L., Mueller, J. F., Mortimer, M., Symons, R., Stevenson, G. & Gaus, C. 2006. Assessment of concentrations of polybrominated diphenyl ether flame retardants in aquatic environments in Australia. *In:* HERITAGE, A. G. D. O. T. E. A. (ed.). Canberra.

Tue, N. M., Takahashi, S., Suzuki, G., Isobe, T., Viet, P. H., Kobara, Y., Seike, N., Zhang, G., Sudaryanto, A. & Tanabe, S. 2013. Contamination of indoor dust and air by polychlorinated biphenyls and brominated flame retardants and relevance of non-dietary exposure in Vietnamese informal e-waste recycling sites. *Environment International*, 51**,** 160-167.

U.S. EPA 2007, Method 1614. Brominated Diphenyl Ethers in Water, Soil, Seiment and Tissue by HRGC/HRMS,. Washington, DC. http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_09_11_methods_method_1614.pdf [accessed 10/09/2013]

U.S. EPA. 2008a. IRIS Toxicological Review of Decabromodiphenyl Ether (2008 Final). Washington, DC: U.S. Environmental Protection Agency.

U.S. EPA. 2008b. Toxicological Review of 2,2',4,4'-Tetrabromodiphenyl ether (BDE-47). Washingtond, DC. http://www.epa.gov/iris/toxreviews/1010tr.pdf [accessed: 05/06/2013]

U.S. EPA. 2008c. Toxicological Review of 2,2',4,4',5-Pentabromodiphenyl ether (BDE-99). Washington, DC. http://www.epa.gov/iris/toxreviews/1008tr.pdf [accessed: 05/06/2013]

U.S. EPA. 2008d. Toxicological Review of 2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153). Washington, DC: U.S. Environmental Protection Agency. http://www.epa.gov/iris/toxreviews/1009tr.pdf [accessed: 05/06/2013]

U. S. Environmental Protection Agency (EPA) 2011. Exposure Factors Handbook. 2011 ed. USA: EPA.

UNEP 1999. Regionally Based Assessment of Persistent Toxic Substances. *2nd Scientific and Technical Evluation Workshop on Persistent Organic Pesticides Used in Agriculture, Human Health and Other Related Sectors and 3rd Scientific and Technical Evaluation Workshop on Organometallics.* Geneva, Switzerland.

Usenko, S., Landers, D. H., Appleby, P. G. & Simonich, S. L. 2007. Current and Historical Deposition of PBDEs, Pesticides, PCBs, and PAHs to Rocky Mountain National Park. *Environmental Science & Technology*, 41**,** 7235-7241.

Van Den Berg, M., Denison, M. S., Birnbaum, L. S., Devito, M. J., Fiedler, H., Falandysz, J., Rose, M., Schrenk, D., Safe, S., Tohyama, C., Tritscher, A., Tysklind, M. & Peterson, R. E. 2013. Polybrominated Dibenzo-p-Dioxins, Dibenzofurans, and Biphenyls:

Inclusion in the Toxicity Equivalency Factor Concept for Dioxin-Like Compounds. *Toxicological Sciences,* 133**,** 197-208.

Vane, C., Ma, Y.-J., Chen, S.-J. & Mai, B.-X. 2010. Increasing polybrominated diphenyl ether (PBDE) contamination in sediment cores from the inner Clyde Estuary, UK. *Environmental Geochemistry and Health,* 32**,** 13-21.

Vives, I., Canuti, E., Castro-Jimenez, J., Christoph, E. H., Eisenreich, S. J., Hanke, G., Huber, T., Mariani, G., Mueller, A., Skejo, H., Umlauf, G. & Wollgast, J. 2007. Occurrence of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Lake Maggiore (Italy and Switzerland). *Journal of Environmental Monitoring,* 9**,** 589-598.

Vonderheide, A. P., Mueller-Spitz, S. R., Meija, J., Welsh, G. L., Mueller, K. E., Kinkle, B. K., Shann, J. R., Caruso, J. A., 2006, Rapid breakdown of brominated flame retardants by soil microorganisms, *Journal of Analytical Atomic Spectrometry*, 21, 1232-1239

Voorspoels, S., Covaci, A., Neels, H. & Schepens, P. 2007. Dietary PBDE intake: A market-basket study in Belgium. *Environment International,* 33**,** 93-97.

Wang, D. L., Cai, Z. W., Jiang, G. B., Leung, A., Wong, M. H. & Wong, W. K. 2005. Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. *Chemosphere,* 60**,** 810-816.

Wang, L.-C., Lee, W.-J., Lee, W.-S. & Chang-Chien, G.-P. 2010a. Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources. *Environmental Pollution*, 158**,** 3108-3115.

Wang, L. C., Tsai, C. H., Chang-Chien, G. P. & Hung, C. H. 2008. Characterization of polybrominated dibenzo-p-dioxins and dibenzofurans in different atmospheric environments. *Environmental Science & Technology,* 42**,** 75-80.

Wang, L. C., Wang, Y. F., Hsi, H. C. & Chang-Chien, G. P. 2010b. Characterizing the Emissions of Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Dibenzo-p-dioxins and Dibenzofurans (PBDD/Fs) from Metallurgical Processes. *Environmental Science & Technology,* 44**,** 1240-1246.

Wang, Z., Ma, X., Lin, Z., Na, G. & Yao, Z. 2009. Congener specific distributions of polybrominated diphenyl ethers (PBDEs) in sediment and mussel (Mytilus edulis) of the Bo Sea, China. *Chemosphere,* 74**,** 896-901.

Wania, F. & Dugani, C. B. 2003. Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of four multimedia models. *Environmental Toxicology & Chemistry,* 22**,** 1252-61.

Weber, R. & Kuch, B. 2003. Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. *Environment International,* 29**,** 699-710.

Webster, L., Russell, M., Adefehinti, F., Dalgarno, E. J. & Moffat, C. F. 2008. Preliminary assessment of polybrominated diphenyl ethers (PBDEs) in the Scottish aquatic environment, including the Firth of Clyde. *Journal of Environmental Monitoring,* 10**,** 463-473.

Webster, T. F., Vieira, V. & Shecter, A. 2005. Estimating Human Exposure to PBDE-47 Via Air, Food and Dust Using Monte Carlo Methods. *Organohalgen Compounds,* 67**,** 505-508.

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

Wilford, B. H., Thomas, G. O., Jones, K. C., Davison, B. & Hurst, D. K. 2008. Decabromodiphenyl ether (deca-BDE) commercial mixture components, and other PBDEs, in airborne particles at a UK site. *Environment International,* 34**,** 412-419.

Wong, F., Kurt-Karakus, P., Bidleman, T., Fate of Brominated Flame Retardants and Organochlorine Pesticides in Urban Soil: Volatility and Degradation. *Environmental Science & Technology,* 46, 2668-2674

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

World Health Organization (WHO) 1998. International Programme on Chemical Safety. Environmental Health Criteria 205: Polybrominated dibenzo-p-dioxings and dibenzofurans. Geneva: WHO.

Wu, N., Herrmann, T., Paepke, O., Tickner, J., Hale, R., Harvey, E., La Guardia, M., McClean, M. D. & Webster, T. F. 2007. Human Exposure to PBDEs: Associations of PBDE Body Burdens with Food Consumption and House Dust Concentrations. *Environmental Science & Technology,* 41**,** 1584-1589.

Wurl, O., Potter, J. R., Durville, C. & Obbard, J. P. 2006. Polybrominated diphenyl ethers (PBDEs) over the open Indian Ocean. *Atmospheric Environment,* 40**,** 5558-5565.

Xiao, H., Shen, L., Su, Y., Barresi, E., Dejong, M., Hung, H., Lei, Y.-D., Wania, F., Reiner, E. J., Sverko, E. & Kang, S.-C. 2012. Atmospheric concentrations of halogenated flame retardants at two remote locations: The Canadian High Arctic and the Tibetan Plateau. *Environmental Pollution,* 161**,** 154-161.

Xiao, Q., Hu, B., Duan, J., He, M. & Zu, W. 2007. Analysis of PBDEs in Soil, Dust, Spiked Lake Water, and Human Serum Samples by Hollow Fiber-Liquid Phase Microextraction Combined with GC-ICP-MS. *Journal of the American Society for Mass Spectrometry,* 18**,** 1740-1748.

Yen, J. H., Liao, W. C., Chen, W. C., Wang, Y. S., 2009, Interaction of polybrominated diphenyl ethers (PBDEs) with anaerobic mixed bacterial cultures isolated from river sediment, *Journal of Hazardous Materials*, 165, 518-524

Yun, S. H., Addink, R., McCabe, J. M., Ostaszewski, A., Mackenzie-Taylor, D., Taylor, A. B. & Kannan, K. 2008. Polybrominated diphenyl ethers and polybrominated biphenyls in sediment and floodplain soils of the Saginaw River watershed, Michigan, USA. *Archives of Environmental Contamination and Toxicology,* 55**,** 1-10.

Zegers, B. N., Lewis, W. E., Booij, K., Smittenberg, R. H., Boer, W., De Boer, J. & boon, J. P. 2003. Levels of Polybrominated Diphenyl Ether Flame Retardants in Sediment Cores from Western Europe. *Environmental Science & Technology,* 37**,** 3803-3807.

Zhang, B.-Z., Guan, Y.-F., LI, S.-M. & Zeng, E. Y. 2009a. Occurrence of Polybrominated Diphenyl Ethers in Air and Precipitation of the Pearl River Delta, South China: Annual Washout Ratios and Depositional Rates. *Environmental Science & Technology,* 43**,** 9142-9147.

Zhang, X.-L., Luo, X.-J., Chen, S.-J., Wu, J.-P. & Mai, B.-X. 2009b. Spatial distribution and vertical profile of polybrominated diphenyl ethers, tetrabromobisphenol A, and decabromodiphenylethane in river sediment from an industrialized region of South China. *Environmental Pollution,* 157**,** 1917-1923.

Zhu, L. Y. & Hites, R. A. 2005. Brominated Flame Retardants in Sediment Cores from Lakes Michigan and Erie. *Environmental Science & Technology,* 39**,** 3488-3494.

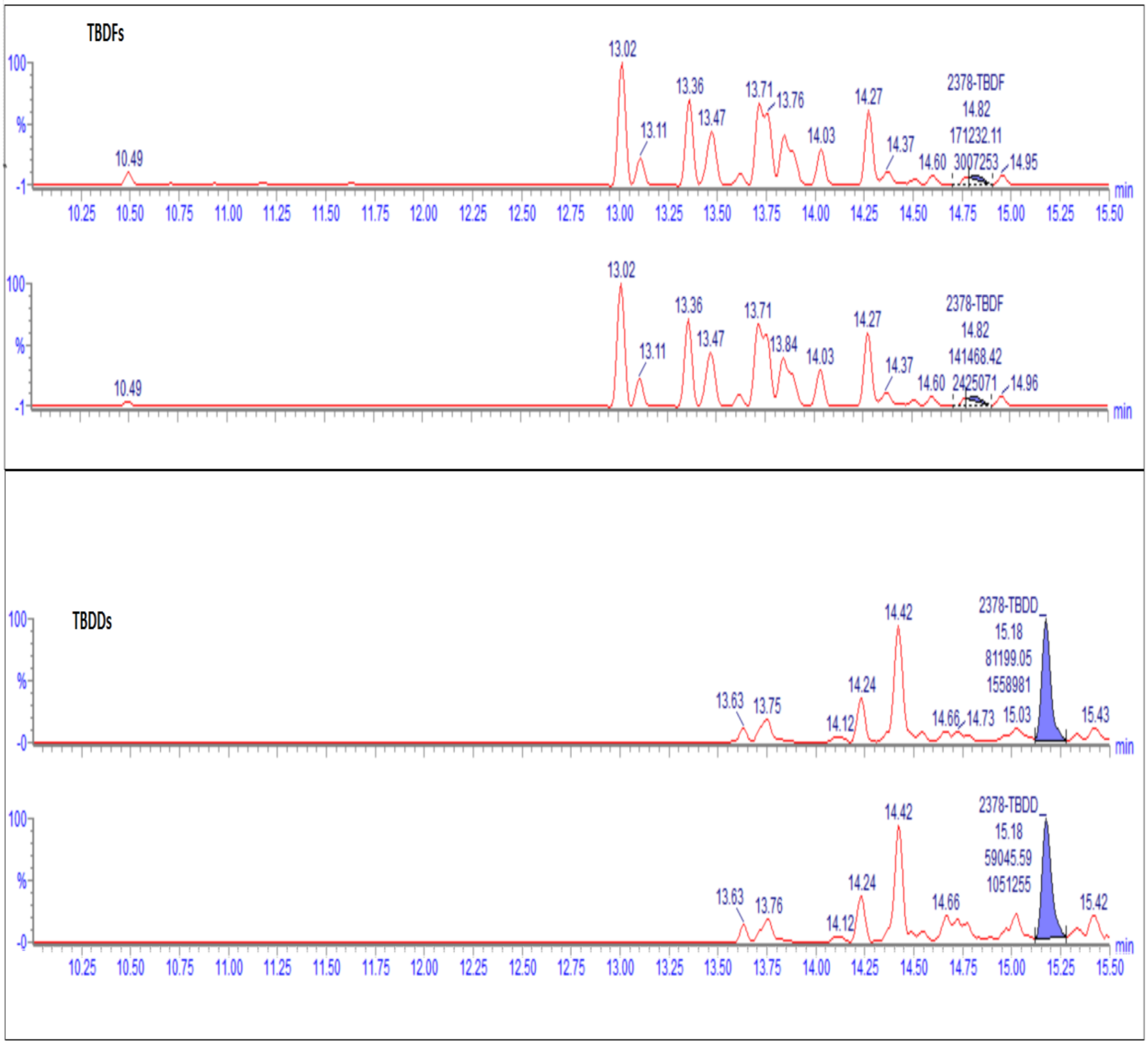
Appendix 1. Concentrations of PBDEs within the vicinity of Scunthorpe Sinter Plant

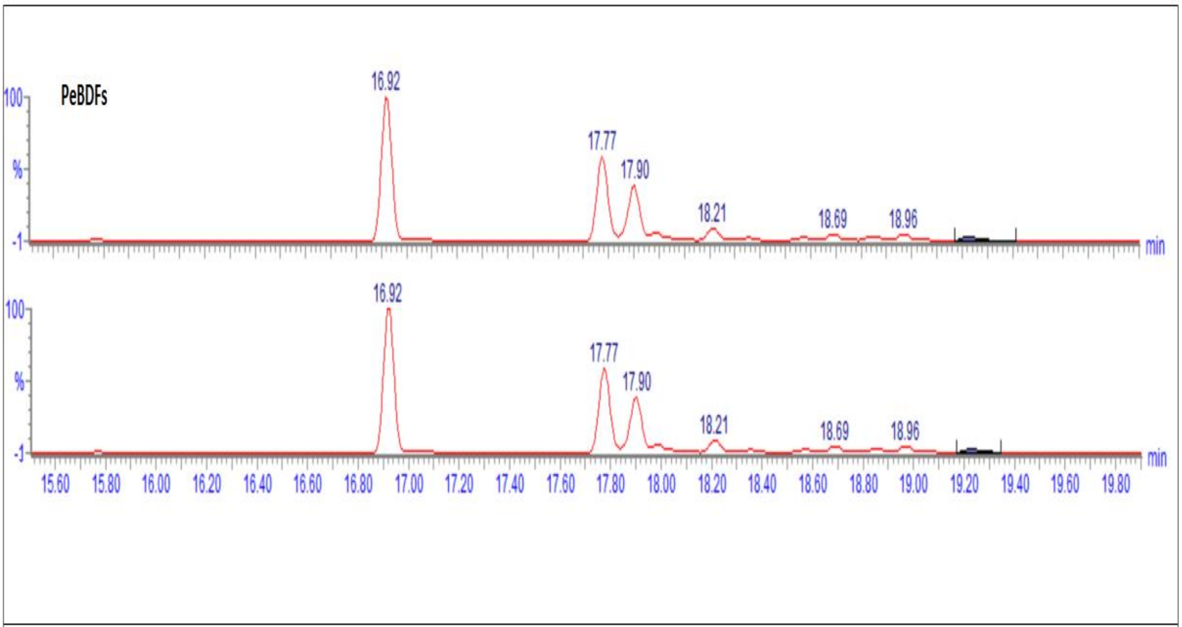
Concentration OF PBDEs in SSP in pg/m^3				
BS	BS1	BS2	BS3	BS4
BDE47	17	26	<0.3	2.7
BDE85	0.33	3	1.9	<0.74
BDE99	8.1	4	8.9	11
BDE100	0.4	9.9	0.84	0.83
BDE153	1.7	2.1	1.7	3
BDE154	<0.89	1	<0.89	0.9
BDE183	<0.5	2.2	<1.5	2.8
BDE209	700	340	170	870
∑PBDEs	730	390	180	890
LTOO	LTOO1	LTOO2	LTOO4	
BDE47	93	36	24	
BDE85	3.6	15	3.5	
BDE99	110	65	81	
BDE100	7.7	8	3.3	
BDE153	13.3	9	4.2	
BDE154	2.0	1.9	1.1	
BDE183	<1.5	2	2.1	
BDE209	3000	2200	1600	
∑PBDEs	3200	2300	1700	
SLT	SLT2			
BDE47	8.5			
BDE85	<0.74			
BDE99	7.3			
BDE100	0.77			
BDE153	1.3			
BDE154	1.5			
BDE183	1.2			
BDE209	2200			
∑PBDEs	2200			
ESR	ESR1	ESR2		
BDE47	48	70		
BDE85	<0.75	7.7		
BDE99	26	94		
BDE100	2.3	10		
BDE153	2	17		
BDE154	1.4	1.3		
BDE183	<1.5	1.3		
BDE209	800	4100		
∑PBDEs	880	4300		

DLCO	DLCOO1	DLCOO2	DLCOO3	DLCOO4
BDE47	1200	1500	520	180
BDE85	72	180	23	6.5
BDE99	1300	2100	300	310
BDE100	84	170	17	12
BDE153	170	360	51	47
BDE154	35	86	12	4
BDE183	2.8	2.6	4	15
BDE209	970	2200	290	1100
∑PBDEs	3800	6600	1200	1700

AT	AT1	AT2	AT3
BDE47	11	6.1	2
BDE85	2.1	0.37	0.64
BDE99	1.8	0.15	6.2
BDE100	<0.45	<0.45	0.51
BDE153	<0.9	1	0.67
BDE154	<1.1	0.61	0.65
BDE183	<0.5	<0.5	1.74
BDE209	530	390	1400
∑PBDEs	550	400	1400

Appendix 2: PBDD/Fs chromatograms from Sinterpot Study, Experiment 1

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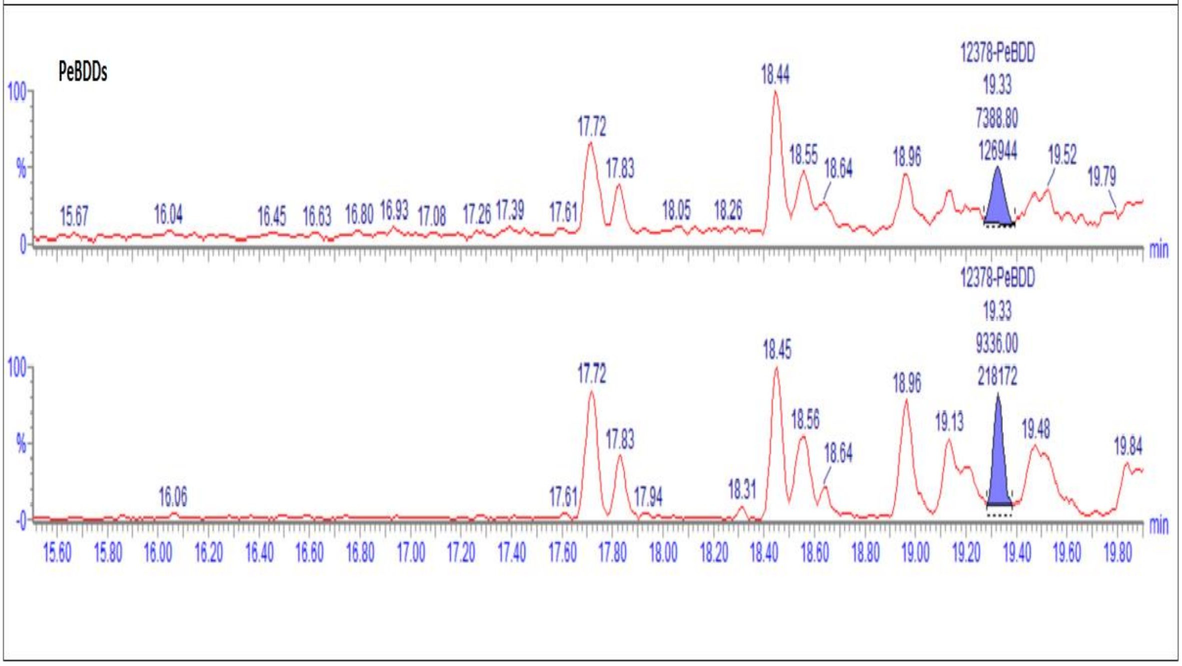
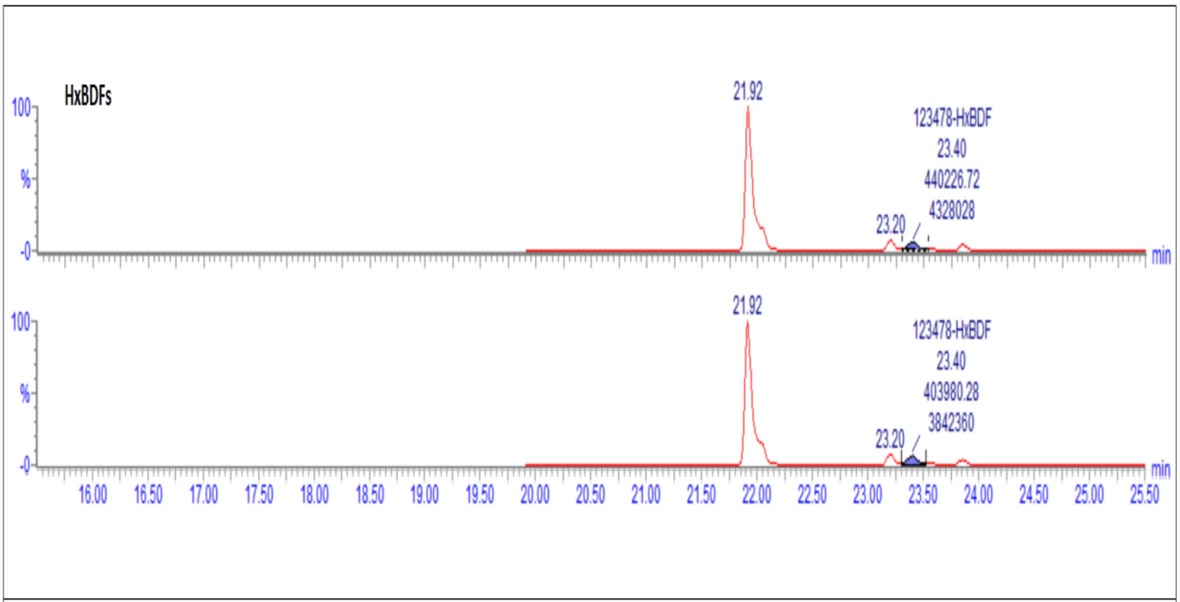
100
%
-1
16.92
17.77
17.90
18.21
18.69
18.96
min
100
%
-1
16.92
17.77
17.90
18.21
18.69
18.96
min
15.60
15.80
16.00
16.20
16.40
16.60
16.80
17.00
17.20
17.40
17.60
17.80
18.00
18.20
18.40
18.60
18.80
19.00
19.20
19.40
19.60
19.80


PeBDDs
100
%
0
15.67
16.04
16.45
16.63
16.80
16.93
17.08
17.26
17.39
17.61
17.72
17.83
18.05
18.26
18.44
18.55
18.64
18.96
12378-PeBDD
19.33
7388.80
126944
19.52
19.79
min
100
%
-0
16.06
17.61
17.72
17.83
17.94
18.31
18.45
18.56
18.64
18.96
19.13
12378-PeBDD
19.33
9336.00
218172
19.48
19.84
min
15.60
15.80
16.00
16.20
16.40
16.60
16.80
17.00
17.20
17.40
17.60
17.80
18.00
18.20
18.40
18.60
18.80
19.00
19.20
19.40
19.60
19.80


HxBDFs
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%
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21.92
123478-HxBDF
23.40
440226.72
4328028
23.20
min
100
%
0
21.92
123478-HxBDF
23.40
403980.28
3842360
23.20
min
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
20.00
20.50
21.00
21.50
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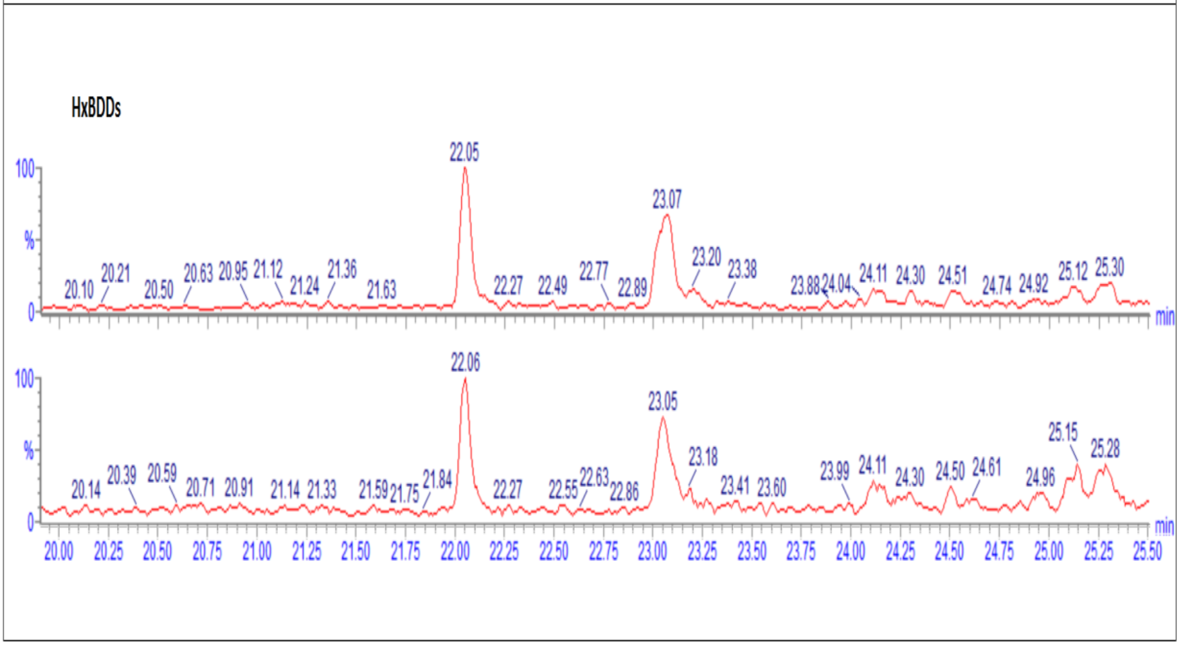
24.00
24.50
25.00
25.50


HxBDDs
100
%
0
22.05
23.07
20.10
20.21
20.50
20.63
20.95
21.12
21.24
21.36
21.63
22.27
22.49
22.77
22.89
23.20
23.38
23.88
24.04
24.11
24.30
24.51
24.74
24.92
25.12
25.30
min
100
%
0
22.06
23.05
20.14
20.39
20.59
20.71
20.91
21.14
21.33
21.59
21.75
21.84
22.27
22.55
22.63
22.86
23.18
23.41
23.60
23.99
24.11
24.30
24.50
24.61
24.96
25.15
25.28
min
20.00
20.25
20.50
20.75
21.00
21.25
21.50
21.75
22.00
22.25
22.50
22.75
23.00
23.25
23.50
23.75
24.00
24.25
24.50
24.75
25.00
25.25
25.50

Appendix 3. Concentrations of PBDEs in ambient air samples from the West Midlands, UK

Worcester	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	0.4	1.5	0.8	<0.21	<0.21	<0.21
BDE-28	0.5	4.2	0.3	0.9	<0.23	1.3
BDE-47	<0.3	2.3	1.3	2.4	4.5	0.8
BDE-66	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
BDE-100	1	<0.45	<0.45	2.2	<0.45	<0.45
BDE-99	<0.49	<0.49	<0.49	3.5	<0.49	<0.49
BDE-85	<0.74	<0.74	<0.74	<0.74	<0.74	<0.74
BDE-154	1.4	2.6	1.5	<0.89	<0.89	<0.89
BDE-153	1.7	<1.1	2.3	<1.1	<1.1	<1.1
BDE-183	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
BDE-209	<2.2	58	13	82	110	300
∑PBDEs	5	69	19	91	110	300
∑tri-heptaPBDEs	5	11	6.2	9	4.5	2.1
Droitwich	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	0.6	2.4	<0.21	0.3	0.7	<0.21
BDE-28	0.9	6.3	0.5	0.5	1.8	2
BDE-47	<0.3	6.2	1.1	0.6	0.9	1.6
BDE-66	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
BDE-100	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
BDE-99	<0.49	<0.49	<0.49	1.3	<0.49	<0.49
BDE-85	<0.74	<0.74	<0.74	<0.74	<0.74	<0.74
BDE-154	<0.89	8.7	<0.89	<0.89	<0.89	<0.89
BDE-153	<1.1	9.5	<1.1	<1.1	<1.1	<1.1
BDE-183	<1.5	11	<1.5	<1.5	<1.5	<1.5
BDE-209	<2.2	59	56	<2.2	56	380
∑PBDEs	1.5	100	58	2.7	59	380
∑tri-heptaPBDEs	1.5	44	1.6	2.7	3.4	3.6

Bromsgrove	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	7.9	0.8	1.5	<0.21	<0.21	<0.21
BDE-28	9.4	7.4	1.9	<0.23	1.3	1.5
BDE-47	18	1.3	2.8	0.9	4.5	1.6
BDE-66	4.4	2	<0.45	<0.45	<0.45	<0.45
BDE-100	15	<0.45	<0.45	<0.45	<0.45	<0.45
BDE-99	36	<0.49	<0.49	<0.49	<0.49	<0.49
BDE-85	6.7	<0.74	<0.74	<0.74	<0.74	<0.74
BDE-154	20	4.6	<0.89	<0.89	<0.89	<0.89
BDE-153	31	8.2	<1.1	<1.1	<1.1	<1.1
BDE-183	29	<1.5	<1.5	<1.5	<1.5	<1.5
BDE-209	1500	210	<2.2	120	63	350
∑PBDEs	1700	230	6.2	120	69	350
∑tri-heptaPBDEs	180	24	6.2	0.9	5.8	3.1
Bournville	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	6.4	1	3.3	0.4	<0.21	<0.21
BDE-28	6.4	6.8	4.4	1.5	1.4	1.5
BDE-47	11	6.8	7.2	1.9	3.7	0.5
BDE-66	6.6	5.1	3.7	<0.45	<0.45	<0.45
BDE-100	10	<0.45	1.5	<0.45	<0.45	<0.45
BDE-99	13	<0.49	6.4	1.8	<0.49	<0.49
BDE-85	11	<0.74	3.8	<0.74	<0.74	<0.74
BDE-154	18	<0.89	5	<0.89	<0.89	<0.89
BDE-153	26	<1.1	7.8	1.5	<1.1	<1.1
BDE-183	21	<1.5	8.8	<1.5	<1.5	<1.5
BDE-209	<2.2	140	58	27	120	510
∑PBDEs	130	160	110	34	130	510
∑tri-heptaPBDEs	130	20	52	7.1	5.1	2

Edgbaston	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	42	1.3	0.3	<0.21	<0.21	0.3
BDE-28	26	3.4	0.9	<0.23	1.4	0.8
BDE-47	31	5.8	2	2.1	4	0.4
BDE-66	<0.45	4.5	<0.45	<0.45	<0.45	<0.45
BDE-100	30	<0.45	1.3	<0.45	<0.45	<0.45
BDE-99	43	<0.49	1.8	<0.49	<0.49	<0.49
BDE-85	<0.74	<0.74	<0.74	<0.74	<0.74	<0.74
BDE-154	57	<0.89	9.4	7.3	<0.89	<0.89
BDE-153	62	<1.1	1.9	<1.1	<1.1	<1.1
BDE-183	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
BDE-209	<2.2	180	SAMPLING[a] ERROR	92	26	270
∑PBDEs	290	200	-	100	31	270
∑tri-heptaPBDEs	290	15	18	9.4	5.4	1.5
Digbeth	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	25	1	0.3	2.5	<0.21	<0.21
BDE-28	26	2	0.5	4.1	1.8	0.9
BDE-47	27	3.9	1.9	10	3.1	1.3
BDE-66	16	0.8	<0.45	2.1	<0.45	<0.45
BDE-100	14	<0.45	0.6	<0.45	<0.45	<0.45
BDE-99	27	1.7	0.9	6.1	<0.49	<0.49
BDE-85	<0.74	<0.74	<0.74	<0.74	<0.74	<0.74
BDE-154	42	2	<0.89	2.9	<0.89	3.2
BDE-153	70	3.7	<1.1	6.5	<1.1	1.7
BDE-183	57	<1.5	<1.5	<1.5	<1.5	11
BDE-209	<2.2	34	97	180	170	360
∑PBDEs	300	49	100	210	170	380
∑tri-heptaPBDEs	310	15	4.2	34	4.9	18

[a] GFF not present upon collection of samplers. Therefore particulate phase (and thus BDE-209) not measured

Sutton Coldfield	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	3.7	0.9	0.9	<0.21	<0.21	<0.21
BDE-28	2.7	3.9	1.3	<0.23	1	1.3
BDE-47	2.5	8.3	4	2.2	0.7	0.6
BDE-66	2.1	<0.45	<0.45	<0.45	<0.45	<0.45
BDE-100	1.3	<0.45	1.9	<0.45	<0.45	<0.45
BDE-99	3.5	11	3.3	<0.49	<0.49	<0.49
BDE-85	4.5	<0.74	<0.74	<0.74	<0.74	<0.74
BDE-154	14	9.1	<0.89	3.8	<0.89	<0.89
BDE-153	11	<1.1	<1.1	4.1	<1.1	<1.1
BDE-183	<1.5	<1.5	<1.5	17	<1.5	<1.5
BDE-209	17	370	16	48	120	220
∑PBDEs	62	400	27	75	120	220
∑tri-heptaPBDEs	45	33	11	27	1.7	1.9
Tamworth	**Jun-Jul**	**Jul-Aug**	**Aug-Oct**	**Oct-Nov**	**Nov-Dec**	**Dec-Jan**
BDE-17	15	<0.21	0.5	1.8	<0.21	0.5
BDE-28	9.9	2.2	1.2	2.3	<0.23	1.4
BDE-47	14	6.1	3.3	5.1	1.8	0.5
BDE-66	<0.45	<0.45	<0.45	1.9	<0.45	<0.45
BDE-100	8.1	2.2	1.8	<0.45	<0.45	<0.45
BDE-99	11	5	3.7	3.9	<0.49	<0.49
BDE-85	<0.74	<0.74	<0.74	<0.74	<0.74	<0.74
BDE-154	<0.89	<0.89	<0.89	2.2	<0.89	<0.89
BDE-153	<1.1	<1.1	14	3.9	<1.1	<1.1
BDE-183	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
BDE-209	<2.2	97	18	47	38	440
∑PBDEs	58	110	43	68	40	440
∑tri-heptaPBDEs	58	16	25	21	1.8	2.4

STUDIES INTO THE FORMATION OF PBDEs AND PBDD/Fs IN THE IRON ORE SINTERING PROCESS

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Introduction

In recent years, several studies have been published showing that the steel industry could be a potential source of Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) to the environment[1, 2, 3]. Amongst the processes involved in steelmaking, the EAF (Electric Arc Furnace) steelmaking process was pointed out as the main potential source of PBDEs and PBDD/Fs from the steel industry. For instance, Odabasi et al. have highlighted the recycling of scrap metal containing PBDE impurities as a potential source of PBDEs in the environment[3]. Wang et al. measured the emissions of PBDEs and PBDD/Fs in both carbon steel EAFs and stainless steel EAFs in Taiwan showing that carbon steel EAFs exhibited emission factors of PBDEs and PBDD/Fs three to eighteen times higher than those of stainless steel EAFs owing to the fact that the production of stainless steel requires scrap with fewer impurities than carbon steel[2]. In the same study, the iron ore sintering process was highlighted, for the first time, as a potential source of PBDEs in the environment because PBDEs (sum of 30 congeners) were found at higher concentrations (ca. 35 ng / m^3) than EAFs (ca. 15 ng / m^3). Based on these results, it was hypothesized that PBDEs could be formed in the sintering process through similar formation conditions than PCDD/Fs (ie. *de novo* formation), however the bromide content and the potential PBDE content of raw materials were not measured. The presence of PBDEs in sinter plant emissions could also have implications with regard to the mechanism of formation of PBDD/Fs in iron ore sintering since the formation of PBDFs from PBDEs requires only an intra-molecular elimination of Br_2 or HBr, which occur within the temperature range 510 to 630ºC[4]. Considering that the mechanisms involved in PBDEs and PBDD/Fs formation in iron ore sintering remains unclear, the aim of this study was to investigate into more details their potential formation in sintering through a series of laboratory sinter pot experiments and the measurement of PBDEs in raw material inputs and emissions from commercial sinter plants operated by Tata Steel in the UK.

Materials and methods

The sinter pot experiments were performed using a laboratory sinter pot which has a raw sinter mix capacity of 1.0 kg, with a bed diameter and height of 100 and 150 mm, respectively (Fig. 1). The raw sinter mix was charged as micro-pellets onto a layer of hearth material, approximately 25 mm thick, consisting of sinter cake pieces supported on a 3-mm thick stainless steel mesh. On each day of operation, sufficient raw mix was prepared for single test firing by mixing the raw materials and additives in a drum mixer/pelletiser together with water to give the required moisture content (6%-wt). The ore blend contained a base mixture of several high-grade iron ores, coke breeze (3.3%-wt) as fuel and additions of limestone and olivine. In the experiments, the potential for PBDE and PBDD/F formation was investigated by adding medium and high concentrations of potassium bromide (KBr) and PBDE Technical mixtures (both Penta- and Deca-BDE). PBDEs and PBDD/Fs were measured in the raw sinter mix and sinter product at the start and end of each experimental run, and also in the volatile emissions collected on PUF plugs.

Table 1 - Sinter pot experimental conditions to study PBDE and PBDD/F formation in iron ore sintering.

Experiment 1	"Base Case" – Standard Raw Sinter Mix / no KBr / no PBDE technical mixture
Experiment 2	Standard Raw Sinter Mix + 74.5 mg/kg KBr
Experiment 3	Standard Raw Sinter Mix + 224 mg/kg KBr
Experiment 4	Standard Raw Sinter Mix + 100 µg/kg PBDE Technical Solutions (Penta / Deca)
Experiment 5	Standard Raw Sinter Mix + 224 mg/kg KBr + 100 µg/kg PBDE Technical Solutions (Penta / Deca)

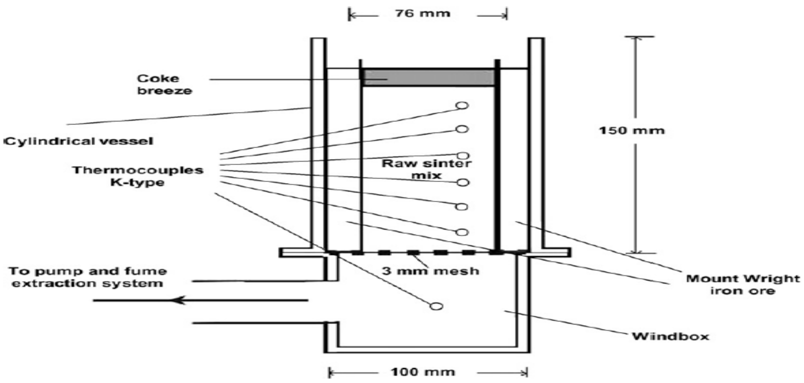


Fig. 1 - A schematic diagram of the laboratory sinter pot apparatus

PBDEs were also measured in a series of raw material input and output samples taken from two commercial scale sintering plants in the UK including 6 raw sinter mix (ie. input samples); 9 electrostatic precipitator (ESP) dusts ; 6 sinter product samples and 1 stack emission sample (output samples). All samples, except for the stack emissions and the sinter pot PUF samples underwent pressurized liquid extraction PLE as previously used by our research group[5]. Stack emissions and sinter pot PUF samples were extracted using PLE according to Tata Steel ISO 17025 method accredited for PCDD/F analysis. For these samples, 90% (by volume) was retained for PBDD/F analysis, whilst the remaining 10% was used for PBDE analysis. Samples were measured for tri-hexa-PBDEs using GC-EI/MS[6]. All PBDD/F samples were analysed using HRGC/HRMS for tetra-hexa PBDD/Fs.

Results and discussion

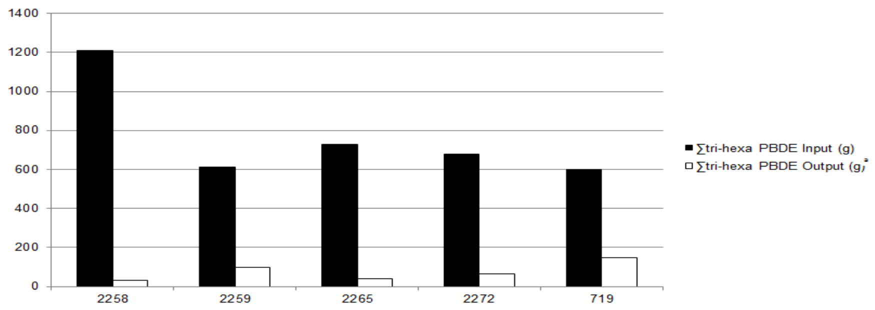
Analysis of input / output materials used in commercial sinter plants.

The results of the PBDE content of the initial raw mix entering the sintering process for five different beds are shown in Table 2 and revealed a substantial input of PBDEs, with the sum of the measured congeners ranging from 2,600-20,000 ng/kg. For Bed 2272, PBDE emissions were measured and a total concentration of 96 ng/m^3 was found for the sum of the 6 congeners analysed. This value was used to calculate a mass balance by comparing the total PBDE input to the total PBDE output (ie. ESP dust + Sinter Product + Emissions), for each bed. The results of the mass balance are depicted in Fig. 2 and showed a total input of 600-1200 g PBDE per sintering bed (Fig. 2). In comparison, the total PBDE outputs were estimated only at 33-150 g PBDE per sintering bed, which represented a 75-97% reduction of the total input. This reduction showed that the PBDEs that were already present in the raw materials prior to sintering were destroyed during the process.

Table 2 - PBDE concentrations (ng/kg) of key congeners in raw sinter six samples (ie. input) from sinter plants in the UK.

	Bed 2258	**Bed 2259**	**Bed 2265**	**Bed 2272**	**Bed 719**
BDE-28	390	190	230	180	38
BDE-49	2000	940	1100	940	180
BDE-47	3800	1900	2300	2300	700
BDE-99	10000	5100	6500	5600	1050
BDE-100	1400	760	200	710	270
BDE-153	2600	1300	1700	1400	350
$\sum_{\textbf{tri-hexa}}$**PBDEs**[a]	**20000**	**10000**	**12000**	**11000**	**2600**

[a] Sum of individual congeners may not be the same as ΣPBDEs due to rounding to 2 significant figures.



*emission sample from bed 2272 used as an emission estimate for output calculations in all other beds

Fig. 2 - Measured PBDE inputs and outputs (g) in sinter plants in the UK.

Analysis of PBDD/F emissions in sinter plants in the UK

A series of emission samples from UK sinter plants were analysed for their PBDD/F concentrations, and the results were compared with the emissions of their chlorinated homologues (PCDD/Fs). The results are presented in Fig. 3. For this study, PBDD/F emissions concentrations were reported as WHO-TEQ emission concentrations, by assuming that PBDD/F and PCDD/F would have identical toxic equivalency factors (WHO-TEFs). Fig. 3 shows WHO-TEQ concentrations for both types of compounds indicating that PBDD/Fs were detected in quantifiable levels in all emission samples within the range 0.03 - 0.39 ng WHO-TEQ/m^3. These concentrations were substantially lower than those of their chlorinated analogues (0.39 - 1.9 ng WHO-TEQ/m^3). This suggests that, although PBDD/Fs are emitted from the sintering process, the magnitude of these emissions was substantially lower than that of the PCDD/Fs (ie. less than 10%). It is believed that PBDD/F emissions are significantly lower than PCDD/F emissions because soluble bromide concentrations in the raw sinter mix are substantially lower (typically below 5 mg / kg) than soluble chloride concentrations (typically within the range 20 to 80 mg/kg).

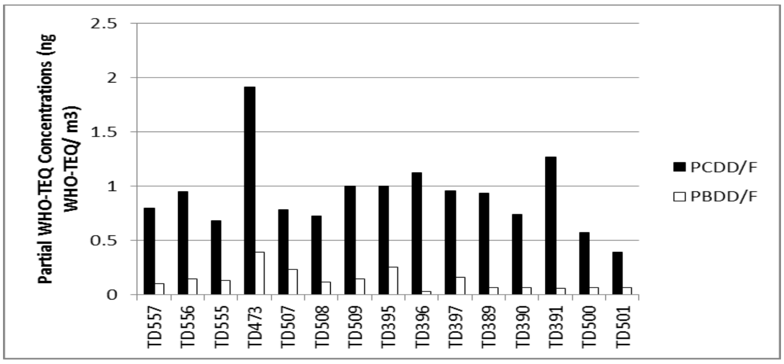


Fig. 3 - WHO-TEQ concentrations (ng WHO-TEQ/ m^3) of PCDD/Fs and PBDD/Fs in sinter plant stack emission samples.

Results of sinter pot tests experiments -

The results obtained with regard to PBDD/Fs in sinter pot experiments are shown in Fig. 4. The results are expressed in ng WHO-TEQ / kg raw sinter mix for each experiment. As may be seen from Fig. 4, very low PBDD/F emissions were observed in experiment 1 where no KBr was added to the raw sinter mix. However, a significant increase in PBDD/F emissions was observed in experiments 2, 3 and 5 when KBr was added to the raw sinter mix. These results showed that PBDD/Fs can be formed in the iron ore sintering process, provided that sufficient soluble bromide is available in the raw mix (ie. non–standard conditions), following a similar pathway to their chlorinated homologues (ie. *de novo* formation). Interestingly, no significant increase in PBDD/F emissions was observed in experiment 4 where large amounts of PBDE technical mixtures were added to the raw sinter mix. This result ruled out the possibility that PBDD/Fs could be formed via PBDEs as precursors in iron ore sintering, although the conversion of PBDEs into PBDFs has been demonstrated previously in laboratory experiments using pure chemical conmpounds[4].

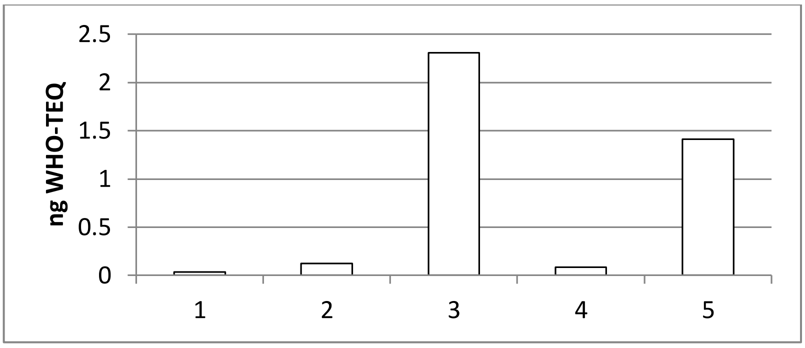


Fig. 4 – Mean tetra- through to hexa-PBDD/Fs amounts (expressed in WHO-TEQ / kg raw sinter mix) formed during the sinter pot experiments.

The results obtained with regard to PBDEs in sinter pot experiments are shown in Fig. 5. As shown in Fig. 5b, the addition in increasing amounts of KBr to the raw sinter mix did not result in a significant rise in PBDE emission concentrations in experiments 2 and 3, suggesting that there was no formation of PBDEs in the iron ore sintering following a pathway similar to the formation of PCDD/Fs and PBDD/Fs (ie. *de novo* formation). For the sinter pot experiments, PBDE mass balances were also carried out by comparing the total PBDE input (ie. raw sinter mix) to the total PBDE output (ie. Sinter product + emissions). As shown in Fig. 5a, the results indicated that the addition of KBr did not result in any increase in PBDE output with percentage decreases of 90%, 79% and 92%, respectively. Similarly, the addition of the penta- to the raw mix resulted in very high percentage reduction in PBDEs (94% and 92%). This result suggested strongly that PBDEs are actually destroyed rather than formed in the sintering process due to the consistent fall in PBDE output for all the experiments.

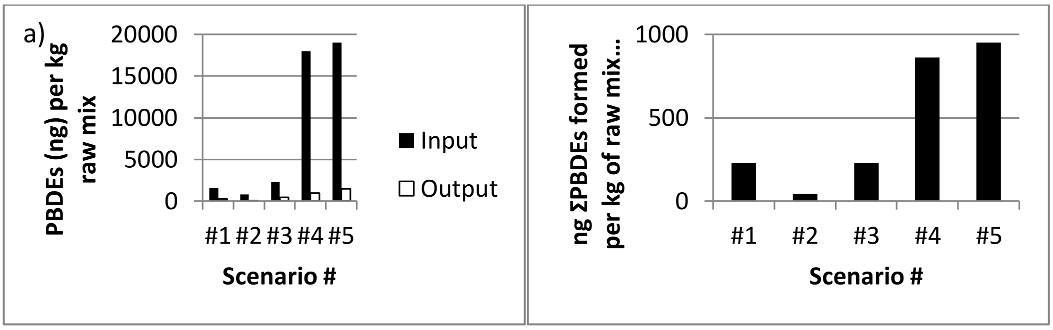


Fig. 5 – Total input and output of PBDEs (ng) per kg of raw mix used; and 5b total PBDE emissions (ng) per kg of raw mix used in sinter pot tests

Acknowledgements

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References

1. Cetin, B.; Odabasi, M., Particle-phase dry deposition and air-soil gas-exchange of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Environ. Sci. Technol.* **2007,** *41*, (14), 4986-4992.

2. Wang, L. C.; Wang, Y. F.; Hsi, H. C.; Chang-Chien, G. P., Characterizing the Emissions of Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Dibenzo-p-dioxins and Dibenzofurans (PBDD/Fs) from Metallurgical Processes. *Environ. Sci. Technol.* **2010,** *44*, (4), 1240-1246.

3. Odabasi, M.; Bayram, A.; Elbir, T.; Seyfioglu, R.; Dumanoglu, Y.; Bozlaker, A.; Demircioglu, H.; Altiok, H.; Yatkin, S.; Cetin, B., Electric Arc Furnaces for Steel-Making: Hot Spots for Persistent Organic Pollutants. *Environ. Sci. Technol.* **2009,** *43*, (14), 5205-5211.

4. Buser, H. R., Polybrominated dibenzofurans and dibenzo-para-dioxins - Thermal reaction products of polybrominated diphenyl ether flame retardants. *Environ. Sci. Technol.* **1986,** *20*, (4), 404-408.

5. Harrad, S.; Abdallah, M. A.-E., Brominated flame retardants in dust from UK cars - Within-vehicle spatial variability, evidence for degradation and exposure implications. *Chemosphere* **2011,** *82*, (9), 1240-1245

6. Harrad, S.; Hunter, S., Concentrations of polybrominated diphenyl ethers in air and soil on a rural-urban transect across a major UK conurbation. *Environ. Sci. Technol.* **2006,** *40*, (15), 4548-4553.

SUMMARY OF ANALYTICAL METHODS AND ASSOCIATED QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROCEDURES FOR SEMI-VOLATILE ORGANIC COMPOUNDS

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1. Overview

This document describes the generically applicable methods and procedures that all researchers within the group must follow to ensure the reliability of their analytical data. Methods that apply only to a specific group of pollutants are not covered here. If you have any questions about anything relating to analysis, please ask your supervisor or an experienced member of the Research Group for advice.

2. Instrument Calibration

A full 5-point calibration must be conducted at the beginning of any measurement campaign. The exact concentrations and content of the calibration standard mixes will vary according to the pollutant class being measured but as a guide, the table below gives a typical example.

Compound	*Standard A Concn (pg μl^{-1})*	*Standard B Concn (pg μl^{-1})*	*Standard C Concn (pg μl^{-1})*	*Standard D Concn (pg μl^{-1})*	*Standard E Concn (pg μl^{-1})*
All “native”[1] standards	20	50	200	500	1000
Internal standards, Sampling Evaluation standards, recovery determination standards	200	200	200	200	200

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[1] “native” refers to the ^{12}C or ^{1}H isotope of the target compound. The term is used to distinguish it from the ^{13}C or ^{2}D (deuterated) isotope used as the internal standard.

These standards are used to calculate relative response factors (RRFs) for each of the "target" compounds. The RRF is defined as the instrument response for a unit amount of target pollutant relative to the instrument response obtained for the same amount of the internal standard (IS). For example, if the response of a unit amount of the target compound is 1.5 times that for the same amount of the internal standard, the RRF =1.5. It is calculated as in equation 1.

$$RRF = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{IS}}{C_{NAT}} \quad \text{(equation 1)}$$

where A_{NAT} is the peak area for the "native" compound in the standard; A_{IS} is the peak area of the internal standard in the standard; C_{NAT} is the concentration of the "native" compound in the standard; and C_{IS} is the concentration of the internal standard in the standard.

Calculation of RRFs for each of the standards A-E, should reveal them to be essentially identical in each standard. Ideally, the relative standard deviation (*i.e.* (σ_{n-1}/average) x 100%) of RRFs for a given target compound should not exceed 10%. If they do, consult your supervisor before proceeding.

A full 5 point calibration typically only needs to be conducted infrequently, or when an on-going accuracy check proves unsatisfactory. The average RRF for any subsequent full calibration should be within ± 10% of the average RRF obtained for the 1st 5-point calibration. If they do not, then you must consult your supervisor immediately.

Before each batch of samples are analysed on the GC/MS, one of the calibration standards (usually Standard C, but others are fine) must be run. The RRFs obtained from this analysis must be within ± 25% of the RRFs obtained for that standard in the initial 5-point calibration. If they do not, please consult your supervisor before proceeding. At the end of each batch of samples, the same calibration standard must be run. The RRFs obtained from this analysis must be within ±25% of the RRFs obtained for that standard in the initial 5-point calibration. The RRFs that must be used for calculating concentrations in samples in that batch will be an average of those obtained for the 2 standards run for that batch.

3. GC/MS tuning tips

At the start of each session, an autotune should be run. The results should be printed out and a record kept. Following the autotune (which should detect any major problems with the GC/MS), a manual tune must be conducted. The purpose of the manual tune is to maximise sensitivity and instrument performance for the particular group of compounds you are targeting. As a general rule, while during tuning the detector voltage should be set at 200V, you should set the detector voltage to 450V (*i.e.* that necessary to detect compounds in the concentration range 10-1000 pg/component) in your acquisition file used when running standards and samples. You should also tune with the oven temperature at a temperature similar to that at which your target compounds will elute form the GC column. Typically for a DB-5 type column it will be 250^{o}C, but may be lower for other columns (DO NOT EXCEED THE MAXIMUM ALLOWABLE ISOTHERMAL OPERATING TEMPERATURE FOR THE COLUMN). You should choose the m/z values most appropriate to the mass range of the pollutants which you are targeting – your supervisor will be able to advise you on the best choice. The autotune uses m/z 69, 219, and 502 – this is not appropriate for PCBs for example, which lie in the mass range 256 to 394, and the manual tune should be based on tuning masses 219, 264, and 414.

4. Determination of Internal Standard Recoveries

It is important to note that use of the internal standard quantification method means that NO correction of concentrations for recovery is required. However, it is important that recoveries of internal standards are calculated for each sample as a QA/QC measure. Typically such recoveries should be around 70%, but they may routinely fall in the range 30%-150%. If values exceed 150%, the sample extract should be re-analysed and the recovery recalculated. If recoveries are below 30%, then the signal to noise (S:N) ratio of the internal standard must be calculated. The data are acceptable provided that the S:N ratio exceeds 20:1. If it is less than 20:1 the sample extract should be re-analysed and the recovery recalculated. If the recovery percentage and S:N ratio is still unacceptable then data for that sample must be considered invalid.

Internal standard (IS) recoveries are calculated thus:

$$\% \text{ IS Recovery} = \left[\left(\frac{A_{IS}}{A_{RDS}} \right)_S \times \left(\frac{A_{RDS}}{A_{IS}} \right)_{STD} \times \left(\frac{C_{IS}}{C_{RDS}} \right)_{STD} \times \left(\frac{C_{RDS}}{C_{IS}} \right)_S \right] \text{x } 100 \text{ (equation 2)}$$

where $(A_{IS}/A_{RDS})_S$ = ratio of internal standard peak area to recovery determination standard peak area in the sample; $(A_{RDS}/A_{IS})_{STD}$ = ratio of recovery determination standard peak area to internal standard peak area in the calibration standard (the average of values obtained for both calibration standards run for a batch of samples is used); $(C_{IS}/C_{RDS})_{STD}$ = ratio of concentration of internal standard to concentration of recovery determination standard in the calibration standard; and $(C_{RDS}/C_{IS})_S$ = ratio of concentration of recovery determination standard to concentration of internal standard in the sample (assuming 100% recovery). Note that this can be calculated as the amount of internal or recovery determination standard added to the sample divided by the volume of the sample extract used for GC/MS analysis (typically 25-50 µ1).

5. Determination of Sampling Evaluation Standard Recoveries

Recoveries of sampling evaluation standards (*i.e.* those added to the PUF plug in air or aqueous sample analysis) are calculated for each sample as QA/QC measure. Note that SESs are NOT added to solid samples like soil or grass. Typically such recoveries should be around 70%, but they may routinely fall in the range 30%-150%. Note that although SES recoveries should be recorded for every sample, they are a QA/QC check only, and are NOT used to correct concentrations for sampling losses. If values exceed 150%, the sample extract should be re-analysed and the recovery recalculated. If it still exceeds 150%, then data for that sample must be considered invalid. If recoveries are below 30%, then the signal to noise (S:N) ratio of the sampling evaluation standard must be calculated. The data are acceptable provided that the S:N ratio exceeds 20:1. If it is less than 20:1 the sample extract should be re-analysed and the recovery recalculated. If the recovery percentage and S:N ratio is still unacceptable then data for that sample must be considered invalid.

Sampling evaluation standard (SES) recoveries are calculated thus:

$$\%\ \text{SES Recovery} = \left[\left(\frac{A_{SES}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{SES}}\right)_{STD} \times \left(\frac{C_{SES}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{SES}}\right)_S\right] \text{x 100 (equation 3)}$$

where $(A_{SES}/A_{RDS})_S$ = ratio of sampling evaluation standard peak area to recovery determination standard peak area in the sample; $(A_{RDS}/A_{SES})_{STD}$ = ratio of recovery determination standard peak area to sampling evaluation standard peak area in the calibration standard (the average of values obtained for both calibration standards run for a batch of samples is used); $(C_{SES}/C_{RDS})_{STD}$ = ratio of concentration of sampling evaluation standard to concentration of recovery determination standard in the calibration standard and $(C_{RDS}/C_{SES})_S$ = ratio of concentration of recovery determination standard to concentration of sampling evaluation standard in the sample (assuming 100% recovery). Note that this can be calculated as the amount of sampling evaluation or recovery determination standard added to the sample divided by the volume of the sample extract used for GC/MS analysis (typically 25-50 µ1).

6. Determination and On-Going Monitoring of Accuracy

The principal means of determining method accuracy is *via* analysis of one or more certified or standard reference materials (CRMs or SRMs). Your supervisor will recommend a suitable CRM/SRM. Before you commence analysis of any samples as part of your research, you must conduct 5 replicate analyses of a suitable CRM or SRM, and obtain satisfactory data for these analyses. Essentially a CRM or SRM is a sample that has been analysed a large number of expert laboratories worldwide and that has had agreed concentrations of target pollutants assigned to it. These values are usually cited as an average ± a standard deviation. The values you obtain will be compared with these. You must discuss your data with your supervisor and will only be allowed to proceed with analysis of your samples once acceptable accuracy of data are obtained.

As an ongoing measure of accuracy, you must analyse 1 aliquot of the same CRM/SRM for every 20 samples – *i.e.* every 21st sample you analyse must be a CRM/SRM. If satisfactory data are not obtained, then you must consult your supervisor immediately.

Additional means of evaluating accuracy include participation in interlaboratory comparisons. Your supervisor will advise you as and when such comparisons are to take place.

7. Determination of Precision

This is defined as the relative standard deviation (*i.e.* 100 x σ_{n-1}/average) of concentrations obtained from 5 replicate analyses of the same sample. Usually, this is a CRM/SRM. Typically, precision should be no more than 30%, but you must discuss your data with your supervisor.

8. Determination of Blank Concentrations

This is defined as the concentration of a target pollutant present in an analysis where the sample is omitted, but internal standards etc. are added. Note that for air analyses, a blank should consist of analysis of a clean PUF plug and filter paper. For calculation of blank sample concentrations, you should assume the sample mass or volume to be that typically used – *e.g.* 1,000 m^3 for air samples, 50g for soil or grass samples. One blank analysis must be conducted for every 5 samples – *i.e.* every 6th analysis you perform must be a blank. Where the concentration of a target pollutant in a blank for a given batch of samples is 5-20% of the concentration in a sample from that batch, the blank concentration must be subtracted from that in the sample. Where the concentration in the blank exceeds 20% of that in a sample from that batch, data for that target pollutant in that sample must not be reported.

9. Determination of Detection limits

Two categories of detection limits exist.

1. instrument detection limit (IDL)
2. sample detection limit (SDL)

The IDL is defined as that amount of pollutant that gives a signal to noise ratio of 3:1. It is best determined by calculating the signal to noise ratio for the pollutant in your calibration standard A. To illustrate, if the concentration of a target pollutant in that standard = 20 pg/µ1 and 1 µ1 is injected, then if a signal to noise ratio of 50:1 is obtained, then the IDL = 20 x (3/50)= 1.2 pg/injection.

The SDL can then be calculated as in equation 4:

$$\text{SDL} = \frac{IDL \times FEV}{VFEI \times SS} \times \frac{100}{\%IS\ \mathrm{Re}\cos very} \quad \text{(equation 4)}$$

Where FEV = final extract volume (µ1), VFEI = volume of final extract injected (µ1); SS = sample size (m^3 or g); and %IS recovery = percentage recovery of internal standard used to quantify the target pollutant in a particular sample.

To illustrate, if the IDL = 1.2 pg/injection, the final extract volume for a sample is 50µl, 1 µ1 is injected; the sample size is 1,000 m^3, and the percentage internal standard recovery in that sample = 70%, then the SDL = ((1.2 x 50)/ (1 x 1000)) x 100/70 = 0.086 pg m^{-3}.

Where the concentration in the sample blank exceeds the SDL calculated as above, the effective SDL is the blank concentration. This is not an unusual occurrence.

10. Calculation of concentrations in samples

Concentrations in samples may be calculated *via* the equation below:

$$\textit{Concn.} = \frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS} \quad \text{(equation 5)}$$

Where A_{IS} = peak area of internal standard in sample; A_{NAT} = peak area of target pollutant in sample; RRF = relative response factor for the target pollutant (see equation 1); M_{IS} = mass of internal standard added to sample (pg) and SS = sample size (m^3 or g).

To illustrate, where A_{NAT} = 10,000 units; A_{IS} = 20,000 units; RRF = 1.5; M_{IS} = 20,000 pg; and SS = 50 g, the concentration of the target pollutant will be (10,000/20,000) x (1/1.5) x (20,000/50) = 133.33 pg g^{-1}.

11. Correct Storage of Calibration and internal standards

Once prepared in CERTAN vials, all standards should be stored in a freezer unless required for analysis. You should record the weight of the CERTAN vial and contents before and after each use. Before weighing, allow the vial and contents to reach room temperature, and wipe off any condensation before weighing. If at any time, the weight before use is less than 5% of the weight after recorded after the previous use, you must consult your supervisor immediately.

12. Criteria for Quantification of a Peak as a Target pollutant

For a given peak to be identified as a target pollutant in a sample, various criteria must be met. These are:

1. the signal to noise ratio of the peak must exceed 3:1
2. the relative retention time (RRT) of the peak in the sample must be within 0.2% of the average value determined for the 2 calibration standards run for the sample batch. Note RRT = retention time of target pollutant/retention time of internal standard used to quantify target pollutant.

The above criteria apply to all target pollutants. For organochlorine and organobromine pollutants, the following criterion also applies.

- the isotope ratio of the peak in the sample must be within 20% of the average value determined for the 2 calibration standards run for that sample batch. If it falls outside this range, then you must consult your supervisor, but it is likely that the peak cannot be quantified due to a co-eluting interference. For example, for trichlorinated PCBs, where 2 m/z values are monitored (*i.e.* 255.95 and 257.95) the isotope ratio = area of peak for 255.95 trace/area of peak for 257.95 trace. Note that for calculating RRFs and concentrations, the m/z value providing the largest peak must be used.

Congener Group (no. of Br)	Bromine Sites	Common Name	Congener Group (no. of Br)	Bromine Sites	Common Name	Congener Group (no. of Br)	Bromine Sites	Common Name
Mono-BDE	2	BDE-1	Tri-BDE	2, 2', 3	BDE-16	Tetra-BDE	2, 2', 3, 3'	BDE-40
	3	BDE-2		2, 2', 4	BDE-17		2, 2', 3, 4	BDE-41
	4	BDE-3		2, 2', 5	BDE-18		2, 2', 3, 4'	BDE-42
Di-BDE	2, 2'	BDE-4		2, 2', 6	BDE-19		2, 2', 3, 5	BDE-43
	2, 3	BDE-5		2, 3, 3'	BDE-20		2, 2',3, 5	BDE-44
	2, 3'	BDE-6		2, 3, 4	BDE-21		2, 2',3, 6	BDE-45
	2, 4	BDE-7		2, 3, 4'	BDE-22		2, 2', 3, 6'	BDE-46
	2, 4'	BDE-8		2, 3, 5	BDE-23		2. 2',4 ,4'	BDE-47
	2, 5	BDE-9		2, 3, 6	BDE-24		2, 2', 4, 5	BDE-48
	2, 6	BDE-10		2, 3', 4	BDE-25		2, 2', 4, 5'	BDE-49
	3, 3'	BDE-11		2, 3', 5	BDE-26		2, 2', 4, 6	BDE-50
	3, 4	BDE-12		2, 3', 6	BDE-27		2, 2', 4, 6'	BDE-51
	3, 4'	BDE-13		2, 4, 4'	BDE-28		2, 2', 5, 5'	BDE-52
	3, 5	BDE-14		2, 4, 5	BDE-29		2, 2', 5, 6'	BDE-53
	4, 4'	BDE-15		2, 4, 6	BDE-30		2, 2', 6, 6'	BDE-54
				2, 4', 5	BDE-31		2, 3, 3', 4	BDE-55
				2, 4', 6	BDE-32		2, 3, 3', 4'	BDE-56
				2, 3', 4'	BDE-33		2, 3, 3', 5	BDE-57
				2, 3', 5'	BDE-34		2, 3, 3', 5'	BDE-58
				3, 3', 4	BDE-35		2. 3. 3' 6	BDE-59
				3, 3', 5	BDE-36		2, 3, 4, 4 '	BDE-60
				3, 4, 4'	BDE-37		2, 3, 4, 5	BDE-61
				3, 4, 5	BDE-38		2, 3, 4, 6	BDE-62
				3, 4', 5	BDE-39		2, 3, 4', 5	BDE-63
							2, 3, 4', 6	BDE-64

Congener Group (no. of Br)	Bromine Sites	Common Name
Tetra-BDE	2, 3, 5, 6	BDE-65
	2, 3', 4, 4'	BDE-66
	2, 3', 4, 5	BDE-67
	2, 3', 4', 5	BDE-68
	2, 3', 4, 6	BDE-69
	2, 3', 4', 5	BDE-70
	2, 3', 4', 6	BDE-71
	2, 3', 5, 5'	BDE-72
	2, 3', 5', 6	BDE-73
	2, 4, 4', 5	BDE-74
	2, 4, 4', 6	BDE-75
	2, 3', 4', 5'	BDE-76
	3, 3', 4, 4'	BDE-77
	3, 3', 4, 4'	BDE-78
	3, 3', 4, 5'	BDE-79
	3, 3', 5, 5'	BDE-80
	3, 4, 4', 5	BDE-81
Penta-BDE	2, 2', 3, 3', 4	BDE-82
	2, 2', 3, 3', 5	BDE-83
	2, 2', 3, 3', 6	BDE-84
	2 ,2', 3, 4, 4'	BDE-85
	2, 2', 3, 4, 5	BDE-86
	2, 2', 3, 4, 5'	BDE-87
	2, 2', 3, 4, 6	BDE-88
	2, 2', 3, 4, 6'	BDE-89
	2, 2', 3, 4', 5	BDE-90
	2, 2', 3, 4', 6	BDE-91
	2, 2', 3, 5, 5'	BDE-92
	2, 2', 3, 5, 6	BDE-93
	2, 2', 3, 5, 6'	BDE-94
	2, 2', 3, 5', 6	BDE-95
	2, 2', 3, 6, 6'	BDE-96
	2, 2', 3, 4', 5'	BDE-97
	2, 2', 3, 4', 5	BDE-98
	2, 2', 4, 4', 5	BDE-99
	2, 2', 4, 4', 6	BDE-100
	2, 2', 4, 5, 5'	BDE-101
	2, 2', 4, 5, 6'	BDE-102
	2, 2’, 4, 5’, 6	BDE-103
	2,2’,4,6, 6	BDE-104
	2,3,3’,4, 4’	BDE-105
	2,3,3’,4, 5	BDE-106
	2,3,3’,4’,5	BDE-107
	2,3,3’,4 ,5’	BDE-108
	2,3,3’,4,6	BDE-109
	2,3,3’,4’, 6	BDE-110
Penta-BDE	2,3,3’,5,5’	BDE-111
	2,3,3’,5,6	BDE-112
	2,3,3’,5', 6	BDE-113
	2,3,4,4’,5	BDE-114
	2,3,4,4’,6	BDE-115
	2,3,4,5,6	BDE-116
	2,3,4’,5,6	BDE-117
	2,3’,4,4’,5	BDE-118
	2,3’,4,4’,6	BDE-119
	2,3’,4,4’,5	BDE-120
	2,3’,4,5’,6	BDE-121
	2,3,3’,4’,5’	BDE-122
	2,3’,4,4’,5’	BDE-123
	2,3’,4’,5,5’	BDE-124
	2,3’,4’,5',6	BDE-125
	3,3’,4,4’,5	BDE-126
	3,3’,4,5,5’	BDE-127

Congener Group (no. of Br)	Bromine Sites	Common Name
Hexa-BDE	2,2’,3,3’,4,4’	BDE-128
	2,2’,3,3’,4,5	BDE-129
	2, 2’, 3, 3’, 4, 5’	BDE-130
	2, 2’, 3, 3’, 4, 6	BDE-131
	2, 2’, 3, 3’, 4, 6’	BDE-132
	2, 2’, 3, 3’, 5, 5’	BDE-133
	2, 2’, 3, 3’, 5, 6	BDE-134
	2, 2’, 3, 3’, 5, 6’	BDE-135
	2, 2’, 3, 3’, 6, 6’	BDE-136
	2, 2’, 3, 4, 4’, 5	BDE-137
	2, 2’, 3, 4, 4’, 5’	BDE-138
	2, 2’, 3, 4, 4’, 6	BDE-139
	2, 2’, 3, 4, 4’, 6’	BDE-140
	2, 2’, 3, 4, 5, 5’	BDE-141
	2, 2’, 3, 4, 5, 6	BDE-142
	2, 2’, 3, 4, 5, 6’	BDE-143
	2, 2’, 3, 4, 5’, 6	BDE-144
	2, 2’, 3, 4, 6, 6’	BDE-145
	2, 2’, 3, 4’, 5, 5’	BDE-146
	2, 2’, 3, 4’, 5, 6	BDE-147
	2, 2’, 3, 4’, 5, 6’	BDE-148
	2, 2’, 3, 4’, 5’, 6’	BDE-149
	2, 2’, 3, 4’, 6, 6’	BDE-150
	2, 2’, 3, 5, 5’, 6	BDE-151
	2, 2’, 3, 5, 6, 6’	BDE-152
	2, 2’, 4, 4’, 5, 5’	BDE-153
	2, 2’, 4, 4’, 5, 6’	BDE-154
Hexa-BDE	2, 2’, 4, 4’, 6, 6’	BDE-155
	2, 3, 3', 4, 4' 5	BDE-156
	2, 3, 3’, 4, 4’, 5’	BDE-157
	2, 3, 3’, 4, 4’, 6	BDE-158
	2, 3, 3’, 4, 5, 5’	BDE-159
	2, 3, 3’, 4, 5, 6	BDE-160
	2, 3, 3’, 4, 5’, 6	BDE-161
	2, 3, 3’, 4’, 5, 5’	BDE-162
	2, 3, 3’, 4’, 5, 6	BDE-163
	2, 3, 3’, 4, 5’, 6	BDE-164
	2, 3, 3’, 5, 5’, 6	BDE-165
	2, 3, 4, 4’, 5, 6	BDE-166
	2, 3', 4, 4’, 5, 5’	BDE-167
	2, 3’, 4, 4’, 5’, 6	BDE-168
	3, 3’, 4, 4’, 5, 5’	BDE-169
Hepta-BDE	2, 2’, 3, 3’, 4, 4’, 5	BDE-170
	2, 2’, 3, 3’, 4, 4’, 6	BDE-171
	2, 2’, 3, 3’, 4, 5, 5’	BDE-172
	2, 2’, 3, 3’, 4, 5, 6	BDE-173
	2, 2’, 3, 3’, 4, 5, 6’	BDE-174
	2, 2’, 3, 3’, 4, 5’, 6	BDE-175
	2, 2’, 3, 3’, 4, 6, 6’	BDE-176
	2, 2’, 3, 3’, 4, 5’, 6’	BDE-177
	2, 2’, 3, 3’, 5, 5’, 6	BDE-178
	2, 2’, 3, 3’, 5, 6, 6’	BDE-179
	2, 2’, 3, 4, 4’, 5, 5’	BDE-180
	2, 2’, 3, 4, 4’, 5, 6	BDE-181
	2, 2’, 3, 4, 4’, 5, 6’	BDE-182
	2, 2’, 3, 4, 4’, 5’, 46	BDE-183
	2, 2’, 3, 4, 4’, 6, 6’	BDE-184
	2, 2’, 3, 3’, 5, 5’ 6	BDE-185
	2, 2’, 3, 4, 5, 6, 6’	BDE-186
	2, 2’, 3, 4’, 5, 5’, 6	BDE-187
	2, 2’, 3, 4’, 5, 6, 6’	BDE-188
	2, 3, 3’, 4, 4’, 5, 5’	BDE-189
	2, 3, 3’, 4, 4’, 5, 6	BDE-190
	2, 3, 3’, 4, 4’, 5’, 6	BDE-191
	2, 3, 3’, 4, 5, 5’, 6	BDE-192
	2, 3, 3’, 4’, 5, 5’, 6	BDE-193

Congener Group (no. of Br)	Bromine Sites	Common Name
Octa-BDE	2, 2’, 3, 3’, 4, 4’, 5, 5’	BDE-194
	2, 2', 3, 3', 4, 4', 5, 6	BDE-195
	2, 2’, 3, 3’, 4, 4’, 5, 6’	BDE-196
	2, 2’, 3, 3’, 4, 4’, 6, 6’	BDE-197
	2, 2’, 3, 3’, 4, 5, 5’, 6	BDE-198
	2, 2’, 3, 3’, 4, 5, 5’, 6’	BDE-199
	2, 2’, 3, 3’, 4, 5, 6, 6’	BDE-200
	2, 2’, 3, 3’, 4, 5’, 6, 6’	BDE-201
	2, 2’, 3, 3’, 5, 5’, 6, 6’	BDE-202
	2, 2’, 3, 4, 4’, 5, 5’, 6	BDE-203
	2,2’,3,4,4’,5,6,6’	BDE-204
	2,3,3’,4,4’,5,5’,6	BDE-205
Nona-BDE	2, 2’, 3, 3’, 4, 4’, 5, 5’, 6	BDE-206
	2, 2’, 3, 3’, 4, 4’, 5, 6, 6’	BDE-207
	2, 2’, 3, 3’, 4, 5, 5’, 6, 6’	BDE-208
Deca-BDE	2, 2’, 3, 3', 4, 4', 5 , 5', 6, 6'	BDE-209