UNIVERSITY OF BIRMINGHAM

EXTENT AND MECHANISMS OF BROMINATED AND CHLORINATED FLAME RETARDANT EMISSIONS ASSOCIATED WITH THE TREATMENT OF WASTE ELECTRONICS, FURNISHINGS AND BUILDING MATERIALS

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Abstract.

The work conducted in this thesis examines the potential for emissions of flame retardants (FRs) from a range of treated end-of-life materials during and following disposal. A series of standardised leaching experiments were developed and conducted to study FR leaching from a range of waste flame retarded products, including: textiles, EPS and XPS building insulation foams, cathode-ray tube plastics and polyurethane furniture foams (PUF). The leaching tests were conducted using a range of leaching fluids, with the view of simulating the characteristics of real landfill leachates. A number of different test parameters were examined, such as a variety of dissolved humic matter concentrations, landfill relevant pHs between 5.8 and 8.5, landfill relevant temperatures, the effect of agitation, contact durations and longer term cycles of periodic wetting and draining of waste. It is apparent from these experiments that despite the relatively hydrophobic physicochemical properties of brominated FRs (BFRs), they are able to leach from waste materials at substantial concentrations. Concentrations of ΣPBDEs (polybrominated diphenyl ethers) in the leachate from the leaching experiments in this study ranged from 14,000 – 200,000 ng L^{-1}, while concentrations of ΣHBCDD (hexabromocyclododecane) ranged from 170 ng L^{-1} – 13,000 ng L^{-1} in textile leaching experiments and from 13,000 ng L^{-1} – 4,200,000 ng L^{-1} in building insulation foam experiments. BFR leaching appears to be a second order process, whereby a period of initially intense dissolution of more labile BFR is followed by a slower stage corresponding to external diffusion of the soluble residue in the material. Tris (chloro*iso*propyl) phosphate (TCIPP) is more readily soluble in water than the BFRs studied, and leaching of TCIPP from PUF appears to be a first order process. Concentrations of TCIPP in the leachate from the leaching experiments in this study ranged from 13 mg L^{-1} – 130 mg L^{-1}. In serial batch leaching experiments, >95 % of TCIPP was depleted from the flexible PUF after the sixth batch (168 h total contact). Hence, leaching is potentially a very significant pathway for TCIPP emissions to the environment. A small survey of waste soft furnishings from a variety of UK domestic and office locations was also conducted, to help determine the total FR content entering the UK waste stream as a result of the disposal of soft furnishings. The predominant FR detected was TCIPP. Closed test chamber experiments investigating the effect of temperature on volatilisation of TCIPP from polyurethane foam were conducted. These experiments show volatilisation of TCIPP from PUF to increase exponentially with temperature and to constitute an additional potentially significant pathway for emissions from UK MSW landfills, with TCIPP emissions via volatilisation from landfilled PUF estimated to range between ~200 and ~3,800 tonnes yr^{-1}.

Table of contents.

Chapter I: Introduction.

Chapter II: Sampling and Analytical Methodology.

Chapter III: Leaching behaviour of HBCDD from treated textile curtains.

Chapter IV: Leaching behaviour of HBCDD from EPS and XPS building insulation foams.

Chapter V: Leaching behaviour of PBDEs from cathode ray tube (CRT) plastics.

Chapter VI: Leaching behaviour of TCIPP from furniture PUF.

Chapter VII: Survey of flame retardants in the UK soft furnishings waste stream, 2011-12.

Chapter VIII: Closed chamber volatilisation experiments for TCIPP from furniture PUF.

List of tables.

Chapter I: Introduction.

Chapter II: Sampling and Analytical Methodology.

Chapter III: Leaching behaviour of HBCDD from treated textile curtains.

Chapter IV: Leaching behaviour of HBCDD from EPS and XPS building insulation foams.

Chapter V: Leaching behaviour of PBDEs from cathode ray tube plastics.

Chapter VI: Leaching behaviour of TCIPP from furniture PUF.

Chapter VII: Survey of flame retardants in the UK soft furnishings and furniture waste stream, 2011-12.

Chapter VIII: Closed chamber volatilisation experiments for TCIPP from furniture PUF.

List of figures.

Chapter I: Introduction.

Chapter II: Sampling and Analytical Methodology.

Chapter III: Leaching behaviour of HBCDD from treated textile curtains.

Chapter IV: Leaching behaviour of HBCDD from EPS and XPS building insulation foams.

Chapter V: Leaching behaviour of PBDEs from cathode ray tube plastics.

Chapter VI: Leaching behaviour of TCIPP from furniture PUF.

Chapter VIII: Closed chamber volatilisation experiments for TCIPP from furniture PUF.

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Abbreviations.

ABS	Acrylonitrile-butadiene-styrene.
APPI	Atmospheric pressure photoionisation.
BFR	Brominated flame retardant.
BSEF	Bromine science and environmental forum.
CRM	Certified reference material.
CRT	Cathode ray tube.
ECNI	Electron capture negative ionisation.
EDC	Endocrine disrupting chemical.
EI	Electron impact.
EPA	Environment protection agency.
EPS	Expanded polystyrene.
ESI	Electrospray ionisation.
GC	Gas chromatography.
HBCDD	Hexabromocyclododecane.
HIPS	High impact polystyrenes.
HPLC	High pressure liquid chromatography.
IS	Internal standard.
$\mathbf{K_{ow}}$	n-octanol/water partition coefficient.
LC	Liquid chromatography.
LDPE	Low density polyethylene.
LOD	Limit of detection.
LOQ	Limit of quantification.
m/z	Mass to charge ratio.
MLRA	Multiple linear regression analysis.
MRM	Multiple reaction monitoring.
MS	Mass spectrometry.
MSW	Municipal solid waste.
PBDE	Polybrominated diphenyl ether.
PP	Polypropylene.
PFR	Phosphorus flame retardants.
PL	Percentage leached.
PLT	Percentage leached relative to time.
POP	Persistent organic pollutant.
PUF	Polyurethane foam.
QA/QC	Quality assurance/quality control.
RDS	Recovery determination (syringe) standard.
RPM	Revolutions per minute.
RRT	Relative retention time.
RSD	Relative standard deviation.
SD	Standard deviation.
SRM	Standard reference material.

TBBP-A	Tetrabromobisphenol A.
TCEP	Tris(2-chloro*ethyl*)phosphate.
TCIPP	Tris(chloro*iso*propyl)phosphate.
TDCIPP	Tris(1,3-dichloro-2-propyl)phosphate.
TnBP	Tri (*n*-butyl) phosphate**.**
TPhP	Tri-phenyl-phosphate.
WWTP	Waste water treatment plant.
XPS	Extruded polystyrene.

Chapter I: Introduction.

1.1.1. Halogenated flame retardants.

Flame retardants (FRs) include many different groups of chemicals used to slow the ignition and spread of fires and have been used in polymers since the 1960s (Kemmlein et al., 2003). One category of FRs are organohalogen compounds that incorporate bromine or chlorine into organic molecules that do not naturally exist. Brominated flame retardants (BFRs) are a group of synthetic chemical additives that have been applied to a wide range of consumer products such as: building materials, electronics and electrical goods, textiles and furnishings, to meet and comply with fire safety codes, standards and regulations. Currently there are more than 75 different commercially-recognised BFRs (WHO, 1997). Moreover, BFRs have historically been the most widely used organic flame retardants due to their low cost and high efficacy (Covaci et al., 2008b). The five classes of BFR that have found most widespread use are tetrabromobisphenol-A (TBBP-A), hexabromocyclododecane (HBCDD), and three technical mixtures of polybrominated diphenyl ethers (PBDEs): Penta-BDE, Octa-BDE, and Deca-BDE (Leonards et al., 2008). In an environmental context, BFRs are highly resistant to degradation whether through chemical, biological, or photolytic processes and are therefore capable of long range transport, bioaccumulation in human and animal tissues and potential trophic magnification. As a result, widespread contamination of air, water, soil, sediment, and terrestrial and marine biota by BFRs has been widely documented (Law et al., 2006; Law, 2010; Harrad et al., 2009b; Harrad et al., 2010a; Muir and de Wit, 2010). Another widely used group of FRs are the chlorinated phosphorous flame retardants (PFRs) also known as phosphinates, such as Tris(2-chloroisopropyl)phosphate (TCIPP), Tris(2-chloroethyl)phosphate (TCEP) and Tris(1,3-dichloroisopropyl)phosphate (TDCIPP). PFRs have also been applied to a wide range of commercial products such as: textiles, rubber, polyurethane foam (PUF), cellulose, cotton, electronic equipment cables, casting resins, glues, engineering thermoplastics, epoxy resins, and phenolic resins, to meet and comply with fire safety codes, standards and regulations (van der Veen and de Boer, 2012). TCEP is also reported to be used as a plasticiser in the production of polyvinyl chloride (Björklund et al., 2004). TCIPP has been found to be resistant to degradation (Leisewitz et al., 2000; Kawagoshi et al., 2002). Contamination of indoor air and dust, lakes, river sediment and marine biota across Europe, USA and Japan is well documented (Carlsson et al., 1997;

Marklund et al., 2003; Andresen et al., 2004; Björklund et al., 2004; Stapleton et al., 2009; Leonards et al., 2011). Detection of TCIPP and TCEP in groundwater older than 20 years indicates considerable persistence in aquifers (Regnery et al., 2011). In laboratory experiments, Regnery and Püttmann (2010) demonstrated that TCEP and TCIPP appeared resistant to photodegradation by sunlight. Furthermore, it has been demonstrated that particulate-bound TDCIPP is capable of mid to long-range transport due to its highly persistent nature in the atmosphere with regard to OH radical oxidation (Liu et al., 2014).

These considerations are exacerbated by evidence of the toxicity of some BFRs and PFRs. HBCDD has been identified as an endocrine disrupting chemical (EDC) that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects in humans at relatively low exposure levels (Darnerud, 2003, 2008; Yamada-Okabe et al., 2005; van der Ven et al., 2006, 2009). With respect to PBDEs, acute toxicity studies have suggested that they can be hepatotoxic at relatively high doses (Zhou et al., 2002; Bruchajzer et al., 2011). Moreover, several studies have indicated that Penta- and Octa-BDE mixtures, as well as several of the major individual congeners present in wildlife and people, can alter liver enzymes, disrupt thyroid homeostasis, and are associated with early onset of puberty, reduced fertility, and impaired neurological development (Viberg et al., 2007). This latter effect is illustrated by two cohort studies of *in utero* and early life PBDE exposure in New York City and California, in which prenatal PBDE exposure (as indicated by cord blood PBDE levels) was associated with lower mental and physical development test scores for children aged 1, 4, and 6 years (New York City) and poorer attention, fine motor coordination, and cognition for children aged 5 and 7 years (California) (Herbstman et al., 2010; Eskenazi et al., 2013). In general, the lower brominated congeners are more acutely toxic than the higher ones (Darnerud, 2003). Decabromodiphenyl ether (BDE-209) is relatively less persistent and bioaccumulative than the lower brominated congeners and has been shown to have very low acute toxicity when given by the oral, inhalation and dermal route (Kelly et al., 2008; Tomy et al., 2008; Wu et al., 2009). Moreover, BDE-209 does not appear to be genotoxic, is not teratogenic, and does not seem to cause developmental toxicity (Hardy et al., 2009; Wang et al., 2010). Nonetheless, work by Johansson et al., (2008) suggests that BDE-209 can be as potent as the lower brominated PBDEs in causing developmental neurotoxic defects. Results of a study by Fitzgerald et al. (2012) suggest that PBDEs and polychlorinated biphenyls (PCBs) may interact to affect verbal memory and learning among persons 55-74 years old. In contrast, TBBP-A is relatively less persistent and bioaccumulative than most other BFRs (Domínguez et al., 2011). Furthermore, it is not acutely toxic (WHO, 1995) and the toxicity and teratogenicity of TBBP-A appeared low in experimental *in vivo* studies (Darnerud, 2003). However, TBBP-A is a potential EDC, acting as a thyroid hormone and oestrogen agonist (Meerts et al., 2000; Kitamura et al., 2002, 2005), and additionally has been reported to be immunotoxic as a result of its *in vitro* inhibition of a key T-cell receptor (Mariussen and Fonnum, 2003).

Of the halogenated PFRs, TCIPP accumulates in the liver and kidneys (Leisewitz et al., 2000). Work by Dishaw et al., (2011) shows that TCIPP decreases cell number and alters neurodifferentiation. TCIPP is irritating to the skin and eyes of rats (Leisewitz et al., 2000) and it is considered potentially carcinogenic (Ni et al., 2007); TCEP is toxic to aquatic organisms, causes reduced fertility and neurotoxic effects in rats and mice and is carcinogenic to animals (Sigma-Aldrich, 2011; WHO, 1998; Chapin et al., 1997). Within the EU it is classified as a “potential human carcinogen” and has been listed as a “known carcinogen” by the Californian EPA since 1992 (Regnery and Püttmann, 2010; Cal/EPA, 2011); TDCIPP is also thought to be carcinogenic and tumours were observed in the liver, kidneys and testes of rats which were fed with TDCIPP for 2 years (ATSDR, 2009; Andresen et al., 2004; WHO, 1998). TDCIPP has been classified in the EU as a level 2 carcinogen (EU RAR, 2008c). A study on the neurotoxicity of TDCIPP showed concentration-dependent neurotoxicity, inhibited DNA synthesis, and decreased cell number and altered neurodifferentiation (Dishaw et al., 2011).

Concerns over the toxicology and persistence of these chemicals are further compounded by evidence of FRs inside the human body. Numerous studies have reported the presence of BFRs in human adipose tissue, blood serum, liver, placenta, cord blood and breast milk worldwide (Noren and Meironyte, 2000; Choi et al., 2003; Petreas et al., 2003; Covaci et al., 2008a; Toms et al. 2009; Harrad and Abdallah, 2010).

PBDEs are known to accumulate in fatty tissues due to their hydrophobicity. In contrast, very few studies exist measuring levels of halogenated PFRs within the human body. In Eastern Canada, 115 human adipose tissue samples were taken from 9 cadavers during autopsy, TDCIPP was detected in 31 samples and concentrations ranged from <1 to 251 ng g^{-1} (LeBel and Williams, 1986; LeBel et al., 1989).

Human exposure to BFRs occurs predominantly via indoor dust and food ingestion (mainly oily fish, meat, dairy products, and the neonatal sources of human milk and placental transfer), with a minor contribution from inhalation and dermal absorption (Abdallah and Harrad, 2009; Covaci et al., 2009; Frederiksen et al., 2009; Abdallah et al., 2015). Concentrations of BFRs are higher in indoor air than outdoor air; this is likely due to the usage and slow release of BFRs from consumer products and building materials (Sjödin et al., 2001; Takigami et al., 2007; Abdallah et al., 2008; Toms et al., 2011).

There has been very little research addressing the potential human exposure pathways for halogenated PFRs, although it has been assumed that they will be very similar to those outlined for BFRs due to their equivalent use in consumer products. However, this assumption should be questioned due to differences in the physicochemical properties of chlorinated PFRs. Halogenated PFRs are more volatile and hydrophilic when compared to BFRs, therefore dermal absorption and inhalation are likely to have more significance. Ali et al., (2014) compared a range of organic pollutants from indoor dust and blood serum samples and demonstrated that while elevated concentrations of TCIPP, TCEP and TDCIPP concentrations were detected in dust samples they were not detected in blood serum. This does not necessarily rule out indoor dust as an exposure pathway but does question if serum samples are an adequate biomarker of PFR body burdens in humans. Predicted metabolites of chlorinated PFRs have been measured in urine samples and provide important biomarkers for their presence in humans (Dodson et al. 2014; Hoffman et al., 2015).

These concerns about their adverse environmental impacts have meant that production of the Penta- and Octa-BDE commercial mixtures ceased in the EU and North America in 2004, and their use in all applications in 2006. Likewise, Deca-BDE was restricted severely in the EU in 2008, with US manufacturers voluntarily committing to phase it out from most uses in the USA by the end of 2012, and to end all uses by 31 December 2013 (BSEF, 2014). As a further reflection of concern about their use, the Penta- and Octa-BDE commercial mixtures (Tetra-, Penta-, Hexa- and Hepta-BDEs) and HBCDD are listed as persistent organic pollutants (POPs) by the United Nations Environment Programme (UNEP) under the Stockholm Convention on Persistent Organic Pollutants, while Deca-BDE is under active consideration for listing (UNEP, 2014). Meanwhile, other groups of flame retardants such as the chlorinated PFRs continue to be used in a variety of applications.

1.1.2. FR production and applications.

In 2005, the total annual usage of BFRs was estimated to be about 311,000 tonnes (metric ton, i.e. 1000 kg), 130,000 tonnes of which was TBBP-A (Harju et al., 2008). HBCDD annual production was estimated at up to 28,000 tonnes (9,000 to 15,000 tonnes in China, 13,426 tonnes in Europe and the US) (UNEP, 2011). Total historic production of PBDEs (including Deca-BDE) has been estimated to amount to 1.3 million to 1.5 million tonnes between 1970 and 2005 (UNEP, 2010a). In 1999, it was reported that North America represented 50.6 % of total PBDE consumption; 97.5 % of Penta-BDE (8,290 tonnes), 35.9 % (1,375 tonnes) of Octa-BDE, and 44.3 % (24,300 tonnes) of Deca-BDE (Hale et al., 2003). In Asia, 53 % (2,030 tonnes) of Octa-BDE and 42 % (23,038 tonnes) of global Deca-BDE was used, but no Penta-BDE was produced in 1999 (Hale et al., 2003). Europe accounted for the remaining global demand of 2.5 % (213 tonnes) Penta-BDE, 12 % (460 tonnes) Octa-BDE and 13.7 % (7,515 tonnes) Deca-BDE (Hale et al., 2003).

There are essentially two modes via which FRs are incorporated into polymers. One is referred to as additive; in this instance the FR is added to the molten polymer. This “additive” mode means that the FR is not tightly bound to the polymer and therefore its migration to the environment is relatively facile. The alternative approach is where the FR is covalently-bound to the polymer via reaction. Release to the environment of FRs incorporated via this “reactive” process is comparatively restricted (Law, 2010). A caveat however, is that during the process of incorporation into the treated product, a proportion of the reactive FR used may not polymerise, and this residual fraction has potential to be released to the environment (de Wit, 2002). When both halogens and phosphorus are present within a polymer, they act independently and therefore additively (WHO, 1997).

TBBP-A is primarily used as a reactive FR in epoxy, polycarbonate and phenolic resins in printed circuit boards (58 %), but has also been used as an additive BFR in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins (18 %), and was “possibly” used as an additive in high impact polystyrene (HIPS) (BSEF, 2013; EFRA, 2007). Concentrations of TBBP-A commonly found in these applications are between 10 % and 20 % by weight, depending on the polymer (Covaci et al., 2009). Moreover, during the 1990s, TBBP-A was increasingly used as a replacement for Octa-BDE in ABS polymers (Watson et al., 2010).

The available data indicates that in general PBDEs (all congeners) were added to materials at concentrations between ~3-30 % by weight (WHO, 1994). The exact concentration applied was determined by several considerations such as the degree of flame retardancy required, the efficacy of the FR selected, whether it is applied in conjunction with a synergist (e.g. antimony oxide), physical attributes of the end product (e.g. colour, density, stability, etc.), and its specific application (European Chemicals Bureau, 2000).

In Europe, approximately 95 % of Penta-BDE was used in flexible PUF, mainly used for furniture upholstery and automotive applications (European Chemicals Bureau, 2000). The UNEP initially reported treated PUF to usually contain 10-18 % by weight of Penta-BDE, however they have subsequently revised these estimates to be around 3-5 % by weight for upholstery, cushions, mattresses, and carpet padding (UNEP, 2006a; UNEP 2010a). A similar concentration range of between 6-18 % by weight of Penta-BDE in PUF was provided in the Plastics Additives Handbook (Zweifel, 2001; cited in European Commission, 2011). The remaining minor uses of Penta-BDE (totalling 5 % of total use in Europe) include: textiles, printed circuit boards, insulation foam, cable sheets, conveyor belts, lacquers, and possibly drilling oils (UNEP, 2007). UNEP reported that the approximate distribution of global Penta-BDE use was 60 % in furniture and 36 % in transport, with the remaining 4 % deployed in other articles (UNEP, 2010b).

Historically, around 95 % of Octa-BDE supplied in the EU was used in ABS (globally ~70 %), to which it was typically added at concentrations between 10-18 % by weight (EC, 2011). The main uses for BFR-treated ABS were predominantly in housings of electrical and electronic equipment (EEE), particularly for cathode ray tube (CRT) housings (e.g. PC monitors and TVs), and office equipment (e.g. copying machines and business printers). The remaining ~5 % of minor uses were in HIPS, polybutylene terephthalate (PBT), and polyamide polymers, with typical concentrations between 12-15 % by weight. Other possible uses were in: nylon, low density polyethylene, polycarbonate, phenolformaldehyde resins, and unsaturated polyesters, as well as in adhesives and coatings (UNEP, 2010a; 2010b).

Widely used due to its relatively low cost, Deca-BDE was employed in a range of plastics/polymers and textiles. In plastics, Deca-BDE was used for EEE housings, in the automotive and aeronautic sectors and in construction, in applications such as wires and cables, pipes and carpets, typically loaded at 13-15 % by weight (BSEF, 2014). It was also applied as a back coating on a wide range of fabrics, including: nylon, polypropylene, acrylics, and many other blends such as polyester-cotton (Weil and Levchik, 2008). In textiles, Deca-BDE was typically added at about 10-25 % by weight in a 2:1 weight ratio with antimony oxide (Weil and Levchik, 2008). Important applications were in: automotive upholstery, draperies for hotels and public buildings, and institutional (e.g. office) upholstered furniture (Weil and Levchik, 2008).

The principal use of HBCDD (90 %) is in the building industry, typically added at <3 % by weight into expanded polystyrene (EPS) or extruded polystyrene (XPS) foam in rigid insulation panels/boards (EC, 2011; Marvin et al., 2011), with a further ~2 % deployed in HIPS used for electric and electronic equipment (distribution boxes for electrical lines and electrical housings) (EC, 2011). HBCDD is also used in the automotive industry in a small number of EPS applications, such as foot supports in carpets, as well as noise, vibration and harshness (NVH) materials in bulkheads (or partitions) and bonnet liners. HBCDD is also used as a textile coating agent in polymer dispersions applied to cotton or cotton/synthetic blends for upholstery fabrics, e.g. residential and commercial upholstered furniture and transportation seating, bed mattress ticking, draperies and wall coverings, interior textiles, e.g. roller blinds, and vehicle interior textiles. HBCDD can also be used in thermosol treatment of polyester, polypropylene and nylon fabrics, where it is applied as an aqueous suspension or emulsion at a loading of 8-11 % by weight (Weil and Levchik, 2008).

In 2000 the total TCIPP production in Europe was 36,000 tonnes, with the primary (66.5 %) use being in rigid foams in the production of construction blocks and panels used for insulation purposes, accounting for 26,650 tonnes of TCIPP consumption (EU RAR, 2008a). 90 % of all external roof and wall panels used on modern commercial and industrial buildings use rigid PUF (EPIC, 2002). In 2000, TCIPP accounted for 90 % of the usage of additive FR in PUF insulation foams i.e. flexible-faced laminate, sandwich panels, discontinuous panels, block foam, injected foams (Leisewitz et al., 2000). There is no evidence to suggest that the usage of TCIPP in PUF has changed since. A further 6,800 tonnes (18 %) of TCIPP are used in the production of flexible PUF with a further ~5,200 tonnes (14.3 %) used in the production of spray and one component foams (EU RAR, 2008a). TCIPP is used in slabstock (block) foam for soft furnishings and mattresses for the UK market to fulfil UK flammability regulations. TCIPP has limited use in the rest of Europe and in the USA. TCIPP was not used in products meeting the requirement of the recently repealed California Technical Bulletin 117 flammability standard because it could not meet the heat-ageing requirements due to its volatility. TCIPP is rarely used in the automotive industry because of its potential for 'fogging'; when TCIPP treated foam is heated, the condensation of volatile products on the inside of a car windscreen occurs. Considering the nature of the foam market, TCIPP could well be present in UK-produced foams for other applications. For example, waste from the production of rigid foam is used for adhesive pressing in the production of moulded boards for use in kitchen furniture and flooring (ISOPA, 2001). It is assumed that imports of furniture to the UK from outside the EU could account for an additional 10 % of TCIPP usage (i.e. up to approximately 680 tonnes per annum) (EU RAR, 2008a). TCIPP is a "drop-in" replacement for TCEP (EU RAR, 2008a).

Industry has moved away from use of TCEP but it was estimated that ~1000 tonnes per annum were consumed in Europe when it was in peak usage (EU RAR, 2008b). TCEP is used primarily (approx. 80 %) as an additive plasticiser and viscosity regulator with flame-retarding properties for the production of unsaturated polyester resins. Other fields of application are acrylic resins, adhesives and coatings. The primary uses of TCEP as a flame-retardant plasticiser are in furniture, textiles and roof insulation. Other minor uses include the manufacture of cars, trains, aircraft and as flame resistant paints and varnishes (EU RAR, 2008b). This includes polyvinyl acetate or acetyl cellulose and it can also be used as a secondary plasticiser for polyvinyl chloride to suppress the flammability resulting from primary plasticisers such as phthalates (EU RAR, 2008b). TCEP was not used in rigid PUF, however TCEP is also formed as a reaction by-product in the manufacture of other commercial flame retardants in which TCEP has been declared an impurity (EU RAR, 2008b).

The vast majority of TDCIPP is used in the production of flexible PUF. In 2000, less than 10,000 tonnes of TDCIPP were consumed in the EU (EU RAR, 2008c). In the USA, TDCIPP was used between 2004-2012 as a replacement for Penta-BDE to flame retard furniture foams (pers. comm. 17th September 2014, Luedeka). A 2012 report estimated that approximately 50 % of residential sofas in use in America were treated with TDCIPP (Stapleton et al., 2012). In Europe, TDCIPP is primarily used in the automotive industry, with some use in furniture. TDCIPP is a more expensive FR to use than TCIPP (almost twice the price) (EU RAR, 2008c), therefore TDCIPP is only used in applications where a more efficient flame retardant is required to meet specific standards (EU RAR, 2008c). Due to its relatively lower volatility, TDCIPP was able to meet the California Technical Bulletin of Home Furnishings 117 standard requiring that foam is heat-aged at 104°C for 24 hours where TCIPP was unable to.

The above underlines the extensive global use of BFRs and halogenated PFRs in a wide range of applications, and demonstrates that while deployment in electronic and electrical equipment (EEE) is substantial; use in soft furnishings and insulation foams is extensive also. Soft furnishings are items made of cloth, such as curtains, chair coverings, etc., used to decorate a room. While attention to date has understandably focused largely on emissions during the production and use phases of the product life cycle; the fact that a considerable proportion of the BFR inventory has either entered or is moving towards the end-of-life phase, means that attention is increasingly turning towards the environmental implications of FRs associated with waste materials. In particular, considerable interest has been aroused in potential FR contamination from landfilled waste. At the beginning of the 21st century, the majority of FR-containing consumer products ended up as untreated waste in landfill, with Alcock et al. (2003) estimating that >80 % of total BFR-containing waste was landfilled in the UK and North America. The lifespans of the principal products containing TBBP-A, PBDEs, and HBCDD are estimated to be ~10 years for soft furnishings and furniture, ~12 years for cars, but <10 years for EEE; with lifespans of EEE decreasing as the rate of obsolescence for these products accelerates. Consequently, as European use of these BFRs in new goods peaked in the mid 1990s and has ceased since; many articles containing PBDEs (EEE in particular) have most likely already become waste and been treated by the existing waste management infrastructure. Essentially therefore, most products containing PBDEs in Europe have probably been landfilled already. This therefore represents a significant reservoir in landfilled waste. However, studies of emissions of BFRs from such waste are few and studies of emissions of PFRs are fewer.

1.1.3. FRs in WEEE.

Substantial research focus has centred on plastics from waste electronic and electrical equipment (WEEE), as part of 'end-of-life management'. In 1999, the majority of WEEE plastics, as much as 96 %, were landfilled in Western Europe; while only 3 % of waste underwent mechanical recycling and 1 % incineration (Vehlow et al., 2002). In 2006, UNEP estimated global production of electronic waste (e-waste) to total 20-50 million tonnes. Of that total, the EU-27 states generate 8.3-9.1 million tonnes per annum; a quantity estimated to be increasing by 3-5 % year on year (Robinson, 2009). A recent WRAP (2012) report estimates that UK households dispose of 310,000 tonnes of WEEE annually. Morf et al., 2005 measured BFRs in representative small size WEEE, sampled in 2003. Average concentrations were 34 mg kg^{-1} Penta-BDE, 530 mg kg^{-1} Octa-BDE, 510 mg kg^{-1} Deca-BDE, 1420 mg kg^{-1} TBBP-A (as an additive) and 17 mg kg^{-1} HBCDD. Each personal computer (PC) contains approximately 1.7 kg of FR, of which ~ 70 % (1.2 kg) is in the plastic cabinet, with the remainder coating the printed circuit board (Danish EPA, 1997; Menad et al., 1998). The estimated proportion by weight of plastic contained in PCs and monitors is ~ 23 % of the overall computer materials (RCBC, 2001; SVTC, 2004). Prevedouros et al. (2004) estimated that the flow of Penta-BDE in disposed WEEE in the EU was between 17 and 60 metric tonnes per year between 2000 and 2005. Tasaki et al. (2004) analysed PBDEs in waste TV sets in Japan. Their results indicated that Deca-BDE was added to e-plastics between 1987 to 1990 and 1993 to 1996.

WEEE is composed of approximately 60 % metals, 20 % polymers, and 20 % residual materials such as wood or glass (Schlummer et al. 2005). Of the polymers, ABS plastics contain ~18 to 22 % (by weight) of Octa-BDE while polystyrene plastics contain ~10 to 12 % (by weight) of Deca-BDE. Both of these plastics are used as housing for electronic equipment (Nielsen and Christensen 2001). Electrical and electronic equipment typically contain polymers such as thermoplastics, thermosets and elastomers (Menad et al. 1998) that are flame retarded with chemicals such as BFRs. Riess et al., (2000) investigated 108 TV set and 78 PC monitor housings for FRs and identified PBDEs in 78 % and TBBP-A in 3 % of collected samples. Vehlow et al. (2000) measured BFRs in four shredder residue samples in Germany. PBDE concentrations ranged from 100 to 20,000 mg kg^{-1} while TBBP-A concentrations ranged from 100 to 6000 mg kg^{-1}. In another German report, Schlummer et al., (2007) analysed 45 single housings (9 TV set and 36 PC monitor housings) for polymer types and whether or not they contained BFRs. They identified that the housings were composed from a mixture of five different polymer types; ABS, HIPS, blends of ABS and polyvinylchloride (PVC), ABS and polycarbonate, and polyphenylene oxide and polystyrene (PPO/PS). Only 25 % of the plastics contained BFRs, of which 16 % was ABS and 9 % HIPS. The three other polymer types did not contain BFRs. TBBP-A, Deca-BDE, Octa-BDE, 1,2-bis-tribromophenoxyethane (TBPE) and the carbonate oligomer of TBBP-A could be identified as BFR additives. Analysed WEEE shredder residues contained 800 to 7,400 mg kg^{-1} PBDEs and 1,000 to 10,000 mg kg^{-1} TBBP-A. The observed range in concentrations is due to the heterogeneous mix of polymers within the shredded material. These ranges suggest no clear indication of a decrease in PBDE concentrations since those measured by Vehlow et al., (2000); but does indicate a slight increase in the use of TBBP-A perhaps as a replacement for Octa-BDE in ABS. Zhou et al., (2013) determined concentrations of PBDEs and TBBP-A from waste printed circuit board (WPCB) materials with three different particle sizes; >841 µm (ΣPBDEs 3045 mg kg^{-1}; TBBP-A 127 mg kg^{-1}), 420–841 µm (ΣPBDEs 2865 mg kg^{-1}; TBBP-A 108 mg kg^{-1}) and <420 µm (ΣPBDEs 2679 mg kg^{-1}; TBBP-A 101 mg kg^{-1}). Interestingly, the smaller particle sizes with larger surface area to volume ratios yielded slightly decreased BFR concentrations. The authors attribute this to loss of BFRs during the shredding process in the pulveriser.

1.1.4. FRs in waste soft furnishings and furniture.

In the UK alone, WRAP (2012) estimated that around 670,000 tonnes of furniture and 310,000 tonnes of textiles are disposed of by householders annually. This estimate was extrapolated from data collected across the UK during 2010/11. Considering that these products were often treated with FRs at percent levels by weight (UNEP, 2006a; UNEP 2010a; Weil and Levchik, 2008), it is apparent that they constitute a significant potential source of FRs to the environment. Despite this, very little research has been undertaken that examines end-of-life management of FRs associated with waste soft furnishings and furniture.

1.1.5. FRs in waste building insulation foams.

As a result of the Kyoto protocol committing State Parties to reduce greenhouse gases emissions and the 2003 EU Directive on the energy performance of buildings, the use of foam insulation in buildings has massively increased, as thermal insulation is an effective way of reducing carbon footprints by limiting energy consumption. HBCDD is the primary FR used in treating EPS and XPS panels and boards for this application. HBCDD is scheduled to be phased out under the Stockholm Convention on Persistent Organic Pollutants by countries that have ratified the treaty and will be banned for use in Europe as from 21st August 2015 unless an authorisation is granted for a specific use. However, while alternatives to HBCDD in EPS and XPS have already been identified by the chemical industry, they argue that it will take several years before a sufficient volume of HBCDD alternatives covering the need of the market become commercially available (BSEF, 2015). Because of this, specific exemptions for production and use of HBCDD in EPS and XPS foams for buildings were included and are currently due to last for five years, but this period may be shortened or extended.

1.1.6. Overview of UK landfills as a case study for the developed world.

Landfill has been the dominant waste management option in the UK for many years. Introduction of the European Directive 1999/31/EC on the Landfill of Waste (Landfill Directive) aimed to reduce the dependence on landfill as a disposal option. Its intention was to lessen the environmental impact of landfills and diminish the overall risk to human health. Before 2004, the UK disposed of both hazardous and non-hazardous wastes together at the same landfill, a practice known as co-disposal. Since July 2004, co-disposal is no longer practised and instead, landfills are divided into three distinct classes in which only specific waste types may be disposed of: landfills for hazardous waste, landfills for non-hazardous waste, and landfills for inert waste (Council of the European Union, 1999).

From October 2007, it became a requirement that waste sent to landfill be pre-treated. This change aims to increase waste recycling and recovery and reduce pollutant emissions from landfills (Environment Agency, 2011). The process of treatment must change the characteristics of the waste, and it must do so in order to substantially:

(a) Reduce its volume; or

(b) Reduce its hazardous nature; or
(c) Facilitate its handling; or
(d) Enhance its recovery potential.

The treatment of waste can be achieved by many methods depending on the aim of the treatment. These may include: manual sorting to change waste characteristics, physical (mechanical) treatment (crushing, grading, magnetic separation, eddy current separation, ballistic separation, trommeling (a revolving cylindrical sieve used for screening or sizing waste), and sorting, etc.), thermal treatment, and chemical or biological processes (anaerobic/aerobic digestion, biological stabilization of 'black bin' residues) (Environment Agency, 2011; Council of the European Union, 1999).

The Landfill Directive also places more stringent engineering and operation conditions on landfill operators. During the active phase and following closure of a site, a monitoring regime must be implemented to ensure groundwater quality is not compromised. Groundwater protection measures require that there is no discharge of a prescribed range of hazardous substances (including organohalogen compounds such as pesticides and herbicides, but not BFRs) to groundwater and that formal compliance points below a landfill have been established, where both leachate and groundwater composition must be monitored.

It is now mandatory for new landfills in developed nations to be engineered using a liner membrane barrier to separate the landfilled waste from the underlying ground. This membrane retards migration of leachate into surrounding groundwater. It generally comprises a layer of compacted clay with a minimum required thickness and a maximum allowable hydraulic conductivity, overlaid by a high-density polyethylene (HDPE) geomembrane. By doing so, the intention is that in the event of a hole developing, the impact of any leak will be minimised as there will also be clay below the HDPE as a further line of defence. All membranes are slightly porous and over time low volumes of leachate cross the membrane. The landfill membranes are designed such that at these low volumes the leachate should never have a measurable adverse impact on the quality of the receiving groundwater.

However, the US EPA (1988) has voiced concerns that “once the unit is closed, the bottom layer of the landfill will deteriorate over time and, consequently, will not prevent leachate transport out of the unit.” Therefore it can be said that modern landfill designs delay, but do not wholly prevent ground and surface water pollution.

In order to prevent leachate overflow and potential drying and cracking of clay liners, there is a requirement for landfill sites to manage leachate volumes within the landfill.
Laid on top of the membrane is a series of leachate collection pipes to transport the leachate to a collection or treatment location. The failure or abandonment of the leachate collection system poses a significant risk to groundwater. As landfills age they are prone to suffer large internal movements as waste decomposes unevenly. Consequently leachate collection systems are susceptible to internal failure and pipes can buckle and distort. Such failure causes leachate levels to slowly build within the landfill, and given time they may even rise sufficiently high to spill over the top of the containing membrane at uncapped sites. A positive feedback mechanism can then occur, in which further active decomposition and leachate generation can be triggered as leachate levels rise and rehydrate previously dried out waste masses. One of the many problems leachate collection systems can face, is clogging of the conduit pipes with mud or silt. The conditions in leachate collection systems are ideal for micro-organisms to multiply and this growth can exacerbate the clogging problem. Another mechanism via which clogging can occur is by chemical reactions within the leachate which in turn generates solid residues. Furthermore, the pipe walls may be weakened by the chemical composition of the leachate and cause them to fail. During the management of leachate, volumes are monitored via a number of wells and when volumes are too high it is removed for storage at a pond or tank on-site. The leachate is reintroduced to the landfill by being sprayed on top to maintain a steady volume of leachate within. This recycling of leachate through the system also serves to reduce leachate treatment costs, because the leachate is only sent away for treatment at a waste water treatment plant (WWTP) once it has been deemed sufficiently ‘dirty’, thus reducing the final volume of leachate that is sent to treatment (pers. comms. landfill site managers, 2014).

Simulations by Danon-Schaffer et al., (2013a) suggest that even with an immediate ban on adding all products treated with BFRs to landfill, concentrations of PBDEs will continue to persist within landfills beyond 2080, and that PBDEs contained in existing landfilled waste (both e-waste and non e-waste) will persist to nearly 2070. It is predicted that all PBDEs will have virtually disappeared from non e-waste products by ~2090, five years later than for e-waste because electronic goods have shorter lifespans and enter the waste stream quicker than soft furnishings and fabrics. They predict that the larger molecular weight BDEs would disappear more rapidly (e.g. deca-BDE being eliminated in ~36 years), whereas lower molecules would take longer to disappear due to stepwise debromination (e.g. tetra- and tri-BDEs ~60 years).

Within the UK, the waste electronic and electrical equipment (WEEE) Regulations came into force in July 2007. This requires collection of 65 % of e-waste, and recovery of 85 % of the collected material. This means that 35 % of UK e-waste can still be disposed to landfill untreated, augmenting the already substantial quantity of e-waste residing in UK landfills. However, no regulations currently exist that address the disposal of waste soft furnishings, furniture or building insulation foams.

1.2. Mechanisms of FR migration from goods and materials and their behaviour.

The mechanisms via which BFRs and PFRs transfer from waste products to the environment remain an active field of investigation. PBDEs, HBCDD and chlorinated PFRs are used primarily as additives and therefore migrate comparatively readily from products within which they are incorporated into the environment (Deng et al., 2007). In contrast, TBBP-A is used predominantly (though not exclusively) as a reactive BFR and therefore its release from treated goods is much less pronounced than for PBDEs and HBCDD. This contributes to the low concentrations of TBBP-A reported in indoor air, dust and food (Covaci et al., 2009). In addition to migration from waste materials following disposal to landfill, evidence also exists to suggest that transport of waste materials to disposal sites and their subsequent storage before sorting or deposition may also prove to be significant emission pathways for FRs to the environment (Julander et al., 2005; Muenhor et al., 2010). The following sections summarise current knowledge relevant to our understanding of how FRs are emitted to the environment as a result of waste management.

1.2.1. Emissions to air.

Emission chamber experiments conducted by Kemmlein et al., (2003) documented emissions of BFRs and TCIPP via volatilisation from a range of consumer products including insulating materials, assembly foam, upholstery, mattresses, and electronics equipment. An increase of temperature (from 23 to 60 °C) was found to cause a 500-fold increase in emissions of BDE-47 from printed circuit boards. This has relevance for emissions from waste, as within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat released during aerobic degradation (Kjeldsen et al., 2002; Environment Agency, 2002). Consequently, elevated volatile emissions of BFRs from active landfills are plausible, but the migration would be limited by overlying layers of waste. Additionally, it should also be noted that as products age, the rates of emission of BFRs may also change as their overall concentrations within the goods decreases. Much higher area specific emission rates were reported for TCIPP than for the BFRs. However, the study of Kemmlein et al (2003) also showed BFR emissions to vary between products, and of particular relevance to this review, emissions of HBCDD and Deca-BDE from the PUF and textile components of an upholstered stool were not detected over a period of 170 days. Higher TCIPP emissions were exhibited from materials with lower specific densities and, therefore higher solid-vapour interfaces. Conversely, chamber experiments by Wilford et al., (2003) showed that PBDEs volatilise from PUF at significant levels. Both studies showed that different PBDE congeners are released at different rates, determined by their physical properties i.e. higher emissions observed for congeners with higher vapour pressures (Table 1.1 and 1.2 - Kemmlein et al. 2003; Wilford et al., 2003).

More recently, Kajiwara and Takigami (2013) conducted emission chamber tests on three curtain textile samples. Two of the samples were treated with technical HBCDD and one with technical Deca-BDE. Tests were conducted over a range of temperatures (20, 40, 60, and 80 °C) for 120 hours. Both HBCDD and BDE-209 (the least volatile PBDE) were found to volatilise at 20 °C indicating that they are emitted from textiles even at room temperature. At temperatures of 80 °C, HBCDD emission rates were increased twenty-fold compared to the rates at 60 °C, with those of Deca-BDE at 80 ˚C six times greater than at 60 °C. There were no clear differences between the emission rates at 20, 40, and 60 °C for both BFRs. Tables 1.3, 1.4 and 1.5 summarise emission rates to air of PBDEs, HBCDD and TCIPP respectively.

Table 1.1: Selected physicochemical properties of brominated flame retardants.

Compound	log K_{OW}	Aqueous Solubility (mg L^{-1})	log K_{OA}	Vapour Pressure (Pa)
BDE-15	5.48 [a]	0.821 [b]	8.72 [h]	8.80×10^{-3} [j]
BDE-28	5.80 [a]	0.421 [b]	9.50 [i]	1.57×10^{-3} [j]
BDE-47	6.39 [a]	0.112 [b]	10.53 [i]	2.50×10^{-4} [j]
BDE-85	7.37 [b]	0.097 [b]	11.69 [b]	9.86×10^{-6} [k]
BDE-99	6.76 [a]	0.077 [b]	11.31 [i]	5.00×10^{-5} [j]
BDE-100	6.53 [a]	0.085 [b]	11.13 [i]	2.86×10^{-5} [k]
BDE-153	7.08 [a]	0.031 [b]	11.82 [i]	5.80×10^{-6} [j]
BDE-183	8.27 [b]	-	11.96 [i]	4.68×10^{-7} [k]
BDE-209	9.97 [b]	0.002 [b]	15.73 [b]	1.43×10^{-8} [b]
α-HBCDD	5.07 [c]	0.0488 [e]	-	-
β-HBCDD	5.12 [c]	0.0147 [e]	-	-
γ-HBCDD	5.47 [c]	0.0021 [e]	-	-
Σ-HBCDD	5.62 [c]	0.066 [f]	10.46 [f]	6.27×10^{-5} [l]
TBBP-A	5.90 [d]	0.099 [g]	-	4.72×10^{-9} [g]

[a] Wania and Dugani (2003)
[b] Yue and Li (2013)
[c] MacGregor and Nixon (1997)
[d] MacGregor and Nixon (2001)
[e] MacGregor and Nixon (2004)
[f] Marvin et al., (2011)
[g] Kuramochi et al., (2008)
[h] Li et al., (2006)
[i] Harner and Shoeib (2002)
[j] Wong et al., (2001)
[k] Tittlemier et al., (2002)
[l] USEPA (2008)

Nb : estimated values used where not measured;
Reported K_{OW} and K_{OA} values are dimensionless concentration ratios and therefore unitless.

Table 1.2: Selected physicochemical properties of chlorinated PFRs.

Compound	Log K_{OW}	Aqueous Solubility (mg L^{-1})	Vapour Pressure (Pa)
TCEP	1.78 [a]	7,820 [a]	1.14×10^{-3} [a]
TCIPP	2.59 [b]	1,600 [b]	1.40×10^{-3} [c]
TDCIPP	3.69 [d]	18.1 [d]	5.60×10^{-6} [e]

[a] EU RAR, (2008b)
[b] van der Veen and de Boer, (2012)
[c] Tremain, (2002a)
[d] Cuthbert and Mullee, (2002)
[e] Tremain, (2002b)
Nb : estimated values used where not measured.

Table 1.3: Area specific emission rates (SER_a) and unit specific emission rates (SER_u) of PBDEs to air.

Compound	TV housing[a] (23°C) (ng m^{-2} h^{-1})	Printed circuit board[a] (60°C) (ng unit^{-1} h^{-1})	Polyester curtain[b] (20°C) (ng m^{-2} h^{-1})	Polyester curtain[b] (40°C) (ng m^{-2} h^{-1})	Polyester curtain[b] (60°C) (ng m^{-2} h^{-1})	Polyester curtain[b] (80°C) (ng m^{-2} h^{-1})
BDE-17	-	0.6	-	-	-	-
BDE-28	0.2	1.9	-	-	-	-
BDE-47	6.6	14.2	-	-	-	-
BDE-66	0.5	0.4	-	-	-	-
BDE-85	-	0.1	-	-	-	-
BDE-99	1.7	2.6	-	-	-	-
BDE-100	0.5	1.3	-	-	-	-
BDE-153	1.0	0.04	-	-	-	-
BDE-154	0.2	0.1	-	-	-	-
Hepta-BDE	4.5	-	-	-	-	-
Octa-BDE	1.5	-	-	-	-	-
Nona-BDE	0.8	-	-	-	-	-
Deca-BDE	0.3	-	2.5	3.0 - 12.0	6.0	30

[a] Kemmlein et al., (2003)
[b] Kajiwara & Takigami (2013)

Table 1.4: Area specific emission rates (SER_a) of HBCDD to air (ng m^{-2} h^{-1}).

Temperature (°C)	20	23	40	60	80
EPS (0.02 m^3)[a]	-	4	-	-	-
EPS (0.001 m^3)[a]	-	1	-	-	-
XPS (0.02 m^3)[a]	-	29	-	-	-
XPS (0.001 m^3)[a]	-	0.1	-	-	-
Polyester curtain A[b]	100 - 300	-	200 - 3000	200	5800 - 6100
Polyester curtain B [b]	200	-	200	300	6100 - 9000

[a] Kemmlein et al., (2003)
[b] Kajiwara & Takigami (2013)

Table 1.5: Area specific emission rates (SER_a) of TCIPP to air (µg m^{-2} h^{-1}) at 23 °C.

Product / Material	Content (% by weight)	SER_a
Polyisocyanurate foam (80 g L^{-1}) [a]	5	0.21
Polyisocyanurate foam (20 g L^{-1}) [a]	2-3	0.60
Closed cell PUF (rough, new) [a]	20	70
Closed cell PUF (smooth, new) [a]	20	50
Closed cell PUF (rough, stored) [a]	20	140
Closed cell PUF (smooth, stored) [a]	20	50
Upholstery foam: PUF [a]	2	77
Upholstered stool: PUF [a]	9	36
Mattress [a]	unknown	0.012

[a] Kemmlein et al., (2003)   stored = 6 months after manufacture

The few studies that have reported concentrations of BFRs in air at or near landfill sites are summarised in Table 1.6. Weinberg et al., (2011) reported particulate phase concentrations of BDE-183 at both active and closed landfill sites in Germany to fall between 0.001 to 0.011 ng m^{-3} and 0.001 to 0.003 ng m^{-3} respectively. The authors suggested that the significantly higher ($p<0.05$) detection of BDE-183 at the active landfill site compared to the reference site, indicates that BDE-183 might be emitted from waste disposed at the active landfill. However, the study failed to detect PBDEs in the vapour phase at either site, despite other European and UK background studies reporting low concentrations in air, typically sub- to a few pg m^{-3} (Gioia et al., 2006; Lee et al., 2004). In Canada, St-Amand et al., (2008) reported concentrations of PBDEs collected at a sanitary landfill near Ottawa. Vapour and particulate phase total PBDE concentrations were generally below 0.002 and 0.02 ng m^{-3} respectively and ranged from 0.00036 to 0.0069 ng m^{-3} and 0.00072 to 0.145 ng m^{-3}, respectively. These concentrations are in line with those detected at other locations not impacted directly by point sources.

Table 1.6: Concentrations of brominated flame retardants in ambient air in the vicinity of waste treatment facilities.

Compound	**Phase**	**Method of waste disposal**	**Concentrations (ng m^{-3})**	**Country**
ΣHBCDD	Both (total)	WEEE recycling facility	22	UK[a]
ΣHBCDD	Both (total)	Active landfill	0.013 – 0.18	Sweden[b]
Σ_{24}PBDEs	Particulate only	WEEE recycling facility	175.79 – 233.16	Sweden[c]
Σ_{10}PBDEs	Vapour only	WEEE storage facility	0.008 – 0.15	Thailand[d]
BDE-183	Particulate only	Active landfill	0.001 – 0.011	Germany[e]
ΣPBDEs	Both (total)	Active landfill	0.00108 – 0.1519	Canada[f]
BDE-183	Particulate only	Closed landfill	0.001 – 0.003	Germany[e]
ΣPBDEs	Both (total)	Closed landfill	17.3	USA[g]
ΣPBDEs	Both (total)	Incineration plant	2	Canada[h]
Σ_7PBDEs	Both (total)	Incineration plant	0.00224 – 0.02132	Sweden[i]

[a] Harrad et al., (2010)
[b] Remberger et al., (2004)
[c] Julander et al., (2005)
[d] Muenhor et al., (2010)
[e] Weinberg et al., (2011)
[f] St-Amand et al., (2008)
[g] Oliaei et al., (2010)
[h] Alaee, (2001)
[i] Agrell et al., (2004)

In contrast, Oliaei et al., (2010) reported the total ΣPBDE concentration of vapour and particulate phases combined in “ambient air of diffused landfill gas” at a recently closed landfill in Minnesota, USA was 17.3 ng m^{-3}. BDE-47 had the highest concentration (8.23 ng m^{-3}), followed by BDE-209, -99, -28/33, and -100. BDE-209 was found predominantly in the particulate phase, while lower brominated BDEs were principally in the vapour phase. The data of Oliaei et al. suggest strongly that the landfill studied was a source of PBDEs. Vapour and particulate phase HBCDD concentrations (0.013 – 0.18 ng m^{-3}) have been reported once for outdoor air in the vicinity of a Swedish landfill site (Remsberger et al. 2004).

Given the paucity of data related to BFR concentrations in air in the vicinity of landfills; Table 1.6 also summarises other data that illustrate the potential for emissions of BFRs to air from waste products. In the UK, Harrad et al., (2010a) reported elevated concentrations of HBCDD in outdoor air sampled within the boundaries of an e-waste treatment facility (22 ng ΣHBCDDs m^{-3}). Likewise, Julander et al., (2005) detected up to 214.3 ng m^{-3} Σ_{24}PBDEs in airborne particulates sampled in the vicinity of an e-waste recycling facility in Sweden. Moreover, in addition to the data summarised in Table 1.6, other studies have reported elevated concentrations of PBDEs in indoor air and dust within WEEE recycling facilities (Rosenberg et al., 2011; Sjödin et al., 2001; Takigami et al., 2006). Tomko and McDonald, (2013) modelled potential HBCDD emissions from a newly opened electronics recycling facility at a MSW landfill in Canada. The authors estimate that potential emissions of HBCDD up to 500 kg per year may be released, however the emissions estimate model unrealistically assumes that all of the input mass of HBCDD to the facility will become airborne. The real contribution of HBCDD to airborne emissions is unknown but based on physico-chemical properties are likely to be much lower (Table 1.1).

To the author's knowledge there have been no studies that target the presence of TCEP, TCIPP and TDCIPP in outdoor air in the vicinity of waste disposal sites. There are however a limited number of studies that report direct and indirect measurements of these PFRs in outdoor air. Concentration of TCEP (0.52 ng m^{-3}), TCIPP (1 ng m^{-3}) and TDCIPP (<LOD, not given) were reported for particle phase air samples collected over 24 h at an urban site in A Coruña, Spain (Quintana et al., 2007). Marklund et al., (2005) reported concentrations of TCEP (0.0016 ng m^{-3}), TCIPP (0.81 ng m^{-3}) and TDCIPP (0.02 ng m^{-3}) in background air samples collected in Finland. Wet deposition analysis has also been proposed to confirm the presence of PFRs in the outdoor atmosphere. Deposition samples at the same background site in Finland were reported as 550, 510 and <0.5 ng m^{-2} day^{-1} for TCEP, TCIPP and TDCIPP respectively (Marklund et al., 2005). The study also reported concentrations in Swedish snow ranging from 7 to 39 ng kg^{-1} for TCEP, 68 to 210 ng kg^{-1} for TCIPP and 8 to 230 ng kg^{-1} for TDCIPP. Additionally, Laniewski et al., (1998) reported the occurrence of TCEP and TCIPP in precipitation in remote areas at concentrations ranging from 1 to 21 ng L^{-1} in samples of rainwater from Ireland and 1 to 4.5 ng L^{-1} in snow from Poland and Sweden. TCEP has also been detected in rainwater collected in Germany at concentrations of 121 ng L^{-1} (Fries and Püttmann, 2003). In a more recent German study, concentrations in rainwater and snow samples were reported for TCEP (236 to 353 ng L^{-1} and 78 to 234 ng L^{-1}, respectively), TCIPP (226 to 284 ng L^{-1} and 371 to 385 ng L^{-1}, respectively) and TDCIPP (46 and 100 ng L^{-1}, respectively) (Mihajlović and Fries, 2012). Aston et al., (1996) suggested that concentrations of TCEP (1950 ng/g), TCIPP (763 ng/g), and TDCIPP (1320 ng/g) found in pine needles in the Sierra Nevada Mountains, United States, originated from long-range air transport.

Emissions of BFRs are also plausible as a result of combustion of waste. Rupp and Metzger (2005) qualitatively investigated the reaction of BDE-47 and BDE-153 between 250 °C and 500 °C. At such comparatively low temperatures, PBDEs are not destroyed completely and thus may potentially act as precursors for the formation of e.g. polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs). Interestingly, the same study revealed that thermal treatment of both BDE-47 and BDE-153 resulted in the formation of monochlorinated polybrominated diphenyl ethers (CPBDEs) (Rupp and Metzger, 2005).

Such combustion emissions can occur either accidentally (as in landfill fires), or intentionally via incineration of municipal solid waste (MSW). MSW is by nature a heterogeneous mix of waste that will contain varying proportions of waste furniture and fabrics. The concentration of ΣPBDEs (the congeners included not specified) outdoors in Tagish, Yukon, Canada was reported as 2 ng m^{-3}. These elevated concentrations were attributed to waste incineration near the sampling site (Alaee, 2001). Agrell et al., (2004) sampled air outside a MSW incineration plant in Malmö, Sweden. They reported concentrations of ΣPBDEs (BDE-28, -47, -66, -100, -153, -154, -183) for vapour and particulate phases combined that ranged between 0.00224 and 0.02132 ng m^{-3}; with a median value of 0.0063 ng m^{-3}. However, the authors note that the low concentrations were likely due to the sampling having taken place during cool periods (mean 8 °C, 17th October-9th November 2001 and 19th February-15th March 2002) when volatilisation from contaminated surfaces was less likely. Concentrations of ΣPBDEs and BDE-47 in both the particulate and vapour phases were significantly higher at the MSW incineration plant compared to those at an urban background reference site (i.e. *p*-values for particulate and vapour phase ΣPBDEs = 0.0088 and 0.0071 respectively; BDE-47 *p* = 0.0143 and 0.0117 respectively), while concentrations of BDE-209 were significantly higher only in the particulate phase (*p* = 0.004) (Agrell, et al. 2004). In Japan, PBDE output from incinerator stack emissions were reported as 65,000 ng/h, equivalent to an emission factor of 100 ng PBDE emitted per g waste incinerated) (Sakai et al., 2006). Tu et al., (2011) reported emissions of Σ_{30}PBDEs measured in stack flue gas at two MSW incinerators in southern Taiwan. PBDE concentrations were 9.32 ng/Nm^3 and 7.62 ng/Nm^3 again equating to an emission factor of 100 ng PBDE emitted per g waste incinerated. Investigations by Takigami et al., (2014) into the incineration of XPS and EPS insulation foams using a pilot scale rotary kiln incinerator show that HBCDD is destroyed almost entirely during the combustion process and resulting emissions are negligible (destruction efficiency of 99.9999 %). Feeding rates of refuse derived fuel pellets, both EPS-added (3.1 % of pellet; 300 mg kg^{-1} HBCDD) and XPS-added (3.1 % of pellet; 1200 mg kg^{-1} HBCDD) were approximately 2.1 kg h^{-1}. Incineration temperatures of 840 °C and 900 °C were maintained at primary and secondary combustion zones respectively. It appears reasonable to assume that HBCDDs in treated fabrics may exhibit similar behaviour during incineration. Finally, similar investigations by Matsukami et al., (2014) into the incineration of wastes containing approximately 1 % of TCIPP (10,000 mg kg^{-1}) were conducted using the same pilot scale rotary kiln incinerator as detailed above with a feeding rate of 2.21 kg h^{-1}. Final flue gas emissions of TCIPP were reported as 0.02 μg m^{-3}, expressed under dry standard conditions (0 °C, 101.325 kPa). TCIPP was mainly destroyed in the primary combustion with destruction efficiencies greater than 99.999 %.

1.2.2. Leaching to surface and groundwater.

Emissions into surface and groundwater may occur via landfill leachate (Albaiges et al., 1986; Looser et al., 1999; Paxéus, 2000). Percolation of water through almost any material will cause soluble components to be dissolved out and enter the leachate. Insoluble liquids (such as oils) and small particles in the form of suspended solids may also be present in leachate (Environment Agency, 2002). Leachate composition is primarily determined by the composition and solubility of the waste constituents. The composition of waste can be said to change over time as a landfill ages (for example due to weathering or biodegradation) and therefore the leachate composition also changes with time. This is particularly the case in landfills containing non-hazardous municipal waste. Generally, it is accepted that landfilled waste undergoes at least four phases of decomposition and therefore four stages in the generation of leachate. These are: (1) an initial aerobic phase, (2) an anaerobic acid phase, (3) an initial methanogenic phase, and (4) a stable methanogenic phase (Christensen and Kjeldsen, 1995).

1. Leachate produced in the early stages of decomposition of waste is typically generated under aerobic conditions producing a complex solution with near neutral pH. This phase generally only lasts a few days or weeks because oxygen is not replenished once the waste is covered. It is relatively unimportant in terms of leachate quality, as most leachate produced during this phase results from the release of moisture during compaction and bypassing of precipitation through the buried refuse. However, because aerobic degradation produces heat, leachate temperatures can rise, sometimes as high as 80-90 °C, and if this heat is retained it can enhance the latter stages of leachate production (Kjeldsen et al., 2002; Environment Agency, 2002). Elevated temperatures are likely to enhance potential volatilisation and also the aqueous solubility of BFRs.
2. As decomposition processes develop and oxygen sources are depleted, the waste becomes anaerobic, supporting fermentation reactions. The anaerobic phase has two main stages in leachate generation; the acidogenic stage and the acetogenic stage. The acidogenic stage proceeds efficiently over a relatively narrow pH range around neutral. During the acetogenic stage, hydrolytic, fermentative, and acetogenic bacteria dominate, resulting in an accumulation of carboxylic acids, and a pH decrease. This acidic pH leachate is chemically aggressive and increases the solubility of many compounds (Kjeldsen et al., 2002; Environment Agency, 2002).
3. After several months or years, methanogenic conditions are established as the pH of the waste becomes sufficiently neutralised to permit at least limited growth of methanogenic bacteria. The leachate becomes neutral or slightly alkaline as the pH increases and acids are consumed. The overall volume of leachate is lower but still contains significant quantities of some pollutants (e.g. ammonium).

4. As biodegradation nears completion, the pH continues to increase and aerobic conditions may return. Some organic compounds are present in the leachate, mostly recalcitrant compounds such as humic and fulvic acids (Environment Agency, 2002; Kjeldsen et al., 2002). The implication of the continued presence of humic acids is that they enhance the leachability of BFRs from waste materials they contact.

Over time, leachate barrier systems are prone to degradation and ultimately failure. When this occurs, pollution of groundwater becomes possible. Alternatively if leachate is not removed for treatment at sufficiently high rates, seepage to both surface and groundwater may occur (Slack et al., 2007). The processes via which BFRs and PFRs leach from landfilled waste are not yet understood. In order to understand these leaching mechanisms, a full knowledge of the environmental partitioning mechanism at aqueous/solid-phase interfaces is required, as well as the relevant physicochemical properties of BFRs and PFRs (Choi et al., 2009).

PBDEs are hydrophobic, therefore their presence in leachate implies that other constituents present in the leachate have enhanced their leachability. When wastes come into contact with rainwater in a landfill, relatively hydrophilic BFRs such as TBBP-A are more readily dissolved in the leachate (Osako et al., 2004). However, dissolved humic matter (DHM) in the leachate interacts with hydrophobic BFRs such as the higher brominated PBDEs in the waste and can enhance their leachabilities (Osako et al., 2004).

Danon-Schaffer et al., (2013b) conducted a series of leaching experiments contacting e-waste with distilled water and leachate from a major urban landfill in end-over-end contactors at a rotational speed of 8 revolutions per minute. The authors found greatest transfer of PBDEs to the aqueous phase at pH 4 and 5. The authors hypothesised that changes in pH affect the solubility and mechanical properties of the plastic, influencing the dislodgement of fine particles from the polymer. Contacting e-waste with distilled water resulted in a lower transfer of PBDE concentrations to the aqueous phase, compared to when e-waste was contacted with leachate. The duration of contact time (1 to 168 h) appeared to exert little influence on the transfer of PBDEs to the distilled water. Likewise, when leachate was used (over experimental durations of 1 to 654 h), relatively little PBDE was transferred to the leachate after the first 24 h period and the last 630 h of contact appeared to have little further effect on transfer. The authors suggested that there are two potential mechanisms responsible for the observed transfer rates; 1) dislodgement of ultra-fine particles of dust adhering to the surface of the plastic; or 2) abrasion occurring when the chipped e-waste material rubs against each other and against the walls of the columns during end-over-end contacting. The experiment also examined differences between e-wastes separated out into the decades 1980s, 1990s and 2000s. Higher PBDE concentrations in the aqueous phase were found for wastes from the 1980s than for the later decades. Concentrations from the 1990s and 2000s were generally 2–4 orders of magnitude lower than 1980s e-wastes (Danon-Schaffer et al., 2013b).

Brandsma et al., (2013a) compared the leaching behaviour of BDE-209 from three different polymers; polyphenylene ether/high-impact polystyrene (PE/HIPS), polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) and epoxy resins (EPR). BDE-209 was only detected in significant quantities in the leachate from EPR, with a maximum concentration of 27 ng/cm^2 after thirty days. The study demonstrates that the porosity and/or strength of the materials have a high influence on the leaching behaviour of BFRs. The explanation given for the differences in leaching between the polymers, is the relative softness of EPR when compared to PC/ABS and PE/HIPS.

Concentrations of BFRs in European landfill leachates have only been reported for the UK, Netherlands and Sweden (Table 1.7). Morris et al., (2004) analysed landfill leachates collected from nine Dutch and three UK MSW landfill sites. Interestingly, neither HBCDD nor TBBP-A were detected in the UK leachate samples. HBCDD was found only in the particulate phase of Dutch landfill leachates at a mean concentration of 6 mg kg^{-1} (dry weight), with a maximum HBCDD concentration of 36 mg kg^{-1} (dry weight). The most abundant diastereomer was γ-HBCDD which was at least four times greater than α-HBCDD. TBBP-A was detected at a mean concentration of 54 mg kg^{-1} (dry weight) and varied between <0.3 and 320 mg kg^{-1} (dry weight) (Morris et al., 2004). Öman and Junestedt (2008) analysed leachate collected from twelve Swedish municipal landfills containing household waste, industrial waste, construction and demolition waste, as well as ash, slag, sludge, lime, sediment and excavation material. Concentrations of ΣPBDEs ranged from 10.2 ng L^{-1} to 19,463 ng L^{-1}, with those of TBBP-A reaching up to 20 ng L^{-1}. The age of the waste in the landfills varied from a few years to 50 years, but the influence of waste age on leachate concentrations was not reported. Remberger et al., (2004) reported concentrations of HBCDD in landfill leachate at a Swedish landfill receiving construction and demolition waste ranging from 3 ng L^{-1} to 9 ng L^{-1}.

Table 1.7: Concentrations of brominated flame retardants in landfill leachate and related aqueous samples.

Compound	Aqueous medium	Site Category	Concentration (ng L^{-1})	Country
ΣPBDEs	Raw Leachate	Active landfill	10.2 – 19,463	Sweden[a]
ΣPBDEs	Raw Leachate	Active landfill	29 – 248	USA[b]
Σ_{3}PBDEs	Raw Leachate	Active landfill	<0.008 – 4.0	Japan[c]
Σ_{59}PBDEs	Raw Leachate	Active landfill	0.03 – 1,020	Canada[d]
Σ_{30}PBDEs	Raw Leachate	Active landfill	5.67	China[e]
Σ_{22}PBDEs	Treated Leachate	Active landfill	<6.1	China[e]
Σ_{13}PBDEs	Raw Leachate	Active unlined landfill	8.392 – 54.761	S. Africa[f]
Σ_{8}PBDEs	Raw Leachate	Active unlined landfill	2.25 – 17,953	S. Africa[g]
ΣPBDEs	Raw Leachate	Closed landfill	7.1	USA[h]
ΣPBDEs	Groundwater	Closed landfill	0.052	USA[h]
Σ_{46}PBDEs	Raw Leachate	Active waste dump	3.7 – 133,000	S.E. Asia[i]
ΣHBCDD	Raw Leachate	Active landfill	2.5 – 36*	Holland[j]
ΣHBCDD	Raw Leachate	Active landfill	3.0 – 9.0	Sweden[k]
ΣHBCDD	Raw Leachate	Active landfill	7.0 – 12	Japan[l]
ΣHBCDD	Treated Leachate	Active landfill	< 6	Japan[l]
TBBP-A	Raw Leachate	Active landfill	<0.30 – 320*	Holland[j]
TBBP-A	Raw Leachate	Active landfill	<1.0 – 620	Japan[c]
TBBP-A	Treated Leachate	Active landfill	<1.0 – 11	Japan[c]
TBBP-A	Raw Leachate	Active landfill	0.3 – 540	Japan[l]
TBBP-A	Treated Leachate	Active landfill	7.7	Japan[l]
TBBP-A	Raw Leachate	Active landfill	<1.0 – 20	Sweden[a]
TBBP-A	Raw Leachate	Active landfill	15.41	China[e]
TBBP-A	Treated Leachate	Active landfill	<4.50	China[e]

[a] Öman and Junestedt, (2008)
[b] Oliaei et al., (2002)
[c] Osako et al., (2004)
[d] Li et al., (2012)
[e] Zhou et al., (2013)
[f] Odusanya et al., (2009)
[g] Daso et al., (2013)
[h] Oliaei et al., (2010)
[i] Kwan et al., (2013)
[j] Morris et al., (2004)
[k] Remberger et al., (2004)
[l] Suzuki and Hasegawa, (2006)

* mg kg^{-1} (dry weight)

In North America, Oliaei et al., (2002) reported concentrations of PBDEs in leachate sampled from five landfill sites with different waste characteristics (three municipal, one industrial, and one demolition) in Minnesota, USA. Concentrations of ΣPBDE ranged from 29 to 248 ng L^{-1}. The demolition waste landfill had the highest total PBDE concentrations, suggesting that the fate of building material waste warrants serious consideration. BDE-209 was the dominant congener found in leachate, 60 % to 98 % of the total PBDE contamination (Oliaei et al., 2010). The second phase of this study reported total PBDE concentrations of 7.1 ng L^{-1} in leachate from a recently closed landfill in Minnesota, USA (Oliaei et al., 2010). At this site, BDE-47 was the dominant congener found in leachate followed by BDE-99 and BDE-209 respectively. Water sampled from groundwater monitoring wells at the same site contained total PBDE concentrations of 0.052 ng L^{-1} (sum of dissolved and particulate phases).

PBDEs were detected in leachate from 26 out of 28 landfill and dumpsites across Canada (Li et al., 2012). While 59 PBDE congeners were monitored in all samples, only BDEs-47, -99, -100, -153, -154, -183, -206, -207, and -209 were detected frequently. The sum of these 9 congeners constituted more than 99 % of the total PBDEs measured. Concentrations ranged substantially from 0.03 to 1,020 ng ΣPBDEs L^{-1}, with an average of 166 ng ΣPBDEs L^{-1}. The dominant congener was BDE-209 with a mean contribution of 52 %. The authors did not distinguish between emissions from managed and unmanaged landfills.

To put the concentrations of BFRs in leachate into context, Table 1.8 presents a selection of reported BFR concentrations measured from lakes, estuaries and rivers.

In Japan (Osako et al., 2004), leachate samples were taken from seven different landfill sites and concentrations of PBDEs and TBBP-A determined. The study found substantial differences in the concentrations of BFRs in the raw leachate of each landfill site, with PBDE concentrations expressed as the sum of BDE-47, BDE-99 and BDE-100 ranging from <0.008 to 4 ng L^{-1}. In particular, leachate from one section on a site that contained both crushed fragments of bulk wastes such as WEEE, as well as sewage sludge containing a “large amount” of organic matter; showed an extremely high concentration of PBDEs (e.g. 3.2 ng L^{-1} tetra-BDE, 1.8 ng L^{-1} penta-BDE, and 11 ng L^{-1} hepta-BDE). TBBP-A concentrations recorded in this study ranged from <1 to 620 ng L^{-1}, and it was even found in treated leachate at <1 to 11 ng L^{-1}. Furthermore, relatively high correlation coefficients were observed between concentrations of each PBDE homologue group and chemical oxygen demand (COD) (R = 0.73, 0.90 and 0.92 for tri-, tetra- and penta- BDE homologues respectively) and UV260 (R = 0.80, 0.93 and 0.93 for tri-, tetra- and penta- BDE homologues respectively), both important indicators for DHM. The authors stated that DHM has the potential to enhance leachability

Table 1.8: Concentrations of brominated flame retardants in aqueous environments.

Compound	Environment	Concentrations (ng L^{-1})	Country
ΣPBDEs	Lakes (n=9)	0.042 – 0.073	UK [a]
Σ_6PBDEs	Lake	0.0211	USA [b]
ΣPBDEs	Estuary (surface)	0.000601 – 0.006492	USA [c]
ΣPBDEs	Estuary (bottom)	0.000351 – 0.004902	USA [c]
BDE-209	River	17 – 295	UK [d]
ΣPBDEs	River	2.312 – 4.292	France[e]
ΣHBCDD	Lakes (n=9)	0.08 – 0.27	UK [f]
ΣHBCDD	Lake	0.18 – 0.37	China [g]
ΣHBCDD	River	0.19 – 14	Japan[h]
ΣHBCDD	Rivers (n=3)	2.5 – 2100	Japan[i]
TBBP-A	Lakes (n=9)	0.14 – 3.2	UK [d]
TBBP-A	River	< 0.035 – 0.064	France[e]
TBBP-A	Lake	0.36 – 1.12	China [g]

[a] Yang et al., (2014)
[b] Streets et al., (2006)
[c] Sacks & Lohmann (2012)
[d] Cristale et al., (2013)
[e] Labadie et al., (2010)
[f] Harrad et al., (2009b)
[g] Xu et al., (2013)
[h] Ichihara et al., (2014)
[i] Oh et al., (2014)

of hydrophobic organic pollutants (HOPs) by complex interactions. The presence of DHM was shown to significantly raise the leachability of HOPs, once DHM concentrations exceed a critical micelle concentration. Hydrophobic single tail regions are sequestered to the centre of the micelles leaving the hydrophilic head regions in contact with the surrounding solvent. However, the study found no correlation between concentrations of TBBP-A and either UV260 or COD. The authors hypothesised that more hydrophobic HOPs have greater affinity to DHM and suggested that the relatively higher hydrophobicity of PBDEs relative to TBBP-A, may account for the observed enhanced leachability of PBDEs over TBBP-A. Osako et al., (2004) also suggested that this may be one reason why TBBP-A does not correlate with UV260 and COD. However, as Table 1.1 shows, the water solubility of TBBP-A is very similar to that of the lower PBDE homologues which did correlate with COD and UV260, and other factors are thus likely involved. Suzuki and Hasegawa, (2006) analysed concentrations of HBCDD (7 to 12 ng L^{-1}) and TBBP-A (0.3 to 540 ng L^{-1}) in landfill leachates sampled from the influents to WWTPs at five separate Japanese landfill sites.

Choi et al. (2009) conducted leaching tests for PBDEs, polybrominated biphenyls, polybrominated phenols and TBBP-A in plastic samples in the presence of DHM. Their results clearly show that BFRs can be leached by organic matter. While their experiments provide a valuable illustration of the importance of DHM in enhancing the leachability of BFRs, the authors also highlight that conditions within MSW landfills are more complicated, given the high organic matter loadings in leachate and complex interactions between a wide range of heterogeneous BFR waste, non-FR waste, sludge, etc..

Some plausible reasons why DHM has the ability to decrease pollutant/solid-phase interaction include: solubilisation, hydrolysis, catalysis, and photosensitisation mechanisms (Choi et al., 2009). Although it is logical to assume that only the BFRs distributed along the surface of a polymer can be leached by a solvent, other chemical engineering studies have reported sorption, diffusion, and permeation in the polymer matrix (Harogoppad and Aminabhavi, 1991; Gamst et al., 2003; Hansen, 2004; cited in Choi et al., 2009). Such interactions will likely involve multiple processes and vary in accordance with a variety of parameters such as temperature, solvent, and the molecular weight and morphology of the polymer (Choi et al., 2009).

Investigations into BFR leaching behaviours in three large scale lysimeters simulating early stage landfill sites in developing countries, have been conducted in Japan by Kajiwara et al., (2013a). Aerobic, semi-aerobic, and anaerobic conditions were explored. Leachate samples were collected from each lysimeter at bimonthly intervals during the first three and a half years and analysed for PBDEs, HBCDD and TBBP-A. HBCDD was readily leached from the waste early on in the experiment but ceased to be detected after 4 months. The authors propose that the HBCDD in the waste was flushed out by rainfall at the early phase of dumping. The total amount of BFRs leached was highest under anaerobic conditions. The highest concentrations of PBDEs in were in the leachate collected after 42 months under anaerobic conditions. Under aerobic condition, TBBP-A emissions slowly increased over time until reaching a maximum concentration at 24 months. However, under semi-aerobic and anaerobic conditions TBBP-A concentrations peaked within 2 months and decreased from then on until the end of the experiment.

Odusanya et al., (2009) reported concentrations of PBDEs in leachate collected from five MSW landfill sites without adequate liners in South Africa. Expressed as the sum of BDEs-28, -47, -66, -71, -75, -77, -85, -99, -100, -119, -153, -154 and -183, concentrations ranged from

8.4 to 54.8 ng ΣPBDEs L^{-1} across the five sites. The dominant congeners found in the leachate were BDEs-28, -47, -71 and -75. The site with the highest concentrations of PBDEs also had the highest COD value, further supporting the influence of DHM on leaching. More recently Daso et al., (2013) reported PBDE concentrations from leachate at three MSW landfill sites in Cape Town, South Africa. Leachate was collected on six occasions at bi-monthly intervals. Concentrations of the sum of BDEs-28, -47, -99, -100, -153, -154, -183 and -209 ranged from 45 to 17,953 ng ΣPBDEs L^{-1}, 2.25 to 164 ng ΣPBDEs L^{-1} and 13.3 to 9,360 ng ΣPBDEs L^{-1} for the three landfills.

Recently, Zhou et al., (2013) reported BFR concentrations from raw (ΣPBDEs 5.67 ng L^{-1}; TBBP-A 15.4 ng L^{-1}) and treated (ΣPBDEs <6.1 ng L^{-1}; TBBP-A <4.5 ng L^{-1}) landfill leachates from Laogang landfill site, Shanghai, China. Elsewhere in Asia, Kwan et al., (2013) reported PBDEs in leachate from ten MSW dumping sites located within eight tropical countries viz: Laos, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines, and Malaysia. Concentrations ranged from 3.7 to 133,000 ng ΣPBDEs L^{-1}. Debromination of PBDE technical mixtures (including BDE-209) is implied by the presence in leachate of congeners that are either absent from or present only in trace concentrations in commercial formulations (e.g., BDEs-208, -207, -206, -202, -188, -179, -49, -17/25, -8, and -1). Further discussion of such debromination follows in section 1.2.3.

Paxéus (2000) reported measurements of TCIPP in untreated landfill leachate from three MSW landfills in the Goteborg area, Sweden. Concentrations of TCIPP were in the range of 4000 to 50,000 ng L^{-1}. Concentrations of TCEP have been reported in both untreated leachate (<1,000 to 240,000 ng L^{-1}) and leachate leakage (<1,000 ng L^{-1}) collected from a former mining system sited directly below a German MSW landfill in which the underlying containment layer was known to have been breached (Schwarzbauer et al., 2002). In a German study of PFRs in groundwater, Regnery et al., (2010) reported concentrations of TCEP, TCIPP and TDCIPP in four leachate-affected monitoring wells and one groundwater pond next to a landfill site closed since 1968. The highest individual concentrations (>100 ng L^{-1}) were determined in groundwater polluted by infiltrating landfill leachate. The mean concentrations of TCEP (12 ng L^{-1} and 114 ng L^{-1}) and TCIPP (50 ng L^{-1} and 142 ng L^{-1}) were lowest at the deep monitoring wells (9 m and 7.6 m deep respectively) and highest (161 ng L^{-1} and 167 ng L^{-1}) and (267 ng L^{-1} and 256 ng L^{-1}) in the shallow monitoring wells (both 5 m deep). The highest TCEP concentrations were found in the groundwater pond (318 ng L^{-1} and 301 ng L^{-1}) while the highest TCIPP concentrations (343 ng L^{-1} and 335 ng L^{-1}) were found in groundwater of the shallow monitoring wells. Most recently, TCIPP was detected in a qualitative screening study of untreated landfill leachates at two closed modern engineered MSW landfills and one unlined MSW landfill with both active and closed sections in Norway (Eggen et al., 2010).

In 2000, Barnes et al., (2004) monitored groundwater from four wells sited along a transect down-gradient from a closed (1985) and unlined MSW landfill in Oklahoma, USA. Concentration of TCEP (40 ng L^{-1}) and TDCIPP (100 ng L^{-1}) are reported in the contaminated groundwater. The wells closest to the landfill showed the greatest concentrations, this is likely due to factors such as dilution, sorption and degradation having taken place further down-gradient. The detection of these PFRs fifteen years after the closure of the site is demonstrative of their persistence in landfill leachate. In Japan, Kawagoshi et al., (2002) reported concentrations of TCEP, TCIPP and TDCIPP in leachate collected from a storage pond from a sea-based MSW landfill as ranging between 100,000 to 140,000 ng L^{-1}, 100,000 to 140,000 ng L^{-1} and 100,000 to 120,000 ng L^{-1} respectively. Green et al. (2008) reported concentrations of TCEP (2,300,000 ng kg^{-1} to 5,500,000 ng kg^{-1}) TCIPP (9,500,000 ng kg^{-1} to 23,500,000 ng kg^{-1}) and TDCIPP (<250,000 ng kg^{-1} to 8,800,000 ng kg^{-1}) near a car demolition site in Norway. Sediment samples collected at a Norwegian landfill site from the upper sediments in the pump pit before leachate was transported to the WWTP, ranged from 27,000 ng kg^{-1} to 380,000 ng kg^{-1} for TCEP and from 1,500,000 ng kg^{-1} to 4,100,000 ng kg^{-1} for TDCIPP (Green et al. 2008). This contamination of sediments directly in the vicinity of waste treatment facilities demonstrates that they are a source of PFRs to the environment.

Another important route for emissions of FR in landfill leachate may occur after treatment at WWTP. As previously described, as part of leachate management, leachate is transported to WWTP for biological and chemical treatment. Due to their hydrophobic nature, over 90 % of PBDEs sequester into sewage sludge during wastewater treatment (Song et al., 2006). In the USA, Oliaei et al., (2010) reported concentrations of PBDEs in samples taken at the influent, effluent and sludges from a WWTP receiving leachates from landfill. The WWTP employed activated sludge (AS) as the second step in biological treatment. The activated sludge process uses air and a biological floc composed of bacteria and protozoa to degrade organic matter into carbon dioxide, water, and other inorganic compounds (Metcalf and Eddy, 2003).

Total PBDE concentrations from three different influents representing different industrial and domestic discharges to the WWTP ranged from 106.43 to 262.2 ng L^{-1}. The dominant congeners were BDE-209> 47> 99>100. Effluent samples detected PBDE concentrations in dissolved and particulate phases with concentrations for ΣPBDEs reported at 0.91 ng L^{-1}. More than 70 % of total PBDEs were in the particulate phase, with BDE-209 not detected in the dissolved phase. The dominant congeners were BDE-47> 99> 209. The ΣPBDEs in samples in final WWTP sludge was 931.18 ng/g (dry weight), the dominant congeners in sludge samples were BDE-209> 99> 47> 100. Widespread agricultural application of WWTP sludge has the potential to be an important emission pathway for hydrophobic BFRs, transferring PBDEs and HBCDD to soils, ground waters and surface waters (Oliaei et al., 2010). Additionally, WWTP sludges have a number of other disposal routes, for example, Chinese sludge disposal generally occurs via landfill burial (63 %), land application (15 %), incineration (2 %), building materials (3 %), and other (unspecified) methods (17 %) (Zeng et al., 2014). HBCDD has been reported in WWTP sludge, influents and effluents but only once specifically for landfill leachate-receiving WWTPs (Morris et al., 2004; Sukuki and Hasegawa, 2006; Ichihara et al., 2014; Zeng et al., 2014). Sukuki and Hasegawa, (2006) reported HBCDD landfill leachate-receiving WWTPs effluent values were < 2 ng L^{-1} for each diastereomer α-, β- and γ-HBCDD.

In Korea, Ryu et al. (2010) monitored a range of EDCs in samples collected from effluents at 11 WWTP in the Seoul metropolitan areas, three of which receive landfill leachate to treat. Two of the leachate-receiving WWTPs utilised activated sludge as the secondary biological treatment step and the other used biological nutrient removal (BNR) plants as the tertiary treatment step. BNR removes total nitrogen and total phosphorus from wastewater through the use of microorganisms under anaerobic-anoxic-aerobic processes (Metcalf and Eddy, 2003). All three WWTPs used chlorine as a disinfectant. Concentrations of TCEP in WWTP effluents ranged from 230 ng L^{-1} to 430 ng L^{-1}, while TCIPP ranged between 110 ng L^{-1} and 380 ng L^{-1}.

Due to their relatively low log K_{OW} values, (see Table 1.2), TCIPP and TCEP are not expected to bioaccumulate in the environment (EU RAR 2008a; EU RAR 2008b). However, their persistence and high polarity enable them to be potentially readily transportable through conventional landfill leachate receiving wastewater treatment systems. Membrane bioreactor treatment is reported to have no effect on decreasing concentrations of TCEP in WWTP effluents, suggesting that TCEP is relatively persistent during biologically-active filtration and/or MBR processes (Kim et al., 2007). However, membrane filtration processes employing reverse osmosis and nanofiltration showed excellent removal rates (>95 %) for TCEP (Kim et al., 2007).

1.2.3. Debromination and degradation.

There is strong evidence that BDE-209 debrominates over time, forming lower brominated PBDEs with stronger bioaccumulation characteristics and higher toxicity (Danon-Schaffer, 2010; Kajiwara et al., 2008, 2013b; Schenker et al., 2008; Stapleton and Dodder, 2008). Work by Danon-Schaffer and Mahecha-Botero (2010) details a simplified degradation/debromination pathway based on stepwise debromination of each homologue group of congeners to the next (lower) one, beginning with BDE-209 and extending ultimately to low molecular weight congeners (tri-BDEs, di-BDEs and mono-BDEs). PBDE congeners lose bromines due to reductive debromination, photolysis, and microbial degradation in anaerobic environments (Danon-Schaffer and Mahecha-Botero, 2010). Reported BDE-209 photodegradation half-lives range between <15 minutes up to 408 days, depending on the matrix with which it is associated and the radiation wavelengths (Stapleton, 2008). It is unclear to what extent degradation occurs in the natural environment as shielding effects likely limit the amount of UV light to which the PBDEs are exposed (Domínguez et al., 2011). Also of concern, Kajiwara et al. (2013b) showed that exposure to natural sunlight of textiles treated with Deca-BDE, resulted in the formation of polybrominated dibenzofurans (PBDFs) as products of photodecomposition. A maximum total PBDF concentration of 27,000 ng g^{-1} was reached after 329 days of exposure. This was approximately 10 times the initial concentration. The authors also reported that di- to hexa-BDF congener concentrations increased continuously throughout the study. Interestingly, textiles that contained approximately 4 % HBCDD by weight showed no substantial loss of any HBCDD diastereomers during the entire exposure period (371 days). This suggested that debromination and isomerisation of HBCDD diastereomers did not occur and that HBCDD is resistant to sunlight. However, this contrasts with the work of Harrad et al., (2009a) in which dust samples were exposed to light indoors for different periods of time with a control sample kept in darkness. Within the first week of exposure there was a significant shift from γ-HBCDD to α-HBCDD and evidence of HBCDD degradation in the presence of light. The experimental data suggested a rapid photolytically mediated shift in the diastereomer profile and a slower degradative loss of HBCDDs via elimination of HBr to degradation products pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs). The difference between the two studies may be an indication of the influence of the material with which the HBCDD is associated.

Analysis of dust samples from inside TV casings detected elevated concentrations of PBDEs. In one television studied, lower brominated homologues displayed elevated concentrations in dust relative to those in the plastic components (Takigami et al., 2008). While one explanation for this is that lower congeners transfer more efficiently via volatilisation and subsequent deposition to dust, another suggestion proposed by the authors was that the PBDEs detected in the dust might be transformed (e.g., through debromination and oxidation) during the transfer from components to dust. In a similar vein, Harrad et al., (2009a) reported that dust collected from within the casing of a HBCDD flame retarded TV showed a substantially higher ratio of γ-HBCDD to α-HBCDD than dust sampled at increasing distances from the source. This is consistent with a photolytically mediated shift in the diastereomer profile. Chen et al., (2010) reported elevated ratios of BDE-208:BDE-183 and BDE-208:BDE-209 in TV/PC display casings, and PC components sampled in South China. The authors attributed these ratios to the decomposition of higher brominated PBDEs during the process of manufacturing, use and/or recycling of PBDE-containing products, in addition to degradation in the environment. Elevated values of such ratios were also reported by Muenhor et al., (2010) in dust samples taken from e-waste storage facilities in Thailand. The authors suggest that debromination of BDE-209 to BDE-208 had taken place during the lifetime of the e-waste and further hypothesised that the elevated abundances of BDE-208 and of the other nona-BDEs (BDE-206 and BDE-207) found in their dust samples arose largely as a result of direct migration of such congeners from stored e-waste.

Finally, reductive debromination of deca- , nona- and octa-BDEs, to lower brominated congeners can occur in anaerobic environments (akin to landfill conditions) *via* microbial activity (Gerecke et al., 2005; He et al., 2006; Robrock et al., 2008). Gerecke et al., (2006) found that TBBP-A and HBCDD also underwent microbially mediated degradation under anaerobic conditions in digested sewage sludge, with the half-life of α-HBCDD almost twice that of β-HBCDD and γ-HBCDD. Additionally, it has been reported that BDE-209 and nona-BDEs can be debrominated by anaerobic sediment microbes (Parsons et al., 2004; Tokarz et al., 2008).

In Japan, Kawagoshi et al., (2002) tested the degradation of PFRs in leachate from a sea-based MSW landfill in a series of lab based experiments. The study found that TCEP, TCIPP and TDCIPP all showed low degradability and no decrease in the concentration of TCIPP was observed under anaerobic conditions. TCIPP was noted as being particularly stable in the leachate.

In summary, the available evidence suggests that the FR content of landfilled waste will likely change over time, as a result of a variety of degradation processes with the exception of TCIPP which has been shown to be very resistant to degradation in landfill leachate.

1.2.4. Abrasion and weathering.

Hale et al. (2002) conducted weathering experiments on BFR-treated PUF for several weeks under full sunlight conditions in summer. Typical daytime temperatures were as high as 30-35 °C and humidity generally exceeded 80 %. Disintegration of the surface of the PUF occurred within four weeks and resulted in small, low-density fragments easily dispersed by precipitation or wind. Moreover, weathered PUF fragments appeared to preserve the original constituent pattern of Penta-BDE.

Work by Webster et al. (2009) using environmental forensic microscopy, suggests that physical abrasion is a viable mechanism via which BDE-209 can migrate from consumer products to indoor dust. BDE-209 has a very low vapour pressure, therefore the authors hypothesised that abrasion is a more plausible transfer mechanism than volatilisation – particularly in dust samples containing highly elevated concentrations of BDE-209. This was supported by the heterogeneous distribution of the bromine in the dust samples. Furthermore, bromine-rich particles were not observed free in the dust but appeared to be embedded in a polymeric/organic matrix and associated with calcium. Calcium carbonate is a very common additive in plastics. This evidence supports the abrasion hypothesis in that BDE-209 is primarily present in dust samples containing highly elevated concentrations of this congener as inclusions in plastic particles. Given the conditions prevalent in landfills, it is not unreasonable to hypothesise that similar abrasive mechanisms will be at work on landfilled waste and thereby facilitate BFR emissions.

1.3. Data and research gaps.

Currently there appear little or no data on emissions of BFRs from waste soft furnishings, furniture and building insulation foams in the literature. Indeed only a few data exist concerning the emissions of FRs from landfill sites or during the incineration of MSW; as well as the potential for emissions during transport of waste to landfills or incinerators. The absence of data on these aspects constitute major research gaps. Figure 1.1 illustrates the various potential pathways via which BFRs may migrate from waste during transport to and storage at waste treatment facilities as well as during the treatment process itself. The bulk of research into BFR emissions from waste focuses on primitive e-waste dismantling and recycling conducted in areas such as Taizhou, Zhejiang province and Guiyu, Guangdong province in China (Chen et al., 2008; Chen et al., 2009; Han et al., 2009) and is therefore not immediately relevant to disposal of waste under controlled conditions.

A small number of emission chamber experiments have shown that volatilisation of BFRs from a range of products including soft furnishings and building insulation foams are amplified significantly at temperatures above 80 °C (Kajiwara and Takigami, 2013; Kemmlein et al., 2003). However, despite evidence that temperatures within landfills can reach up to 80-90 ˚C; to the authors’ knowledge there have been no experiments conducted that examine the effect of temperature on the leachability of FRs from waste. Concentrations of BFRs found in air around landfill sites are limited to four studies. Only Oliaei et al. (2010) reported data that suggests that landfill sites are a source of PBDEs to the environment. There is also a need for more studies which characterise concentrations of other BFRs such as HBCDD and the chlorinated PFRs in air at landfills, incinerators and other waste management sites.

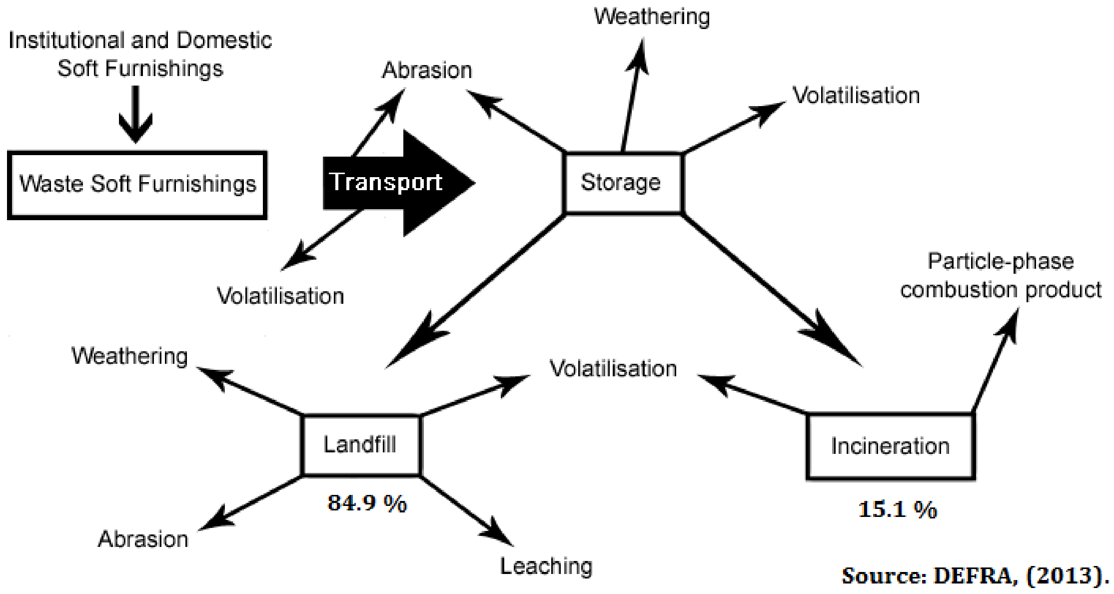

Figure 1.1: Potential BFR migration pathways from waste soft furnishings.

Additionally, further research into effluents from WWTPs that receive leachate from landfill is required to properly assess the potential contribution of emissions of FRs to ground waters, surface waters and drinking waters. Emissions of TCIPP via WWTP effluent is of particular concern due to its persistence in leachate and relatively high concentrations. To the author's knowledge there are have been no reports of HBCDD in effluents from landfill leachate receiving WWTPs.

As well as volatilisation and leaching, an additional migration pathway from waste of BFRs such as BDE-183 and BDE-209, is via fugitive emissions of dust to air by abrasion during waste unloading and/or compacting by on site vehicles. However, there have been no studies to date measuring the extent to which this occurs. Likewise, there exist no studies to date that examine the potential for fugitive (largely, but not exclusively particle-bound) emissions of FRs and as a result of the landfilling of residual bottom and fly ash generated by waste incineration.

As well as limited data on the extent and pathways of FR emissions during waste treatment, our understanding of the factors influencing such emissions is hampered by our limited knowledge of environmentally-relevant physicochemical properties of some FRs, e.g., aqueous solubility, and partition coefficients like K_{OW}, K_{OC}, and Henry's constant. While such physicochemical properties for lower brominated PBDEs are relatively well-characterised, those of BDE-209, TBBP-A, HBCDD, and “novel” BFRs like decabromodiphenyl ethane (DBDPE) are subject to greater uncertainty. Enhanced understanding of these properties – and of the influence on leaching of factors like climate - is needed to facilitate understanding of how BFRs are leached from waste materials in a landfill setting. For example, while Odusanya et al (2009) reported higher concentrations of PBDEs in landfill leachate in winter compared to summer; it still appears likely that hotter climates will enhance the leachability of BFRs in landfill. As a result, compared to much of North America and northern Europe; subtropical and tropical regions such as southern China, Laos, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines, and Malaysia are unlikely to display similar BFR concentrations in landfill leachate.

Further international variability in BFR concentrations in landfill leachate will likely arise due to different waste management practices. For example, the low concentrations detected in leachate from Japanese landfills may well be attributable to the fact that 80 % of MSW is incinerated in Japan. Hence, the proportion of Japanese landfill that is incinerator ash is high, and direct extrapolation of Japanese landfill leachate data to countries such as the UK where incineration is far less prevalent and BFR-containing waste is more likely landfilled untreated, appears unwise.

Given that in many (though not all) studies, BDE-209 is the dominant PBDE congener found in landfill leachates, this suggests that water solubility alone is not the primary factor driving BFR leaching from landfilled waste. Understanding what does drive BFR leaching is important; while there are no reported measurements of HBCDD concentrations in landfill leachates, the evidence for PBDEs suggests that leaching could constitute an appreciable pathway via which HBCDD and related BFRs migrate into the environment. Specifically, Li et al., (2012) estimated average annual emissions from a single urban landfill in Canada to be 3.5 tonnes ΣPBDEs year^{-1}.

Moreover, evidence for reductive debromination of BFRs by microbes under anaerobic conditions suggests this could also occur in landfill, resulting in some instances in more toxic and bioavailable compounds, particularly during phase 2 and 3 of a landfill’s leachate generation (Parsons et al., 2004; Gerecke et al., 2005, 2006; He et al., 2006; Robrock et al., 2008; Tokarz et al., 2008). While this hypothesis has yet to be verified fully; it is supported by the relatively higher abundances in landfill leachate of PBDE congeners that are absent from the commercial formulations (Kwan et al., 2013).

1.4. Conclusions.

The evidence presented here, reveals that to date there has been very little research into the extent of emissions of BFRs and PFRs from waste soft furnishings, furniture and insulation foams. The mechanisms via which FRs migrate from such waste materials remain far from completely understood, and current understanding is almost entirely based on the larger – but still far from complete – database on emissions from WEEE and in-use materials. While – in addition to the burgeoning database on BFR emissions resulting from informal e-waste recycling activities - evidence exists of elevated airborne concentrations of HBCDDs in the vicinity of a UK e-waste treatment facility together with the presence of BFRs (specifically PBDEs and TBBP-A) in landfill leachate; other studies of BFR emissions from regulated waste treatment activities remain few. Although BFRs are hydrophobic, evidence exists that their leachability from waste materials is substantially enhanced when DHM is present in the leachate. There is a need to enhance understanding of the factors influencing emissions and of the potential for BFR degradation under landfill conditions. Moreover, it is clear that more detailed characterisation of BFR and PFR concentrations in landfill leachate is required, to place its significance as a source to the environment into context against other emission pathways. For example, a study by Hope et al., (2011), reported the median ΣPBDE concentration in Oregon wastewater treatment plant effluents to be 43 ng L^{-1}. Landfill sites already constitute an enormous reservoir of FR-containing materials and commercial goods e.g. e-waste, building materials, carpets, furniture and upholstery fabrics. As a result, without careful management, such landfills will continue to act as substantial sources of FRs to the global environment, and the wisdom of continued landfilling of FR-containing waste is questionable. We suggest that remaining FR-containing waste products should be destroyed or managed in an environmentally sound manner. Given the reservoir of FRs already present in landfill, the need to diligently maintain landfills and monitor leachate collection systems well beyond the date of landfill site closure is emphasised. Such measures will help minimise not only release of FRs but those of other landfill contaminants. A thorough cost-benefit analysis of the relative economic and environmental implications of such actions is called for. While hitherto, scientific and societal focus has been on e-waste, evidence suggests that many of the same concerns exist regarding emissions from waste soft furnishings, furniture and insulation foams, and that studies to enhance our currently scant understanding of FR emissions from these important waste streams constitute an urgent research priority.

1.5. Project aims and objectives.

The main aim of this project is to study emissions of as a result of leaching – and to a lesser extent volatilisation – of PBDEs, HBCDDs, and halogenated PFRs from waste electronics, soft furnishings and building materials. The objective is to evaluate the potential contribution made by FR treated waste to overall emissions of such FRs. The emphasis is on landfilled FR treated waste. Another aim was to characterise the FR content of UK soft furnishings currently entering the waste stream.

The project will test the hypothesis that emissions of PBDEs, HBCDD and chlorinated PFRs to air and groundwater from treated end-of-life materials constitute an important source of these FRs to the environment. To test the project hypothesis and achieve its aims, an experimental programme comprising a series of controlled lab-based experiments involving leaching and volatilisation chambers were conducted. A range of waste materials were explored including textiles, furniture foams, building insulation foams and WEEE plastics. A range of landfill relevant parameters were explored to examine a wide spectrum of potential factors that may influence leaching. Furthermore, a range of waste curtains, carpets and furniture foams were sourced from locations across the UK and were screened and analysed for their FR content.

Chapter II: Sampling and Analytical Methodology.

Analytical methodology for determination of BFRs and PFRs in various abiotic samples studied in this thesis generally consists of four major steps: sampling, extraction, clean-up and analysis. In this chapter each of these steps will be discussed in detail. Validation of the developed and applied analytical procedures as well as the quality assurance/quality control measures employed in order to ensure the validity of the generated data will also be presented and explained.

2.1. Sampling.

2.1.1. Waste plastics samples.

One kg grab samples from two separate waste plastic streams; cathode ray tube housings from PC and TV monitors (CRT) and mixed small domestic appliances (SDA) were kindly donated by Sims Recycling Solutions. The SDA sample composed of a range of portable or semi-portable consumer electronic devices including computers, printers, video recorders, DVD players, digital cameras, mobile phones, toasters, stereo equipment, and other small kitchen appliances, to name a few. The SDA category may often contain some of the smaller large household appliances such as microwaves and electric ceiling fans for example. Both samples had been subjected to a size reduction step and were chipped to roughly 5-25 mm diameter.

2.1.2. Waste textile and polyurethane foam samples.

Fabric curtains treated with the HBCDD technical formulation were obtained from the National Institute for Environmental Studies (NIES), Tsukuba, Japan. Concentrations of HBCDDs in these curtains were previously reported at 18,000 mg kg^{-1} for α-HBCDD, 7,500 mg kg^{-1} for β-HBCDD and 17,000 mg kg^{-1} for γ-HBCDD (Kajiwara & Takigami et al., 2013).

A selection of end-of-life office and home curtains, carpets and polyurethane foams and upholstery fabrics from chairs and sofas were kindly donated from friends, family and neighbours across the UK. Some items were collected directly from waste piles at the University of Birmingham. Some items were generously donated by the Ladywood Furniture Project, Birmingham. The FR utilised by the manufacturer was unknown for all items prior to screening.

2.1.3. Building insulation foam samples.

XPS and EPS building insulation foams treated with the HBCDD technical formulation were obtained from the National Institute for Environmental Studies (NIES), Tsukuba, Japan. Concentrations of HBCDDs in these insulation foams were previously reported at 970 mg kg^{-1} and 33,000 mg kg^{-1} for α-HBCDD, 620 mg kg^{-1} and 6500 mg kg^{-1} for β-HBCDD and 3,900 mg kg^{-1} and 3,900 mg kg^{-1} for γ-HBCDD for EPS and XPS respectively (Takigami et al., 2014).

2.2. Test chamber experimental designs.

2.2.1. Leaching chamber experimental design.

Four distinct experimental scenarios were undertaken to examine the effects of: (a) contact time (single batch experiments); (b) duration of serial or periodic wetting and draining of waste (serial batch experiments); (c) temperature; and (d) pH level of the leaching fluid on the leachability of the target analyte from the sample material. In scenario (a) contact time, the treated sample is contacted once with the leaching fluid for a set predetermined time of either, 6 h, 24 h or 48 h. In scenario (b) serial batch, the sample is contacted with the leaching fluid for 168 h in total, with the resulting leachate being extracted from the contact vessel and replenished with fresh leaching fluid 6 times, at intervals of 6 h (batch 1), 24 h (batch 2), 48 h (batch 3), 72 h (batch 4), 96 h (batch 5) and 168 h (batch 6). The leachate was extracted from the contact vessel via pouring or draining through a 0.45 μm pore size glass fibre filter (Advantec, Japan), in which the contact vessel was inverted for approximately 5 mins to ensure as much leachate was removed as possible. In experiments on PUF, where leachate was retained within the foam, it was gently squeezed against the side of the contact vessel using a pre-cleaned stainless steel spatula. Each batch of leachate were analysed for analyte concentrations at the given intervals. PTFE bottles (500 mL) were used as contact vessels during controlled leaching experiments. The whole volume of the contact vessel was not completely filled with leaching fluid and as a result a headspace was present inside the contact vessel. In all textile experiments, 10 g of textile was contacted with 250 mL of Milli-Q purified, deionised water giving a liquid-solid ratio of 25:1 (v/w). In experiments on CRT plastics, 5 g of sample was contacted with 125 mL of Milli-Q water giving a liquid-solid ratio of 25:1 (v/w). In all experiments on foams (PUF, EPS and XPS) 1 g of sample was contacted with 100 mL of Milli-Q water giving a liquid-solid ratio of 100:1 (v/w).

Following addition of the sample and leaching fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired contact time. In scenario (c) experiments examining the influence of temperature, the contact vessels were not agitated and instead were submerged in a water bath for 24 hours at the desired temperature. In scenario (d) experiments were agitated at 200 rpm for 6 h and the initial pH of the leaching fluid before contact with FR materials was recorded. Each of the above leaching experiments were conducted in duplicate. The confidence of the results of these leaching experiments could have been increased further had triplicates or more been conducted. Experiments were limited to duplicates to allow for a greater throughput of laboratory experiments in the limited time available and to enable a more comprehensive study of FR leaching from a broader range of treated products.

2.2.2. Volatilisation chamber experimental design.

A cylindrical in-house designed and built test chamber was utilised for these investigations. Constructed from stainless steel with dimensions of 100 mm diameter and 200 mm height, the total chamber volume was 1,570,000 mm^3, with an internal surface area of 78,500 mm^2 (Rauert et al., 2014). Emissions in both the gas and airborne particulate phases were collected on a polyurethane foam (PUF) disc. The PUF disc used for collection of volatilised PFRs was placed halfway down the chamber supported on a wire mesh, to allow sufficient separation from the TCIPP treated PUF placed at the bottom of the chamber. The TCIPP treated PUF was cut into 50 mm x 50 mm x 40 mm cuboids and a 50 mm x 50 mm side was placed on the floor of the chamber leaving an exposed total surface area of 10,500 mm^2 (0.0105 m^2). After a preliminary test was conducted to ensure that quantifiable concentrations were detected, a test duration of 24 h was chosen. The chamber experimental design for these experiments is illustrated in Figure 2.1.

PUF discs were wrapped in aluminium foil to minimise any analyte contamination prior to extraction. All PUF discs were cleaned before use by pressurised liquid extraction (ASE 350, Dionex Europe, UK) using *n*-hexane:dichloromethane (1:1 v/v). The chamber was maintained at the desired temperature by immersion in a hot water bath with the chamber internal temperature monitored using a LogTag TRIX-8 temperature data logger (LoggerShop Technology, Dorset, UK). Each temperature batch (20 °C (293 K), 40 °C (313 K), 60 °C (333 K) and 80 °C (353 K)) was conducted in duplicate. Post experiment the chamber inner surface (but not the bottom of the chamber, which was in contact with the PUF sample) was rinsed with ethyl acetate and then combined with the PUF disc extract for each experiment before analysis.

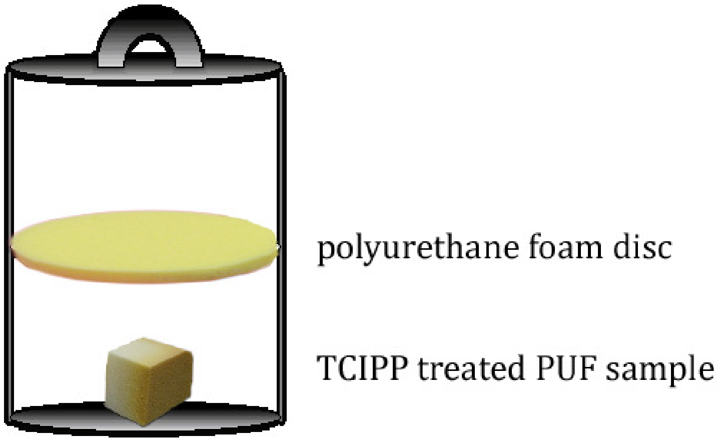

Figure 2.1: Schematic of volatilisation chamber experiment. (Modified from Rauert et al., 2014).

2.2.3. Preparation of leaching fluids for leaching experiments.

Leaching fluids were prepared using deionised distilled Milli-Q water. The pH levels were determined using a pH meter (Hanna, USA) and levels were corrected using either glacial acetic acid (Sigma-Aldrich) or sodium hydroxide (Sigma-Aldrich) solutions. Three pH levels were used in leaching experiments, acidic 5.8, slightly acidic 6.5 and alkaline 8.5. The pH levels used were based on real measured leachate pH levels that with only very few exceptions, lie in the range 5.8 to 8.5 (Renou et al. 2008). Dissolved humic matter (DHM) solution was prepared by dissolving Aldrich humic acid (sodium salt) in Milli-Q water. The solution was stirred for 5 minutes until total dissolution and then the pH was adjusted to the desired level, before finally it was centrifuged at 2000 rpm for 1 min. Concentrations of DHM solutions used in experiments were 100 mg L^{-1} and 1000 mg L^{-1}.

2.2.4. Sample preparation.

In preparation for the leaching experiments, curtain textiles were first cut into 5 x 5 cm squares and 10 g were weighed accurately before addition to the contact vessel. For PUF, EPS and XPS samples, small pieces of foam (approx. 10 mm × 10 mm × 10 mm, equivalent to ~ 1 g) were taken from random points from each sample and weighed accurately.

Chipped CRT and SDA plastic samples were manually separated from additional debris within the waste stream grab sample. Any wood, metal, or wires were removed prior to weighing.

When analysing carpet and curtain textile samples to determine initial concentrations, samples were cut into strips as small as possible (approx. 5 mm × 2 mm) and shaken thoroughly in a sealed plastic bag to ensure homogeneity. Approximately 1 g of each sample was taken from the complete mix.

When analysing PUF, EPS and XPS samples to determine initial analyte concentrations, small pieces of foam (approx. 5 mm × 5 mm × 5 mm) were taken from random points from each sample totalling approximately 50 mg. Approximately 1 g of PUF was used for an alternate pressurised liquid extraction screening method.

The TCIPP treated furniture PUF used in volatilisation experiments was carefully measured and cut into 5 cm x 5 cm x 4 cm subsamples and the weight of each cuboid recorded.

2.3. Extraction.

2.3.1. Leachate samples.

After contacting the leaching fluid, leachate was filtered through a 0.45 μm pore size glass fibre filter (Advantec, Japan) to remove any small particles or fibres of the FR material from the leachate and then spiked with either: 10 ng each of $^{13}C_{12}$-labelled α-, β-, and γ-HBCDDs; 50 ng each of $^{13}C_{12}$--labelled BDE-47, -99, -153 and -209; or 10 µg of d_{15}-labelled Tri-phenyl-phosphate (TPhP), as internal (or surrogate) standards for HBCDD, PBDEs, and TCIPP respectively. The collected filtrate was then extracted in series using 3 x 50 mL DCM by liquid-liquid extraction with mechanical shaking for 10 minutes each time. Approximately 5-10 mL 2% NaCl solution was used on leachates containing no DHM to enhance separation after extraction. When the NaCl solution was used on DHM containing leachates it produced an undesirable emulsion and reduced recovery efficiencies. The combined DCM extracts were dried via filtration through 5 g Na_2SO_4.

The recovery efficiency of three different filter types were explored in preliminary QA/QC trial experiments with HBCDD treated textile samples spiked with ^{13}C-labelled standards and the results are presented in Table 2.1. Glass fibre filters were selected for use in leaching experiments because they facilitated the best recoveries for all five HBCDD diastereomers.

Table 2.1: HBCDD diastereomer recoveries (%) using different filters. (n=2)

	Textile A			**Textile B**		
Filter / Diastereomer	**Mixed cellulose membrane**	**PTFE coated membrane filter**	**Glass fibre filter GC-50**	**Mixed cellulose membrane**	**PTFE coated membrane filter**	**Glass fibre filter GC-50**
α-HBCDD	64	94	101	94	93	117
β-HBCDD	0	43	102	0	42	88
γ-HBCDD	0	44	90	38	37	83
δ-HBCDD	0	75	91	0	81	93
ε-HBCDD	0	23	80	0	28	74

2.3.2. CRT leachate experiment filters.

An additional stage of extraction was performed on the glass fibre filters in experiments on PBDE treated CRT plastics. After filtration of the leachate, filters were desiccated in a glass desiccator jar containing silica gel and this was covered with aluminium foil to prevent any potential photo-degradation of PBDEs. Any visible particles of plastic retained on the filters were carefully removed with tweezers prior to extraction. Filters were then extracted via five cycles of vortexing and ultrasonication. The individual filters for each experiment and 5 mL of a positive azeotropic mixture of *n*-hexane:acetone (3:2 v/v) were added to a pre-washed test tube, vortexed for 1 min and sonicated for 5 mins. The supernatant was transferred to a clean tube, the extraction was repeated and both supernatants were combined (10 mL total) and vortexed for 1 min. The filter extract was then cleaned up by the same method employed for leachate extracts.

2.3.3. Volatilisation chamber samples.

TCIPP sorbed on the PUF discs were extracted using pressurised liquid extraction (ASE 350, Dionex Europe, UK). PUFs were packed into pre-cleaned 66 mL cells using pre-cleaned Hydromatrix (Varian Inc., UK) to fill the void. Each cell was fortified with 10 µg of d_{15}-labelled TPhP as internal (surrogate) standard prior to extraction with *n*-hexane:dichloromethane

(1:1 v/v) at 90˚C and 1500 psi. The cell was heated for 5 min, held static for 4 min and purged for 90 s, with a flush volume of 50%, for 3 cycles. Pressurised liquid extraction was preferred over traditional soxhlet for extraction due to shorter extraction time and lower solvent consumption.

2.3.4. Plastics samples.

PBDEs in hard plastic samples were extracted by means of modified version of the combined ultrasound assisted extraction (UAE) and vortexing method described by Ionas et al. (2012). In order to improve the extraction the hard plastics were submitted to a size reduction step to increase the contact surface area with the solvent. Due to the rigidity of the matrix and size of plastic chips obtained (approx. 2 mm × 5 mm × 5 mm) a Fritsch Pulverisette 0 cryo-vibratory micro mill (Idar-Oberstein, Germany) was employed for this purpose. The samples along with one 25 mm diameter stainless steel ball were added to the stainless steel grinding mortar (50 mL volume), submerged in liquid nitrogen until they reached the temperature of the surrounding liquid (-196 °C) – the liquid nitrogen was added in small increments until the nitrogen began to be expelled from the rear vent of the mill. It was then ground at a vibrational frequency of 30 Hz for 10 min and repeated 3-4 times. The resulting plastic particles varied in size, but typically had very small diameters and most passed though a 250 μm mesh aluminium sieve pre-rinsed with acetone, toluene and *n*-hexane.

The solvents used in the extraction process needed to provide an efficient extraction and at the same time, not dissolve the matrix and for this reason 10 mL *n*-hexane was used in pre-cleaned test tubes. Acetone, dichloromethane, toluene and a *n*-hexane:dichloromethane (9:1 v/v) mixture were all tried but had undesirable effects. The extraction process consisted of consecutive steps of vortexing for 1 min and ultrasonication for 15 min with 10 mL of *n*-hexane. This cycle of vortexing and ultrasonication was repeated 3 times. The samples were left in solvent overnight to ensure high recoveries. No destructive clean-up method was applied to ensure that no degradation of PBDEs took place. The test homogenised plastics were analysed in quintuplicate.

2.3.5. Building insulation foam samples.

50 mg foam and 5 mL of a positive azeotropic mixture of *n*-hexane:acetone (3:2 v/v) were added to a pre-washed test tube, vortexed for 1 min and sonicated for 5 mins before being centrifuged for 2 mins at 2000 rpm. The supernatant was transferred to a clean tube, the extraction was repeated and both supernatants were combined (10 mL total) and vortexed for 1 min. 1 mL of sample was then transferred to a clean tube and diluted using 9 mL *n*-hexane. Finally 10 μL of the first dilution was transferred to and diluted further using 90 μL methanol containing with 50 ng each of $^{13}C_{12}$-labelled α-, β-, and γ-HBCDDs as internal standards. The test foams were analysed in quintuplicate.

2.3.6. Polyurethane foam samples.

50 mg foam and 5 mL of ethyl acetate were added to a pre-washed test tube, vortexed for 1 min and sonicated for 5 mins before being centrifuged for 2 mins at 2000 rpm. The supernatant was transferred to a clean tube, the extraction was repeated and both supernatants were combined (10 mL total) and vortexed for 1 min. 1 mL of sample was then transferred to a clean tube and diluted using 9 mL ethyl-acetate. Finally 10 μL of the first dilution was transferred to and diluted further using 90 μL methanol containing 90 ng d_{15}-labelled TPhP as internal standard (x10,000 dilution in total). The test foams were analysed in quintuplicate.

Additionally a screening method for PBDEs and HBCDD using a pre-packed ASE cell was employed to extract PUF samples during the screening process. A 1 g PUF sample was added to a pre-packed ASE cell (Figure 2.2). The cells were then run using an ASE 350 (Dionex) extracting with dichloromethane:*n*-hexane (3:2 v/v) at 90°C, with three 5 minutes static cycles, with 2 minutes purge time.

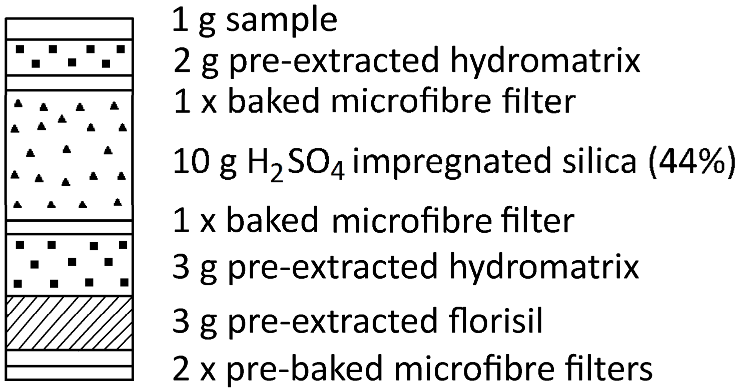

Figure 2.2: Pre-packed ASE cell.

2.3.7. Textile samples.

HBCDD diastereomers in the curtain textiles were extracted by means of the soaking extraction method described by Kajiwara et al. (2009). A textile sample (~0.2 g) was placed in 20 mL of dichloromethane in a glass bottle with a lid; the bottle was shaken by hand and then kept in the dark at room temperature for 2 days. A 200 μL aliquot of the crude extract obtained by this method was diluted with 20 mL toluene. A 50 μL aliquot of the toluene was spiked with 50 ng each of $^{13}C_{12}$-labelled α-, β-, and γ-HBCDDs as internal standards and was further diluted up to 1 mL with methanol. The test textiles were analysed in triplicate.

Additionally the same method as described above using the pre-packed ASE cell was employed to extract carpet and curtain textile samples during the PBDE and HBCDD screening process.

2.4. Clean-up.

2.4.1. Leachate PBDEs and HBCDD samples.

The dried extract was concentrated to 0.5 mL using a Zymark Turbovap II (Hopkinton, MA, USA) with solvent exchange to *n*-hexane before elution through a pre-cleaned acidified silica (22 % concentrated sulfuric acid, w/w for HBCDD and 44 % for PBDEs) and Na_2SO_4 column with 30 mL of *n*-hexane:DCM (9:1 v/v). The eluate was concentrated with solvent exchange to *n*-hexane before evaporation to incipient dryness, addition of either $^{13}C_{12}$-labelled BDE-100 or d_{18}-labelled γ-HBCDDs as recovery (or syringe) standards and dilution in methanol prior to analysis via LC-ESI-MS/MS or LC-APPI-MS/MS, for HBCDD and PBDEs respectively. Sample clean-up with sulfuric acid is necessary to remove interferences. Passing the concentrated extract through acid silica-filled columns was preferred for PBDE and HBCDD clean-up whenever possible due to short processing time.

2.4.2. Leachate TCIPP samples.

The dried extract was concentrated to 0.5 mL using a Zymark Turbovap II with solvent exchange to *n*-hexane before being loaded on to a 2 g pre-cleaned, activated florisil column and washed with 20 mL *n*-hexane. The TCIPP was then eluted using 20 mL ethyl acetate. The eluate was evaporated to incipient dryness and then reconstituted to 100 μL with addition of 25 ng d_{27}-labelled TnBP as recovery standards in methanol. Prior to analysis via LC-ESI-

MS/MS the samples underwent further stages of dilution in which a 10 μL aliquot was taken and diluted with 990 μL of methanol and then the step repeated again to yield a 100,000 times dilution. This was necessary due to the very high concentrations of TCIPP in the sample.

A QA/QC trial experiment was conducted in duplicate to assess the recovery efficiencies of native TCIPP and d_{15}-labelled TPhP IS. A 2 g pre-cleaned, activated florisil column was washed with 10 mL dichloromethane before loading with 1 μg each of the above native and IS. The florisil was then washed with 20 mL *n*-hexane and this was collected, evaporated and reconstituted in methanol for analysis. The TCIPP was then eluted using 2 × 15 mL ethyl acetate and both were separately collected, evaporated and reconstituted in methanol for analysis. The results of the collected *n*-hexane wash and two ethyl acetate elutions are provided in Table 2.2. The quantity of recovered native TCIPP and IS in the *n*-hexane wash was < 5 % and the majority was eluted within the first 15 mL of ethyl acetate. As above, it was necessary to dilute samples prior to analysis.

Table 2.2: TCIPP and d_{15}-TPhP (IS) recoveries (%) in clean-up QA/QC trial experiment performed in duplicate.

Stage/ Target analyte	*n*-hexane wash	1st ethyl acetate elution	2nd ethyl acetate elution	*n*-hexane wash	1st ethyl acetate elution	2nd ethyl acetate elution
TCIPP	1.8	89	4.1	2.3	92	3.9
d_{15}-TPhP (IS)	0.96	91	3.6	1.2	94	2.8

2.4.3. Volatilised TCIPP samples.

The dried extract was concentrated to 0.5 mL using a Zymark Turbovap II with solvent exchange to *n*-hexane before being loaded on to a 2 g of pre-cleaned, activated florisil column and washed with 20 mL of *n*-hexane. The TCIPP was then eluted using 20 mL ethyl acetate. The eluate was evaporated to incipient dryness and then reconstituted to 100 μL with addition of 25 ng d_{27}-labelled TnBP as recovery standard and dilution in methanol prior to analysis via LC-ESI-MS/MS.

2.5. Analysis.

2.5.1. LC-ESI-MS/MS analysis for determination of HBCDD.

Contact time and serial batch experiments on HBCDD treated textiles were conducted at the National Institute for Environmental Studies, Tsukuba, Japan. HBCDD diastereomers were identified and quantified by means of an Alliance 2695 liquid chromatograph equipped with a Quattro Ultima triple quadrupole mass spectrometer (Waters, Tokyo, Japan).

Further analysis of target HBCDD diastereomers was conducted at The University of Birmingham. They were separated using a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a SIL-20A autosampler, and a DGU-20A3 vacuum degasser. A Varian Pursuit XRS3 C18 reversed phase analytical column (150 mm x 4.6 mm i.d., 3 μm particle size) was used for separation of target HBCDDs (α-, β-, γ-). A mobile phase program based upon (mobile phase A) methanol:water (1:1 v/v) and (mobile phase B) methanol at a flow rate of 0.18 mL min^{-1} was applied for elution of the target compounds, as described in Table 2.3 and Figure 2.3.

Table 2.3: Gradient program for HPLC elution of HBCDD diastereomers.

Time (min)	% Mobile Phase A	% Mobile Phase B
0.00	50	50
4.00	0	100
9.00	0	100
10.00	12	88
10.01	50	50
14.00	50	50

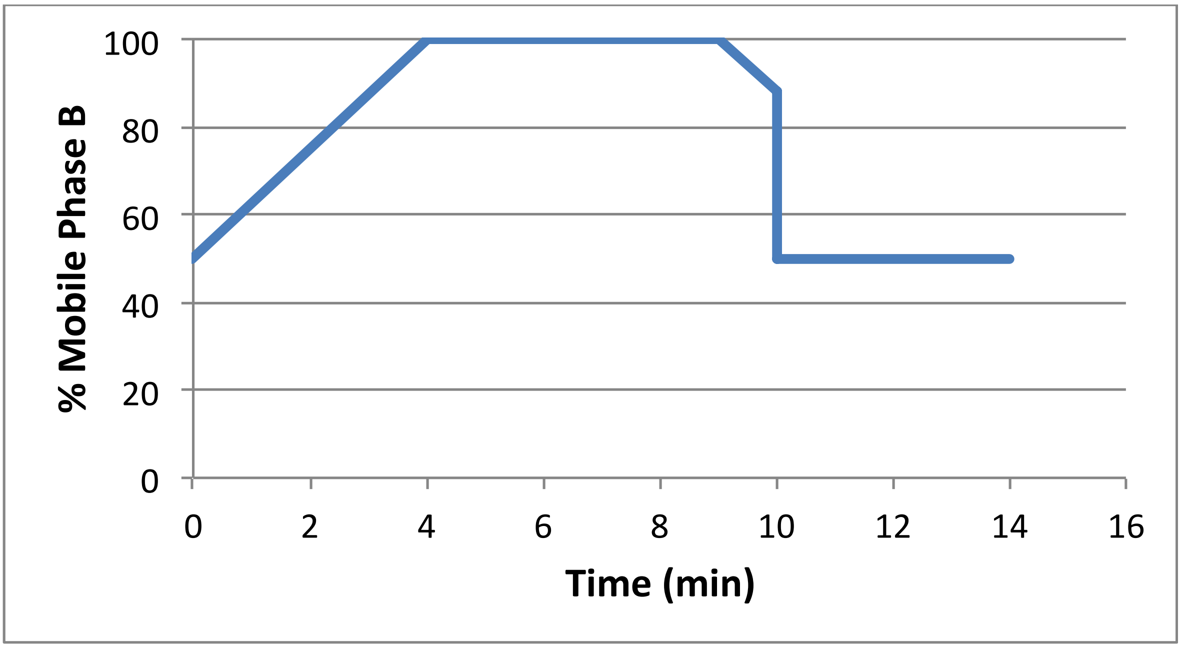

Figure 2.3: Mobile phase gradient program used for HBCDD analysis.

Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an ESI ion source operated in negative ionisation mode. MS/MS detection, operated in multiple reaction monitoring (MRM) mode, was used for quantitative determination of the HBCDD diastereomers and their ^{13}C-, and d_{18}- labelled analogues. Table 2.4 lists the optimised MS/MS parameters and Table 2.5 lists the ion transitions monitored for the HBCDD diastereomers, labelled internal standards (IS) and recovery determination standard (RDS).

Table 2.4: Optimised MS/MS parameters for the analysis of HBCDDs on LC-MS/MS.

Parameter (units)	Value	Parameter (units)	Value
Curtain gas (a.u)	30	Declustering potential (V)	-12
Collision gas (a.u)	5	Focussing potential (V)	-250
Ion spray voltage (V)	-4500	Entrance potential (V)	-10
Temperature (°C)	450	Collision energy (eV)	-40
Ion source gas 1 (a.u)	55	Collision cell exit potential (V)	-6
Ion source gas 2 (a.u)	60	Dwell time (msec)	200

* a.u = arbitrary units

Table 2.5: Parent to product ion transitions (m/z) monitored for native HBCDD diastereomers, IS and RDS.

Diastereomer	Ion transition (*m/z*)
α-, β-, γ-HBCDD	640.6 → 78.9
^{13}C α-, β-, γ-HBCDD *(IS)*	652.4 → 79.0
d_{18} γ-HBCDD *(RDS)*	657.6 → 78.9

2.5.2. LC-APPI-MS/MS analysis for determination of PBDEs.

Target PBDEs were separated with a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a SIL-20A autosampler, and a DGU-20A3 vacuum degasser. A Varian Pursuit XRS3 (Varian, Inc., Palo Alto, CA) C18 reversed phase analytical column (250 mm x 4.6 mm i.d., 3 μm particle size) was used for separation of target PBDEs (47, 85, 99, 100, 153, 154, 183 and 209). A mobile phase program based upon (mobile phase A) 1:1 methanol/water and (mobile phase B) toluene:methanol (1:4 v/v) at a flow rate of 0.4 mL min^{-1} was applied for elution of the target compounds, as described in Table 2.6 and Figure 2.4.

Table 2.6: Gradient program for HPLC elution of PBDE congeners.

Time (min)	% Mobile Phase A	% Mobile Phase B
0.00	15	85
20.00	0	100
30.00	0	100
30.01	15	85
35.00	15	85

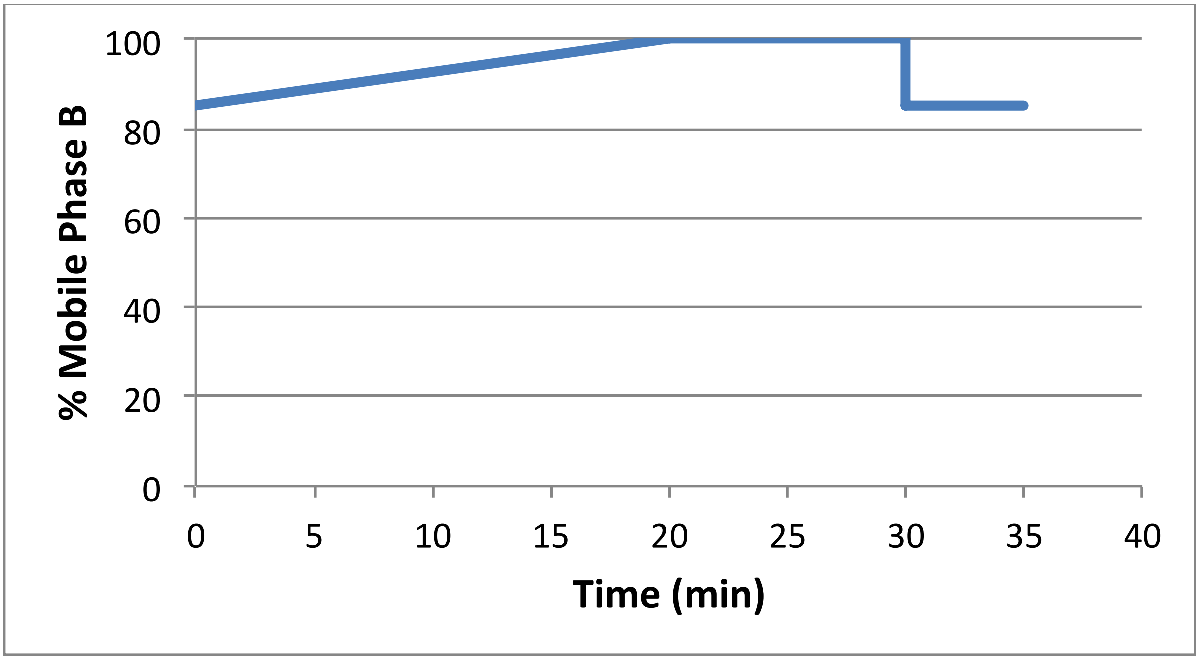

Figure 2.4: Mobile phase gradient program for PBDE analysis.

Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an APPI ion source operated in negative ion mode. MS/MS detection, operated in MRM mode, was used for quantitative determination of the native and labelled ^{13}C-PBDE congeners. Table 2.7 lists the optimised MS/MS parameters and Table 2.8 lists the ion transitions monitored for the PBDE congeners, labelled internal standards (IS) and recovery determination standard (RDS).

Table 2.7: Optimised MS/MS parameters for the analysis of PBDEs on LC-MS/MS.

Parameter (units)	Value	Parameter (units)	Value
Curtain gas (a.u)	25	Declustering potential (V)	-5
Collision gas (a.u)	11	Focussing potential (V)	-250
Ion spray voltage (V)	-1250	Entrance potential (V)	-12
Temperature (^{o}C)	400	Collision energy (eV)	-75
Ion source gas 1 (a.u)	60	Collision cell exit potential (V)	-8
Ion source gas 2 (a.u)	55	Dwell time (msec)	100

* a.u = arbitrary units

Table 2.8: Parent to product ion transitions (m/z) monitored for native PBDE congeners, IS and RDS.

Congener	Ion transition (*m/z*)
BDE-47	420.9 → 78.6
^{13}C BDE-47 *(IS)*	432.9 → 78.8
BDE-85, -99, -100	500.8 → 78.6
^{13}C BDE-99 *(IS)*; 100 *(RDS)*	512.9 → 80.6
BDE-153, -154	578.8 → 78.6
^{13}C BDE-153 *(IS)*	590.7 → 78.8
BDE-183	658.6 → 78.6
BDE-209	486.6 → 78.8
^{13}C BDE-209 *(IS)*	494.7 → 80.6

2.5.3. LC-ESI-MS/MS analysis for determination of PFRs.

PFRs were identified and quantified by means of a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a SIL-20A autosampler, and a DGU-20A3 vacuum degasser. A Varian Pursuit XRS3 C18 reversed phase analytical column (150 mm x 4.6 mm i.d., 3 μm particle size) was used for separation of target PFRs. A mobile phase program based upon (mobile phase A) 1:1 methanol/water and (mobile phase B) methanol at a flow rate of 0.18 mL min^{-1} was applied for elution of the target compounds, as described in Table 2.9 and Figure 2.5.

Table 2.9: Gradient program for HPLC elution of HBCDD diastereomers.

Time (min)	% Mobile Phase A	% Mobile Phase B
0.00	50	50
4.00	0	100
9.00	0	100
10.00	12	88
10.01	50	50
14.00	50	50

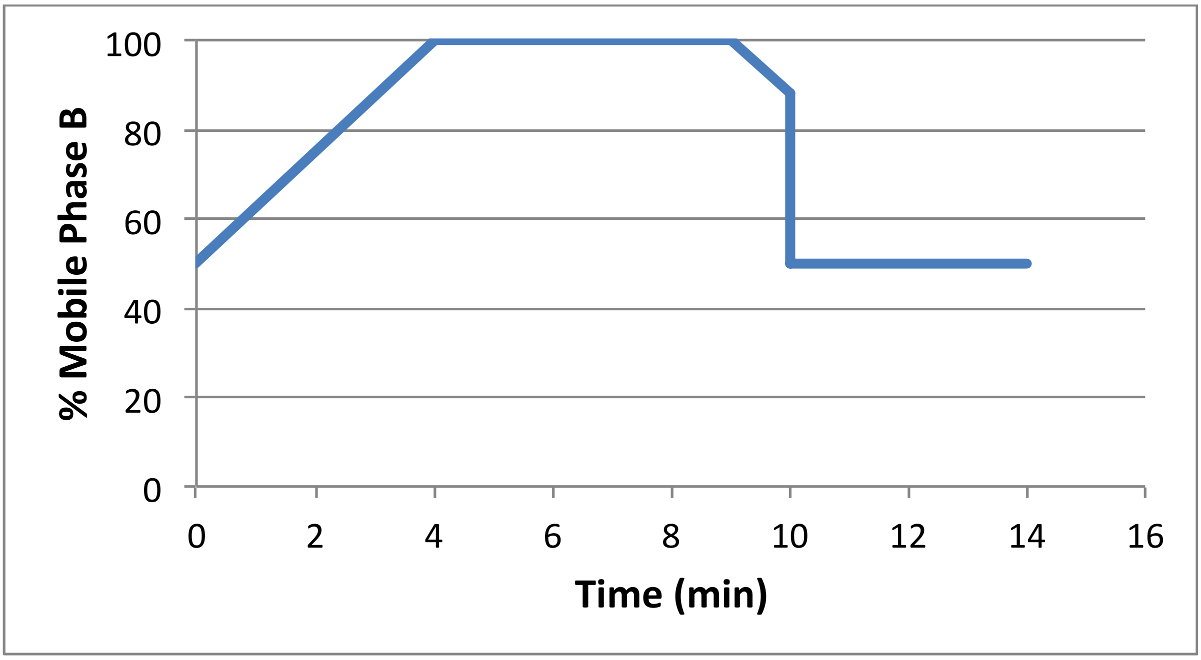

Figure 2.5: Mobile phase gradient program used for PFR analysis.

Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an ESI ion source operated in positive ionisation mode. MS/MS detection, operated in multiple reaction monitoring (MRM) mode, was used for quantitative determination of the PFRs. Table 2.10 lists the optimised MS/MS parameters and Table 2.11 lists the ion transitions monitored for the PFR compounds, labelled internal standards (IS) and recovery determination standard (RDS).

Table 2.10: Optimised MS/MS parameters for the analysis of PFRs on LC-MS/MS.

Parameter (units)	Value	Parameter (units)	Value
Curtain gas (a.u)	30	Declustering potential (V)	-20 / -50 / -28
Collision gas (a.u)	5	Focussing potential (V)	-365 / -400
Ion spray voltage (V)	-4500	Entrance potential (V)	-10
Temperature (^{o}C)	450	Collision energy (eV)	-30
Ion source gas 1 (a.u)	55	Collision cell exit potential (V)	-6
Ion source gas 2 (a.u)	60	Dwell time (msec)	150

* a.u = arbitrary units

Table 2.11: Parent to product ion transitions (m/z) monitored for native PFRs, IS and RDS in LC-MS/MS analysis.

Target compound	Ion transition (*m/z*)
TCIPP	326.6 → 99.1
TCEP	284.9→99.1
TDCIPP	430.9→99.1
d_{15} TPhP *(IS)*	342.2→82.2
d_{27} TnBP *(RDS)*	294.4→ 102.1

2.5.4. GC-ECNI/MS analysis for determination of PFRs in waste soft furnishings and furniture polyurethane foam samples.

The screening of waste soft furnishings and furniture PUFs for PFRs was performed on an Agilent 6890 GC coupled to an Agilent 5973 MS on a 25 m × 0.22 mm × 0.25 mm HT-8 column operated in electron impact ionisation (EI) mode. Injection was performed in pulsed pressure 14.3 psi until 1.5 min and purge flow to split vent of 50 mL min^{-1} after 1.25 min. The GC temperature program was 90 °C, hold 1.25 min, ramp 10 °C min^{-1} to 240 °C, ramp 20 °C min^{-1} to 310 °C, hold 16 min. Helium was used as a carrier gas with a flow rate of 1.0 mL min^{-1}. The mass spectrometer was run in selected ion monitoring (SIM) mode. Dwell times ranged between 20 and 30 ms. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively and the electron multiplier voltage was at 2200 V. d_{15}-labelled TPhP was used as an internal standard to quantify triethyl phosphate (TEP), tri-n-propyl phosphate (TnPP), tri-iso-butyl phosphate (TiBP), TnBP, TCEP, TCIPP, tri (2-butoxyethyl) phosphate (TBEP), TPhP, TDCIPP and tri-cresyl phosphate (TCP). The ion transitions (m/z) monitored for native PFRs, and d_{15}-labelled TPhP (IS) are listed in Table 2.12.

Table 2.12: Parent to product ion transitions (m/z) monitored for native PFRs, IS and RDS in GC-ECNI/MS analysis.

Target compound	Ion transition (*m/z*)
TEP	155
TnPP	183
TiBP	155→211
TnBP	155→211
TCEP	251 → 249
TCIPP	279→277
TBEP	199→299
TPhP	379→381
TDCIPP	325→326
TCP	367→368
d_{15} TPhP *(IS)*	339→341

2.5.5. Rationale for LC-MS/MS use for analysis.

It has been reported previously that thermal isomerisation and degradation of HBCDD diastereomers occurs at the temperatures used during the GC/MS; i.e. above 240 ˚C (Budakowski and Tomy, 2003, Morris et al., 2006; Köppen et al., 2008). Therefore, diastereomer-specific analysis of HBCDD is impossible using GC/MS techniques. Because no high temperatures are required, LC-MS/MS is considered the method of choice (Covaci et al., 2007) for diastereomer-specific determination of HBCDD. LC-MS/MS analysis also allows for the use of isotopically labelled HBCDD diastereomers as internal standards which perform a dual role by compensating for: (a) any variability in instrumental response of the mass spectrometer between injections and (b) matrix related ion suppression or enhancement effects that can occur in the ion source (Tomy et al., 2005; Abdallah et al., 2008b).

Historically, PBDEs have been analysed using GC-MS in electron-capture negative ionisation (ECNI) mode, monitoring the bromine ions fragments (m/z 79 and 81) (Covaci et al., 2007). However, only the bromine ions are monitored, therefore labelled analogues are indistinguishable, with the exception of ^{13}C-BDE 209 which produces $[C_6Br_5O]$- ions from cleavage of the ether bond (Björklund et al., 2003). Electron ionisation (EI) permits the use of isotopically labelled internal standards but lacks sensitivity for congeners containing greater than six bromine atoms. BDE-209 is known to suffer thermal degradation on GC, requiring a meticulously clean injection port and shorter GC columns (Abdallah et al., 2009), as well as injection techniques that minimise time spent in the heated injection zone (Covaci et al., 2007).

Therefore, more recently the measurement of PBDEs via LC-MS/MS using an atmospheric pressure photoionisation (APPI) source has become a more viable option (Debrauwer et al., 2005; Riu et al., 2006; Lagalante and Oswald, 2008; Abdallah et al., 2009). The UV source within the APPI source initiates ionisation of the molecules of a doping agent, and the subsequent radical cation formation allows nonpolar molecules (e.g. PBDEs) to be ionised that otherwise cannot be analysed by electrospray ionisation (ESI) or atmospheric pressure chemical ionisation (APCI) methods on the LC-MS/MS (Abdallah et al., 2009). Negative ionisation mode is more sensitive for the higher brominated compounds, so is more suited for the analysis of BDE-209, as the high electron affinity of the bromine ion means the more brominated the compound, the easier the electron capture and greater sensitivity (Debrauwer et al., 2005). However, in negative ionisation mode a signal is not observed for the di- to tri-PBDEs and only a low signal for the tetra-BDEs (Debrauwer et al., 2005). Therefore, this method is only suitable for the tetra to deca PBDE congeners but most importantly eliminates the degradation of BDE-209 observed in GC/MS methods. The CRT plastic samples were predominantly treated with BDE-209, and thus LC-MS/MS using an APPI source was the method used in this work.

There are several techniques available for the detection and measurement of PFRs in extracts: GC-ECNI/MS-EI, GC with flame photometric detector (GC-FPD), GC with Nitrogen Phosphorous Detector (GC–NPD), GC with atomic emission detection (AED), GC with pulsed flame photometric detector (GC-PFPD), GC with inductively coupled plasma analysis (GC-ICP-MS) and LC–MS/MS.

The disadvantages of NPD detection are an unsatisfactory selectivity for PFRs and that NPD does not offer the possibility for positive identification (García-López et al., 2009). GC-ECNI/MS-EI, is a more powerful identification tool with a higher selectivity and the ability to use isotopically labelled compounds for quantification (Björklund et al., 2004). However a disadvantage of GC-ECNI/MS-EI is the extensive fragmentation of alkylated phosphates that disables a proper identification. GC-MS-PICI can identify the alkylated phosphates but has a limited sensitivity (García-López et al., 2009; Carlsson et al., 1997; Björklund et al., 2004).

GC-AED requires separate injections for oxygen, phosphorus, and carbon/chlorine determination. GC-ICP-MS provides less complex chromatograms, while offering similar recoveries and limits of detections (García-López et al., 2009).

There are no comparative studies available for the analysis of the chlorinated PFRs by GC-ECNI/MS-EI vs LC-MS/MS. There are only comparative studies for analysis of the diester metabolites with LC-MS/MS vs. GC-MS/MS and these show a good correlation between the results (Van den Eede et al., 2013). Both GC-MS and LC-MS/MS analysis for the chlorinated PFRs achieve comparable sensitivity (i.e. low LODs) and accuracy (comparable results of SRM2585) (Brandsma et al., 2013b).

While GC-ECNI/MS-EI inherently provides narrower peaks and a higher number of theoretical plates/peak, LC-MS/MS provides more selectivity *via* monitoring precursor and fragment ions for each compound in addition to higher capacity for sample loading and better accommodation of high analyte concentrations due to a wider linear range. It also shows more tolerance for slightly contaminated samples rather than the GC-MS which requires the laborious process of cleaning the source and changing the liner after each contaminated or highly concentrated sample. Therefore, since the leachate samples were likely to show large concentrations of TCIPP and may contain some extraneous interfering matter even after clean up, this is the main rationale behind the choice of LC-MS/MS for PFR samples in this study.

In view of the above, LC-MS/MS was the method of choice for all target analytes in this study.

2.5.6. Rationale for GC-MS use for analysis.

GC-MS was only used in the screening for PFRs in waste textiles, carpets and furniture foam samples. It was used because of pre-existing and established method set up and development for a wide range of PFRs (Van der Eede, et al., 2011; Brommer, et al., 2012). At the time of screening the LC-MS/MS method was still in development at the University of Birmingham.

2.6. Validation and QA/QC criteria.

2.6.1. Chromatographic selectivity.

For a given chromatographic peak to be identified as a target compound, the following criteria were required to be met. Firstly, the relative retention time (the ratio of the retention time of the analyte to that of its corresponding internal standard) of the analyte in the sample solution had to match that present in the calibration standard within a specified tolerance of ± 2.5 % (EC Directive 2002/657/EC). Secondly, for analytes with the same monitored ion transitions, i.e. PBDE isomers and HBCDD diastereomers, appropriate separation between eluting analyte peaks had to be achieved. Specifically, the peak 'valley' between eluting peaks had to be <20% of the smallest peak height. Concentrations of TCIPP, and TDCIPP were calculated as the sum of all isomers, however the third TCIPP isomer was not measured because of its minor importance, <3%.

2.6.2. Instrument calibration.

A full five point calibration was conducted for each of the studied compounds containing native analytes, labelled internal standards (IS) and labelled recovery determination standards (RDS), to assess the linearity of the MS response. Concentrations of the five PBDE, HBCDD and TCIPP calibration standards are listed in Table 2.13. The calibration standards were run on the LC-MS/MS with every batch of samples before and after the list of samples for a short sample run list, or after every 20-30 samples for a longer sample list, to assess any instrumental drift throughout the analysis. The same IS and RDS standard solutions used for fortification of samples were used for preparation of the calibration standards and when a new IS or RDS standard was prepared, new calibration standards prepared with it, to minimise any inter-standard concentration variation. The calibration standards were also prepared on a regular basis (monthly to bi-monthly, depending on instrument use) in amber vials, and kept in the refrigerator (4 ˚C) when not in use, to reduce any analyte degradation or inter-conversion caused by UV light or age of solution. The BDE-47, ^{13}C BDE-47, BDE-209, and ^{13}C BDE-209 congeners have a higher limit of detection on the LC-MS/MS. All samples and calibration standards were thus fortified with higher concentrations of labelled ^{13}C BDE-47 and ^{13}C BDE-209, and final concentrations of the PBDE IS were in the ratio 4:1:2 for ^{13}C BDE-47, -99, -153, and -209 respectively.

Table 2.13: Concentrations of analyte, IS and RDS compounds in PBDE, HBCDD and PFR calibration standards.

	PBDE Natives (ng mL^{-1})	^{13}C BDE-47 (IS) (ng mL^{-1})	^{13}C BDE-99, -153 (IS) (ng mL^{-1})	^{13}C BDE-209 (IS) (ng mL^{-1})	^{13}C BDE-100 (RDS) (ng mL^{-1})
Std A	20	1000	250	500	200
Std B	50	1000	250	500	200
Std C	200	1000	250	500	200
Std D	500	1000	250	500	200
Std E	900	1000	250	500	200
			HBCDD Natives (ng mL^{-1})	**^{13}C- HBCDD (IS) (ng mL^{-1})**	**d$_{18}$ γ-HBCDD (RDS) (ng mL^{-1})**
Std A			2	20	20
Std B			5	20	20
Std C			20	20	20
Std D			50	20	20
Std E			100	20	20
	TCIPP Native (ng mL^{-1})	**TDCIPP Native (ng mL^{-1})**	**TCEP Native (ng mL^{-1})**	**d$_{15}$- TPhP (IS) (ng mL^{-1})**	**d$_{27}$-TnBP (RDS) (ng mL^{-1})**
Std A	50	50	50	100	500
Std B	100	100	100	100	500
Std C	400	400	400	100	500
Std D	1000	1000	1000	100	500
Std E	2000	2000	2000	100	500

These five calibration standards were 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). RRF is calculated as in equation 2.1.

Equation 2.1: $RRF = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{IS}}{C_{NAT}}$,

Where A_{NAT} is the peak area for the native compound (i.e. the ^{12}C or ^{1}H isotope of the target compound. The term is used to distinguish it from the ^{13}C or deuterated isotope used as internal or recovery determination standards); A_{IS} is the peak area of the internal standard; C_{NAT} is the concentration of the native compound; and C_{IS} is the concentration of the internal standard. The percent relative standard deviation (%RSD) of the RRFs calculated for each target compound at the five points of its calibration curve did not exceed 5 %.

Calibration standard B was injected before and after each batch of ten samples. The average RRFs of the target compounds from these two injections are calculated (These must be within ± 25 % of the average RRFs obtained for that standards in the initial 5-point calibration) and used for calculating the concentrations of the target compounds in samples of this batch using equation 2.2:

Equation 2.2: Concentration = $$\frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS}$$,

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; M_{IS} = mass of internal standard added to sample (ng) and *SS* = sample size (L or g).

2.6.3. Recovery determination (syringe) standard (RDS).

The recoveries of IS during sampling or sample preparation were determined relative to the RDS added to the samples just before MS analysis. In this study, d_{18} γ-HBCDD was used as RDS for α-, β-, γ- HBCDDs, while ^{13}C-BDE100 was used as RDS for PBDEs and **d_{27}**-TnBP was used as RDS for TCIPP, TDCIPP and TCEP. The recoveries of the IS in each sample were calculated using equation 2.3:

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

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 before and after this batch of samples); $(C_{IS}/C_{RDS})STD$ = 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.

2.6.4. Accuracy and precision.

The principal means of determining method accuracy is *via* analysis of one or more certified or standard reference materials (CRMs or SRMs) or *via* inter-laboratory comparisons. There were no known CRMs or SRMs available for PBDEs, HBCDD or TCIPP in aqueous solutions, nor were there any available for TCIPP in air.

Two CRM were used in determining method accuracy in the analysis of PBDEs from plastics; ERM EC590-20G (Low density polyethylene; LDPE) and ERM EC591-20G (Polypropylene; PP). Five replicate analyses of each CRM were conducted before commencement of analysis of any plastic samples and satisfactory recovery data was obtained for these analyses. The mean concentration ± standard deviation (SD), % RSD and certified PBDE values are listed in Table 2.14. As the % RSDs are in all instances below 20 %, the repeatability of the method is acceptable (EC Directive 2002/657/EC). The measured concentration values for ERM EC590-20G (within the limit of the standard deviation) fall within the certified values for all target analytes, except for BDE-47, BDE-100 and BDE-209. The difference in the BDE-100 and BDE-209 value ranges are within ± 10% of the limit of the certified value hence falls within suitable precision criteria and the measurements of the ERMEC590-20G CRM show the method has suitable trueness, precision, and accuracy i.e. is fit for purpose (EC Directive 2002/657/EC). The measured concentration values for ERMEC591-20G (within the limit of the standard deviation) fall within the certified values for all analytes, except for BDE-47 and BDE-99. The difference in the BDE-99 value range is within ± 10% of the limit of the certified value hence falls within suitable precision criteria and the measurements of the ERMEC591-20G CRM show the method has suitable trueness, precision, and accuracy i.e. is fit for purpose (EC Directive 2002/657/EC).

To the author's knowledge, there were at the time of this work, no known SRM or CRM available for HBCDD treated textile or foam materials. However analysis of textiles, EPS and XPS foams (n=5) could be compared to previously conducted and published analyses on the same materials by (Kajiwara and Takigami, 2013; Takigami et al., 2014). In all cases, five replicate analyses were conducted and compared to the previously published values and were found to be satisfactory. The mean concentration ± standard deviation (SD), % RSD and published HBCDD values are provided in Table 2.15. The % RSDs are in all instances below 20 % and therefore the repeatability of the method is acceptable (EC Directive 2002/657/EC). The HBCDD values for the textiles differ from those previously published. This may be due to heterogeneity of the HBCDD treatment of the fabrics or loss of HBCDD from the fabric in the interim between analyses.

Due to the lack of an appropriate reference material for TCIPP, no CRM or SRM analyses were able to be conducted. However, five replicate analyses of the TCIPP concentrations in the PUF material were conducted with a low spread of values with a SD of 13 mg kg^{-1}, 0.077 % RSD and a maximum difference between the highest and lowest values of 34 mg kg^{-1}.

Table 2.14: Mean ± standard deviation of PBDEs in CRMs, % RSD and certified values.

ERM EC590-20G – LDPE

Analyte	Measured mean (g kg^{-1}) ± standard deviation (n = 5)	% RSD	Certified value (g kg^{-1})
BDE-47	0.13 ± 0.010	7.8	0.23 ± 0.04
BDE-99	0.24 ± 0.026	11	0.30 ± 0.030
BDE-100	0.057 ± 0.0044	7.7	0.063 ± 0.005
BDE-153	0.043 ± 0.0041	9.5	0.047 ± 0.006
BDE-154	0.016 ± 0.00084	5.2	0.026 ± 0.0026
BDE-183	0.12 ± 0.0062	5.4	0.13 ± 0.012
BDE-209	0.49 ± 0.036	7.2	0.65 ± 0.10

ERM EC591-20G – PP

Analyte	Measured mean (g kg^{-1}) ± standard deviation (n = 5)	% RSD	Certified value (g kg^{-1})
BDE-47	0.16 ± 0.017	11	0.25 ± 0.023
BDE-99	0.26 ± 0.013	5.1	0.32 ± 0.04
BDE-100	0.067 ± 0.0024	3.6	0.066 ± 0.007
BDE-153	0.045 ± 0.0036	8.0	0.044 ± 0.006
BDE-154	0.022 ± 0.0016	7.5	0.026 ± 0.004
BDE-183	0.083 ± 0.0065	7.9	0.087 ± 0.008
BDE-209	0.67 ± 0.032	4.8	0.78 ± 0.09

Table 2.15: Mean ± standard deviation of HBCDD diastereomers and % RSD compared with previously published values for the same materials.

Material	Analyte	Measured mean (mg kg^{-1}) ± standard deviation (n = 5)	% RSD	Published value (mg kg^{-1})
Textile A	α-HBCDD	11,000 ± 55	0.51	18,000 [a]
	β-HBCDD	4,500 ± 130	2.9	7,500 [a]
	γ-HBCDD	10,000 ± 160	1.5	17,000 [a]
Textile B	α-HBCDD	9,900 ± 200	2.0	19,000 [a]
	β-HBCDD	3,600 ± 100	2.8	6,300 [a]
	γ-HBCDD	10,000 ± 130	1.3	18,000 [a]
EPS	α-HBCDD	960 ± 22	2.3	970 [b]
	β-HBCDD	720 ± 93	13	620 [b]
	γ-HBCDD	3,900 ± 190	4.9	3,900 [b]
XPS	α-HBCDD	40,000 ± 5500	14	33,000 [b]
	β-HBCDD	9,500 ± 530	5.6	6,500 [b]
	γ-HBCDD	6,400 ± 870	14	3,900 [b]

[a] Kajiwara & Takigami (2013)

[b] Takigami et al., (2014)

2.6.5. Analysis of blanks, LODs and LOQs.

Blank values were subtracted from samples in the same batch if the blank contamination was more than 5 % of the sample concentration. If the contamination was below 5 % of that of the sample, it was ignored.

Instrumental limits of detection (LOD) were calculated for each of the studied compounds based on a 3:1 signal to noise ratio and are presented in Table 2.16.

Sample limits of quantification (LOQ) were calculated using equation 2.4:

Equation 2.4: $$LOQ = \frac{LOD \times FEV}{VFEI \times SS} \times \frac{100}{\%IS\,\mathrm{Recov}ery},$$

where *FEV* = final extract volume; *VFEI* = volume of final extract injected; SS = sample size (g or L); and %IS Recovery is % recovery of internal standard used to quantify the target pollutant in a particular sample. Calculated method LOQs for each analyte in leachate, and TCIPP in PUF are listed in Table 2.16.

In leaching experiments, all of the studied BFRs were below the LOQ in method blanks (n=46, leachate was replaced by distilled deionised Milli-Q water) for leachate analysis. TCIPP was detected in all leachate method blanks and the LOQ was 313 ng L^{-1} based on an LOD of 2.5 ng on column. TCIPP was only detected at low concentrations in system blanks (n=2) for volatilisation samples consisting of a pre-cleaned PUF disc treated as a sample. Method limits of quantification (LOQ) for TCIPP was based on the LOD of 2.5 and a PUF disc weight of 0.50 g.

Table 2.16: Calculated LODs (ng on column) and method LOQs for HBCDD diastereomers, PBDE congeners and TCIPP in this study.

Analyte	**LOD (ng on column)**	**Method LOQs**	
		Leachate (ng L^{-1})	**PUF (ng per PUF)**
α-HBCDD	0.029	30	-
β-HBCDD	0.030	49	-
γ-HBCDD	0.028	30	-
BDE-47	1.3	227	-
BDE-85	0.24	12	-
BDE-99	0.23	11	-
BDE-100	0.22	11	-
BDE-153	0.39	37	-
BDE-154	0.55	52	-
BDE-183	0.29	27	-
BDE-209	2.4	152	-
TCIPP	2.5	313	76

2.7. Statistical analysis.

Statistical analysis of the data was conducted using Excel (Microsoft Office 2003) and SPSS version 22.0. The distribution of each data set was evaluated using the Kolmogorov-Smirnov test in SPSS. The results revealed concentrations in all data sets to be normally distributed. One-way ANOVAs with post hoc Tukey test analysis were performed to compare means looking for differences between dependent variables. Paired samples t-tests were employed when looking for significant differences in concentrations between agitated and non agitated samples. Multiple linear regression analysis of whole data sets was performed using the SPSS 22 ‘Automatic linear modeling’ function. All confidence limits were preset to 95% while the significance levels in SPSS were set at 0.05. Because of the limited number of replicates, it is possible that relationships might be missed with this relatively high confidence limit, but a conservative approach was adopted and less statistically significant relationships were not investigated. A standard regression analysis was used for TCIPP volatilisation data. Pearson’s correlation coefficients were calculated using an online statistics calculator: (http://www.danielsoper.com/statcalc3/calc.aspx?id=44).

Chapter III: Leaching behaviour of HBCDD from treated polyester curtains.

3.1. Synopsis.

In this chapter, the leaching behaviour of HBCDD from treated polyester curtain samples donated from Japan is investigated. Concentrations (ng L^{-1}), percentage leached (%), percentage leached per unit time values (*PLT*; % h^{-1}) and leaching kinetics are presented for a range of landfill relevant leaching fluids. These will be then be used to assess the magnitude of this pathway in contributing HBCDD contamination to the environment. Levels of HBCDD will be compared to those reported in landfill leachates and aquatic environments from previous studies. Additional information detailing the experimental set-up of these leaching experiments can be found in section 2.2.1 and extraction, with clean up techniques detailed in sections 2.3.1 and 2.4.1 respectively. A summary of the conditions explored are outlined in Table 3.1.

Table 3.1: Summary of conditions employed in leaching test protocols.

Experimental Scenario / Parameter	**Single batch, variable contact time**	**Serial batch**	**Single batch, variable temperature**
Extraction period (h)	6, 24, 48	6, 24, 48, 72, 96, 168	24
Agitation	200 rpm	200 rpm	None
Temperature (°C)	20	20	20, 50, 80

3.2. Calculation of HBCDD leaching.

The percentage of HBCDDs present in the test textiles that was leached into each leachate sample (PL) was calculated as follows (equation 1):

Equation 3.1: $PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W}\right] \times 100\%$,

PL = percentage leached (%)

$C_{leachate}$ = Conc. of HBCDD collected in leachate (mg L^{-1})

V = volume of leachate (L)

C_{waste} = Conc. of HBCDD in waste sample (mg kg^{-1})

W = total weight of waste sample (kg)

The percentage leached normalised to contact time (PLT, % h^{-1}) is expressed here as the percentage of HBCDD leached from the textile per hour of contact time. PLT is calculated according to equation 2.

Equation 3.2: $PLT = \frac{PL}{t}$,

PL = percentage leached (%)

t = contact time (h)

3.3. Initial HBCDD concentrations and diastereomer profiles in the textile samples.

Table 3.2 displays the initial concentrations of HBCDD and individual diastereomers in the treated textile samples used in this study. The textiles were analysed for α-, β-, γ-, δ- and ε-HBCDD diastereomers. HBCDD is prepared commercially by bromination of *cis,trans,trans*-cyclododecatriene (ctt-CDT) while δ- and ε- are formed by bromination of *trans,trans,trans*-cyclododecatriene (ttt-CDT), a common contaminant in commercial ctt-CDT (Arsenault et al., 2007). However, while traces of δ- and ε- were detected in our textile samples, their concentrations were below the limit of quantitation (<500 mg kg^{-1} and <300 mg kg^{-1} respectively).

Table 3.2: Mean Concentrations (mg kg^{-1}) of HBCDDs in polyester curtains used in this study.

Diastereomer/ Sample	**α-HBCDD**	**β-HBCDD**	**γ-HBCDD**	**δ-HBCDD**	**ε-HBCDD**	**ΣHBCDD**
Textile A	11,000 ± 55	4,500 ± 130	10,000 ± 160	<500	<300	26,000 ± 170
Textile B	9,900 ± 200	3,600 ± 100	10,000 ± 130	<500	<300	24,000 ± 420

Material = polyester; Textile A colour = blue, Textile B colour = black; (n=3)

Depending on the manufacturer and the production method used, technical grade HBCDD consists of 75-95 % γ-HBCDD, 3-13 % α- HBCDD and 0.5-12 % β-HBCDD (Becher, 2005; UNEP, 2011). In contrast, the HBCDD diastereomer pattern in the textiles used in this study was roughly equally distributed between α- and γ- with a smaller proportion of β-HBCDD. The difference between the diastereomer pattern observed in these samples and that reported for technical grade HBCDD is likely due to the processes via which the textiles are flame-retarded. HBCDD is applied via immersion of the textiles in a solution of technical HBCDD. Following removal of the textile from the solution, the textile is desiccated at ~100-190 ºC (Johokiko, 2008). Thermal isomerisation of HBCDD towards a composition relatively enriched in α-HBCD compared to the starting material has been demonstrated previously (Köppen et al, 2008) and appears a plausible explanation for the pattern observed in our textile samples.

3.4. Effects of contact time on leaching (single batch experiments).

The influence of contact time on HBCDD concentrations and mean *PLT* values (% h^{-1}) in leachate in single batch experiments conducted at 20 ˚C is illustrated by Figure 3.1, with HBCDD concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) for the same experiments provided in Table 3.4. The results of one-way ANOVAs with post hoc Tukey tests are provided in Table 3.5.

Only a slight increase in HBCDD concentrations detected in leachate was observed when increasing contact time from 6 to 24 and then 48 h. As a consequence, *PLT* decreases with increasing contact time. This suggests the majority of HBCDD leaching occurs in the first six hours of contact between the fabric source and the leaching fluid, thereafter, *PLT* diminishes. Moreover, in all experiments conducted at 20 ˚C, α-HBCDD leached far more extensively than β-HBCDD or γ-HBCDD. We believe that these diastereomer-specific variations in *PLT* are explicable in terms of the aqueous solubility of HBCDD. Specifically, the aqueous solubility of α-HBCDD (41 µg L^{-1}), exceeds that of both β-HBCDD (15 µg L^{-1}) and γ-HBCDD (2.4 µg L^{-1}) at 20 °C (EC, 2008; Arnot et al., 2009). This is further supported by the results of the ANOVAs, in which highly significant differences in leachate concentrations are only observed for α-HBCDD between 6 h and 24 h and 6h and 48 h in Textile A; and between 6 h and 48 h and 24h and 48 h in Textile B.

Intriguingly, while ε-HBCDD was below the limit of quantitation in the curtain textile samples (Table 3.2), it was detected in the leachate in both single (Figure 3.1) and serial batch experiments (Figures 3.2 & 3.3). This suggests either that ε-HBCDD is present in the textile (but below detection limit) and is substantially more water soluble than other HBCDD diastereomers, and is thus leached more efficiently; or that it is formed as a result of isomerisation processes (Heeb et al, 2008; Köppen et al, 2008). However, ε-HBCDD was not found at quantifiable levels in experiments conducted at different temperatures.

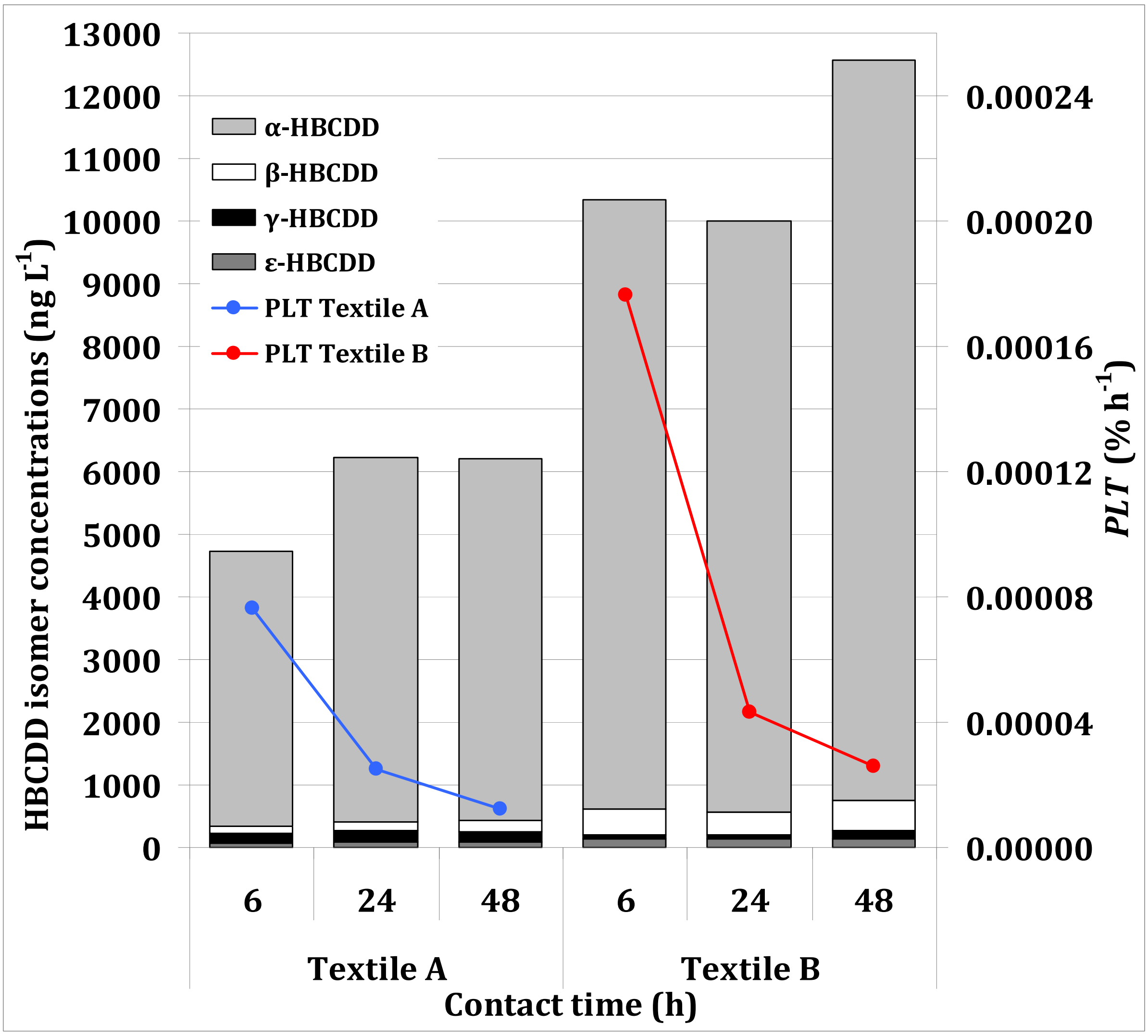

Figure 3.1: Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced from single batch experiments on Textiles A & B for different contact times.

Table 3.4: HBCDD leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean *PL* (%) and mean *PLT* values (% h^{-1}) conducted on Textile A and B polyester curtains at different contact times.

Material	Contact Time (h) /	6			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
Textile A	α-HBCDD	4,200	4,500	0.0010	0.00017
	β-HBCDD	110	120	0.000065	0.000011
	γ-HBCDD	94	200	0.000036	0.0000059
	ε-HBCDD	88	69	-	-
	ΣHBCDD	4,500	4,900	0.00046	0.000076
Textile B	α-HBCDD	9,900	9,600	0.0024	0.00040
	β-HBCDD	400	400	0.00027	0.000044
	γ-HBCDD	90	52	0.000017	0.0000058
	ε-HBCDD	150	140	-	-
	ΣHBCDD	11,000	10,000	0.0011	0.00018

Material	Contact Time (h) /	24			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
Textile A	α-HBCDD	6,000	5,600	0.0013	0.000055
	β-HBCDD	150	160	0.000084	0.0000035
	γ-HBCDD	150	180	0.000039	0.0000016
	ε-HBCDD	100	98	-	-
	ΣHBCDD	6,400	6,000	0.00060	0.000025
Textile B	α-HBCDD	9,600	9,300	0.0024	0.00010
	β-HBCDD	380	340	0.00025	0.000010
	γ-HBCDD	95	69	0.000019	0.00000081
	ε-HBCDD	120	130	-	-
	ΣHBCDD	10,000	9,800	0.0010	0.000043

Material	Contact Time (h) /	48			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
Textile A	α-HBCDD	5,900	5,700	0.0013	0.000028
	β-HBCDD	150	180	0.000091	0.0000019
	γ-HBCDD	140	180	0.000038	0.00000080
	ε-HBCDD	98	91	-	-
	ΣHBCDD	6,300	6,100	0.00060	0.000012
Textile B	α-HBCDD	12,000	12,000	0.0028	0.000059
	β-HBCDD	430	500	0.00030	0.0000063
	γ-HBCDD	130	150	0.000032	0.00000066
	ε-HBCDD	140	150	-	-
	ΣHBCDD	12,000	13,000	0.0012	0.000026

Table 3.5: Results of one-way analysis of variance tests with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in experiments examining the effects of contact time on leaching; performed for both Textile A and Textile B polyester curtains.

Textile A

Diastereomer	Contact time (h)	6 h	24 h
α-HBCDD	24 h	.015	
	48 h	.017	.981
β-HBCDD	24 h	.121	
	48 h	.067	.721
γ-HBCDD	24 h	.949	
	48 h	.964	.999

Textile B

Diastereomer	Contact time (h)	6 h	24 h
α-HBCDD	24 h	.636	
	48 h	.015	.010
β-HBCDD	24 h	.575	
	48 h	.216	.090
γ-HBCDD	24 h	.862	
	48 h	.092	.139

p-values highlighted red = significant ($p<0.05$)

3.5. Effect of cyclical wetting and draining on HBCDD concentrations and leaching behaviour (serial batch experiments).

Mean concentrations of HBCDDs (ng L^{-1}) detected in leachate and mean *PLT* values (% h^{-1}) obtained from these experiments on both textiles A and B are presented in Figures 3.2 and 3.3, with HBCDD concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) for the same experiments provided in Table 3.6. After 24 h cumulative contact time, concentrations of HBCDD leached from both textiles in these serial batch experiments diminish with increasing experimental duration. However, the decline in concentration is not dramatic, and even after a cumulative 168 h of leaching, the ΣHBCDD concentration >50% of that observed after just 6 h leaching. The observed decline in leachate concentration with successive batches may be attributable to removal in the early contact periods of less tightly bound HBCDD present on the surface of the textile. Overall – although longer term experiments are required to confirm this - this serial batch experiment indicates that replenishment of leaching fluid as would be expected in a landfill (e.g. via rainfall) does not result in dramatically diminished HBCDD leaching from textiles over long periods.

The results of one-way ANOVAs with post hoc Tukey tests are provided in Table 3.7 for both textiles A and B. For textile A, the only significant differences (*p*<0.05) observed were in α-HBCDD concentrations in the leachate between the second batch (6-24 h) and the fifth batch (72-96 h), and between the second batch (6-24 h) and the final batch (96-168 h). While for both β-HBCDD and γ-HBCDD, no significant differences were observed between the batches. For textile B, there were highly significant differences (*p*<0.05) in both α-HBCDD and β-HBCDD diastereomer concentrations in the leachate between the second batch (6-24 h) and all other contact durations, the only exception being a weaker significant difference in α-HBCDD concentrations (94.6 % probability) between the first batch (0-6 h) and second batch (6-24 h). In all other instances there were no significant differences observed.

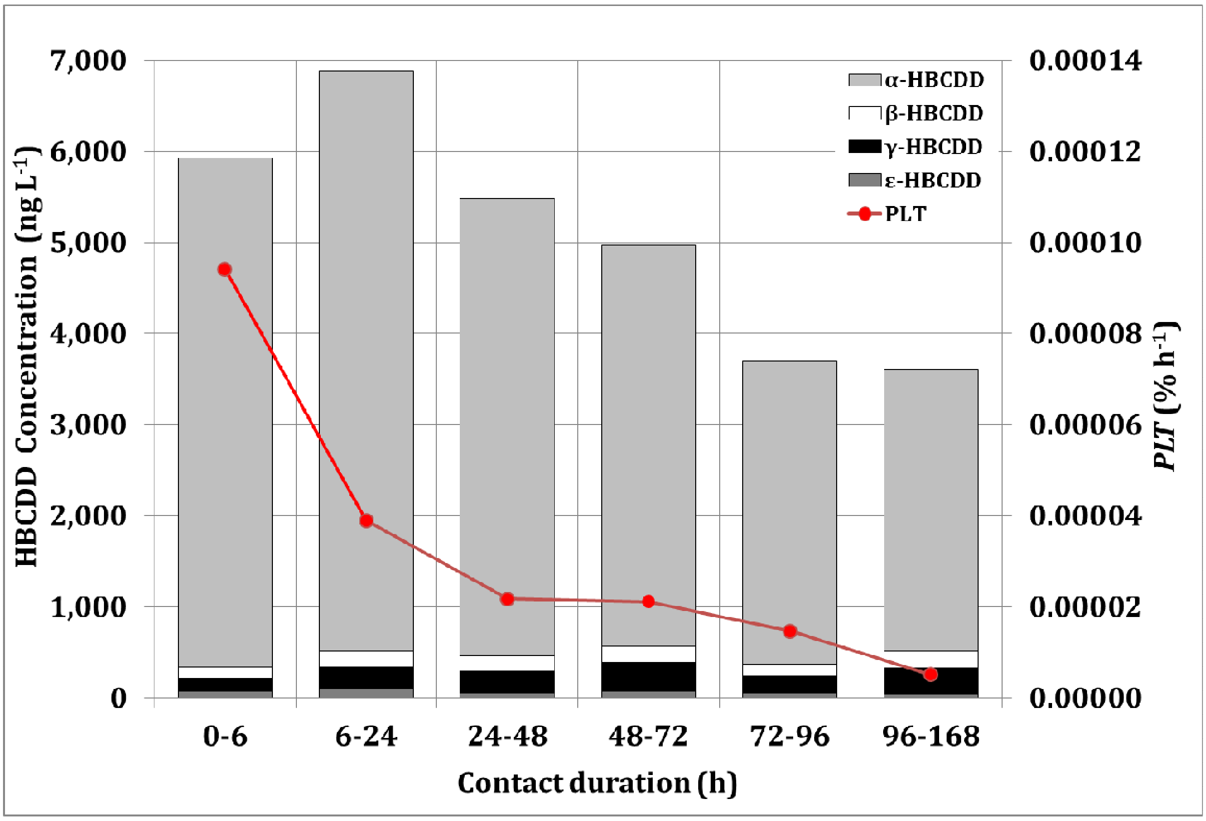

Figure 3.2: Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced during serial batch experiments on Textile A examining the effect of cyclical wetting and draining.

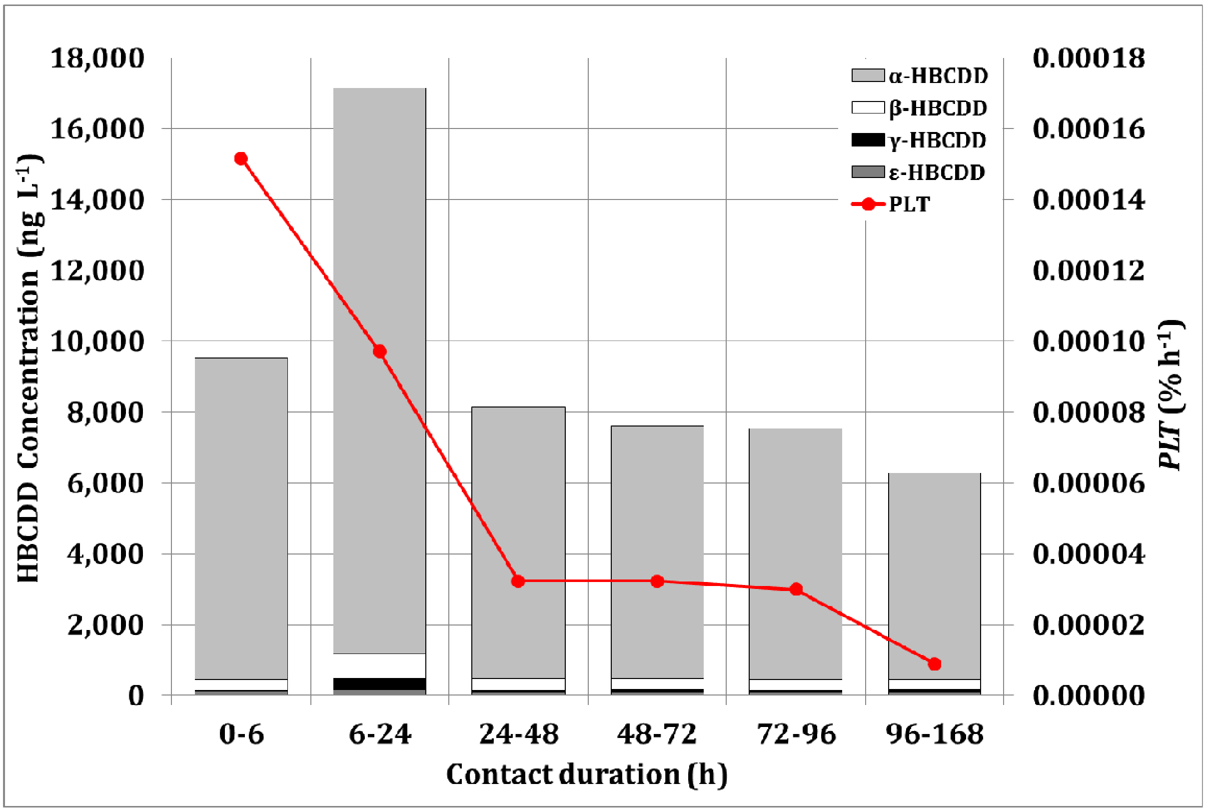

Figure 3.3: Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced during serial batch experiments on Textile B examining the effect of cyclical wetting and draining.

Table 3.6: HBCDD leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on Textile A and B polyester curtains from serial batch experiments.

Material	Contact duration (h) /	0-6				6-24				24-48			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
Textile A													
	α-HBCDD	5300	5900	0.0013	0.00021	6800	5900	0.0015	0.000081	6000	4100	0.0011	0.000048
	β-HBCDD	130	130	0.000070	0.000012	170	190	0.00010	0.0000054	220	110	0.000092	0.0000038
	γ-HBCDD	120	150	0.000032	0.0000054	200	260	0.000054	0.0000030	340	130	0.000055	0.0000023
	ε-HBCDD	74	75			110	96			68	46		
	ΣHBCDD	5600	6300	0.00057	0.000094	7300	6500	0.00066	0.000037	6600	4400	0.00052	0.000022
	Contact duration (h) /	48-72				72-96				96-168			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
	α-HBCDD	4200	4700	0.0010	0.000042	3300	-	0.00076	0.000032	3300	2900	0.00071	0.000010
	β-HBCDD	170	180	0.00010	0.0000041	130	-	0.000071	0.0000030	220	140	0.00010	0.0000014
	γ-HBCDD	280	350	0.000075	0.0000031	190	-	0.000046	0.0000019	410	180	0.000069	0.0000010
	ε-HBCDD	75	69			48	-			39	36		
	ΣHBCDD	4700	5300	0.00048	0.000020	3700	-	0.00035	0.000020	4000	3300	0.00034	0.0000048
	Contact duration (h) /	0-6				6-24				24-48			
Textile B	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
	α-HBCDD	8600	9500	0.0022	0.00037	19000	13000	0.0039	0.00022	7900	7400	0.0019	0.000079
	β-HBCDD	300	300	0.00020	0.000034	850	590	0.00048	0.000027	300	310	0.00020	0.0000084
	γ-HBCDD	41	44	0.000010	0.0000017	380	180	0.000065	0.0000036	61	83	0.000017	0.00000070
	ε-HBCDD	120	100			210	170			100	96		
	ΣHBCDD	9100	10000	0.00091	0.00015	20000	14000	0.0016	0.000091	8400	7900	0.00078	0.000032
	Contact duration (h) /	48-72				72-96				96-168			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
	α-HBCDD	7500	6700	0.0018	0.000073	7800	6400	0.0017	0.000073	5900	5700	0.0014	0.000020
	β-HBCDD	300	280	0.00020	0.0000081	290	280	0.00019	0.0000080	290	260	0.00018	0.0000025
	γ-HBCDD	73	130	0.000024	0.0000010	77	80	0.000018	0.00000076	97	110	0.000024	0.00000034
	ε-HBCDD	110	75			94	87			81	90		
	ΣHBCDD	8000	7200	0.00073	0.000030	8200	6800	0.00072	0.000040	6400	6200	0.00060	0.0000083

Table 3.7: Results of one-way analysis of variance tests with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in serial batch experiments; performed for Textile A and Textile B polyester curtains.

Textile A

Diastereomer	Batch number	1	2	3	4	5
α-HBCDD	**2**	.829				
	3	.944	.415			
	4	.531	.150	.924		
	5	.089	.026	.233	.598	
	6	.061	.018	.158	.434	.999
β-HBCDD	**2**	.796				
	3	.905	1.000			
	4	.796	1.000	1.000		
	5	1.000	.819	.921	.819	
	6	.747	1.000	.999	1.000	.772
γ-HBCDD	**2**	.906				
	3	.891	1.000			
	4	.460	.918	.931		
	5	.986	.998	.997	.762	
	6	.591	.978	.983	1.000	.881

Textile B

Diastereomer	Batch number	1	2	3	4	5
α-HBCDD	**2**	.054				
	3	.957	.024			
	4	.857	.017	.999		
	5	.848	.017	.999	1.000	
	6	.504	.009	.887	.971	.975
β-HBCDD	**2**	.011				
	3	1.000	.011			
	4	1.000	.009	1.000		
	5	1.000	.009	1.000	1.000	
	6	.998	.008	.998	1.000	1.000
γ-HBCDD	**2**	.061				
	3	.995	.102			
	4	.917	.175	.995		
	5	.989	.114	1.000	.998	
	6	.906	.181	.993	1.000	.998

Batch number: 1 = 0–6 h; 2 = 6–24 h; 3 = 24–48 h; 4 = 48–72 h; 5 = 72–96 h; 6 = 96–168 h.

p-values highlighted red = significant ($p<0.05$)

3.6. Leaching kinetics.

Ho et al., (2005) expressed the leaching of water-soluble components from sapwood in terms of the following second-order rate equation:

Equation 3.3: $\frac{Ct}{t} = k(Cs - Ct)^2$,

where k is the second-order leaching rate constant (L ng^{-1} min^{-1}), Cs the leaching capacity, which is the concentration of HBCDD at saturation (ng L^{-1}), and Ct is the concentration of HBCDD (ng L^{-1}) in suspension at any given time, t (min). The leaching capacity, Cs, and the second-order leaching rate constant, k, can be determined experimentally from the slope and intercept by plotting t/Ct against t.

We generated such plots for all our experiments conducted at 20 ˚C. We combined data at that temperature for both single batch and serial batch experiments, by treating our serial batch experiments as a series of single batch experiments. We consider that the total quantity of HBCDD leached from textiles in serial batch experiments were low enough to be used in this manner (e.g. Textile A mean PL in batch 1 = 0.00057 %, etc.; see Table 3.6). However, we acknowledge that with each subsequent batch from batch two onwards will have a slightly reduced HBCDD starting concentration in the textiles and that rather than allowing concentrations to build up, the leaching is reset with each batch. Additionally, a degree of uncertainty is involved in determining leaching kinetics from this data due to the potential for more than just chemical processes taking place (e.g. physical processes such as abrasion). Therefore, the relationship and its constants do not have the same meaning as they would for a conventionally performed kinetic experiment. A positive and highly significant linear correlation between t/C_t and t was observed in all instances, with plots provided for Textile A and Textile B as Figures 3.4 and 3.5 respectively. This apparent fit with second order kinetics confirms our observations above of initial rapid leaching followed by a slower second phase. We suggest that initially there is intense dissolution in which maximum leaching takes place as a result of removal from the fabric of HBCDD that is more loosely associated with easily abraded fibres and present on the fabric surface rather than embedded within the fabric. A second, slower stage follows, which corresponds primarily to external diffusion and is related to the soluble remainder. The slope, Y-intercept, saturated

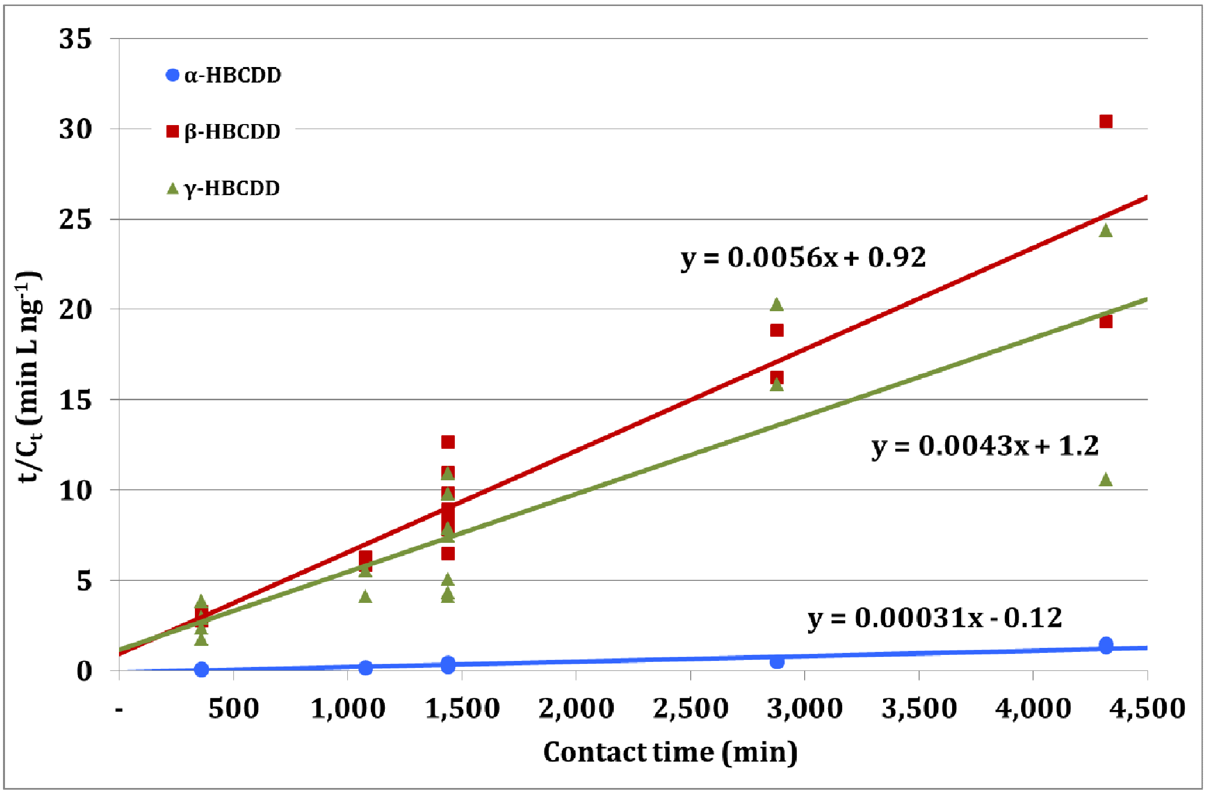

Figure 3.4: Plot of t/C_t versus t for HBCDD leaching from Textile A in single and serial batch experiments.

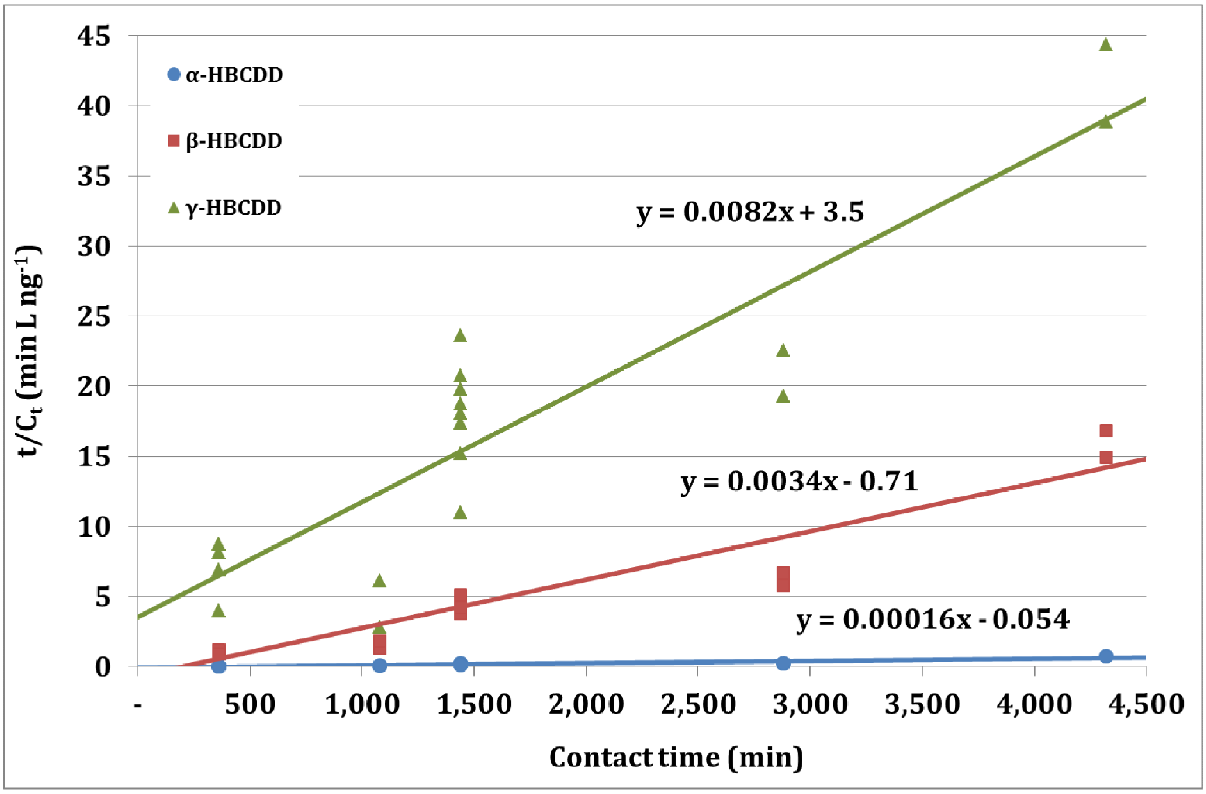

Figure 3.5: Plot of t/C_t versus t for HBCDD leaching from Textile B in single and serial batch experiments.

leaching capacity, *Cs*, the leaching rate constant, *k*, two-tailed *p* values, and Pearson's correlation coefficients, *r*, are given for individual HBCDD diastereomers in Table 3.8.

Table 3.8: Second order leaching rate constants (*k*) and saturated leaching capacities (C_s) obtained for HBCDD diastereomers for Textile A and Textile B polyester curtains[a].

Constant / Compound	**Slope (min L ng^{-1} /min)**	**y-intercept (min L ng^{-1})**	**C_s (ng L^{-1})**	**Observed max. conc. (ng L^{-1})**	***k* (L ng^{-1} min^{-1})**	***Two-tailed P value***	***Correlation coefficient: r***
Textile A							
β-HBCDD	0.0056	0.93	180	220	0.000012	.000	0.945
γ-HBCDD	0.0043	1.2	230	410	0.0000070	.000	0.832
Textile B							
γ-HBCDD	0.0082	3.5	120	380	0.000019	.000	0.896

[a]Data not shown for plots for which y-intercept and thus *k* values were negative.

To further evaluate the hypothesis of second-order rate kinetics, the natural logarithm of the HBCDD leachate concentration data for both single and serial batch experiments conducted at 20 ˚C, were plotted against time to check for linearity and negative slopes that would suggest first order kinetics. The results are presented in Table 3.9 and in all instances the correlation coefficient *r* was insignificant and Pearson's two-tailed probability values also demonstrated no significance.

Table 3.9: First order leaching rate slopes, y-intercepts, constants (*k*), and *r* values obtained for HBCDD for Textile A and Textile B polyester curtains.

Constant / Compound	**Slope (log$_e$ ng L^{-1} /min)**	**y-intercept (log$_e$ ng L^{-1})**	***k* (min^{-1})**	***Two-tailed P value***	***Correlation coefficient: r***
Textile A					
α-HBCDD	-0.000094	8.6	0.0000000010	.058	-0.468
β-HBCDD	0.000076	4.9	0.0000000012	.076	0.442
γ-HBCDD	0.00011	5.1	0.0000000024	.182	0.340
Textile B					
α-HBCDD	-0.000091	9.2	0.00000000089	.138	-0.364
β-HBCDD	-0.000047	6.0	0.00000000037	.465	-0.184
γ-HBCDD	0.00014	4.3	0.0000000044	.207	0.313

3.7. Effect of temperature on leaching.

Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on *PLT* of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated. Concentrations and leaching behaviour of HBCDD from textiles A and B at different temperatures are displayed in Figures 3.6 and 3.7, with the diastereomer pattern in leachate at different temperatures shown in Figure 3.8. HBCDD concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) for the same experiments provided in Table 3.10, with the results of one-way ANOVAs with post hoc Tukey tests presented in Table 3.11. For Textile A, there were significant differences in all three HBCDD diastereomer concentrations in the leachate between the three temperatures explored. However, Textile B showed no significant differences between 20 °C and 50 °C for all three diastereomers. While concentrations of all diastereomers increased with increasing temperature, raising the temperature from 20 °C to 80 °C increased leachate concentrations of γ-HBCDD by a factor of 28 - 33, while α-HBCDD concentrations only increased by a factor of 4.3 - 4.8. One possible explanation for this observation is that at higher temperatures the relatively more hydrophobic isomers (β-HBCDD and γ-HBCDD) become more water soluble compared to α-HBCDD and are therefore more readily leached. Alternatively, isomerisation may occur at lower temperatures than hitherto documented.

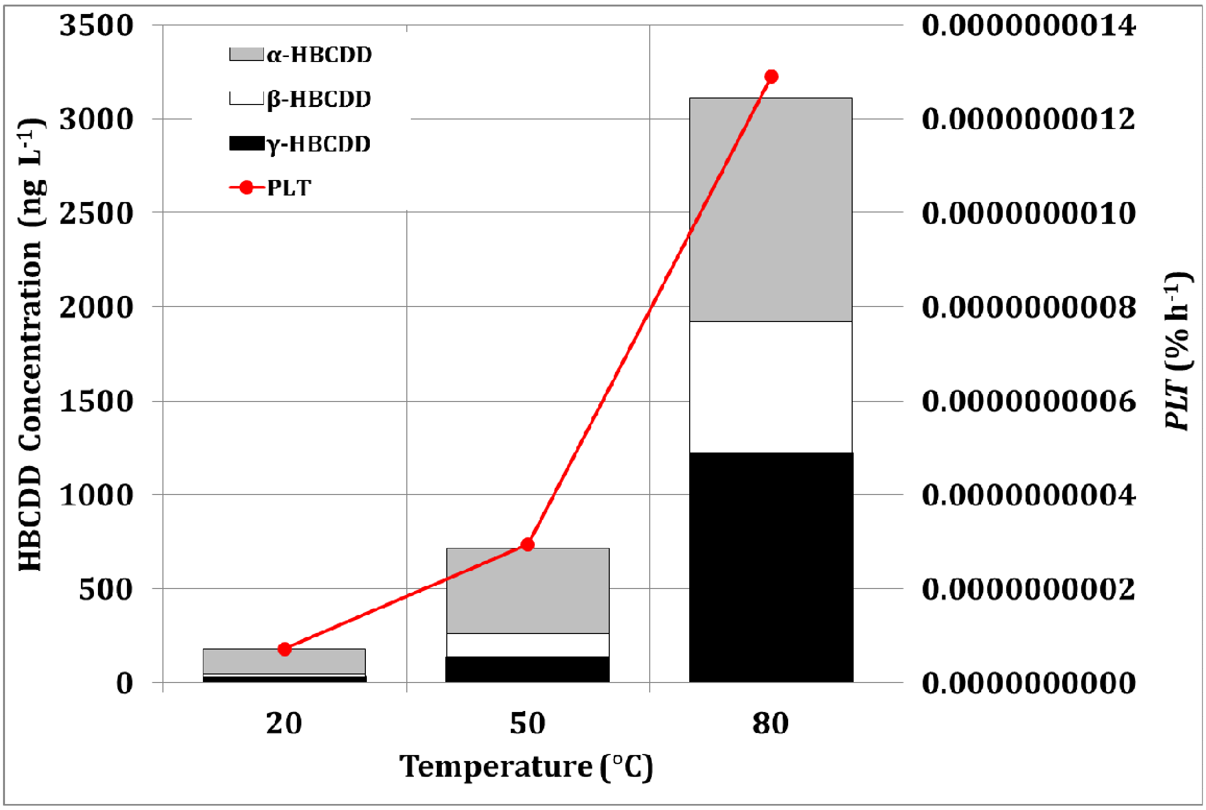

Figure 3.6: Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) from Textile A at different temperatures during 24h single batch experiments.

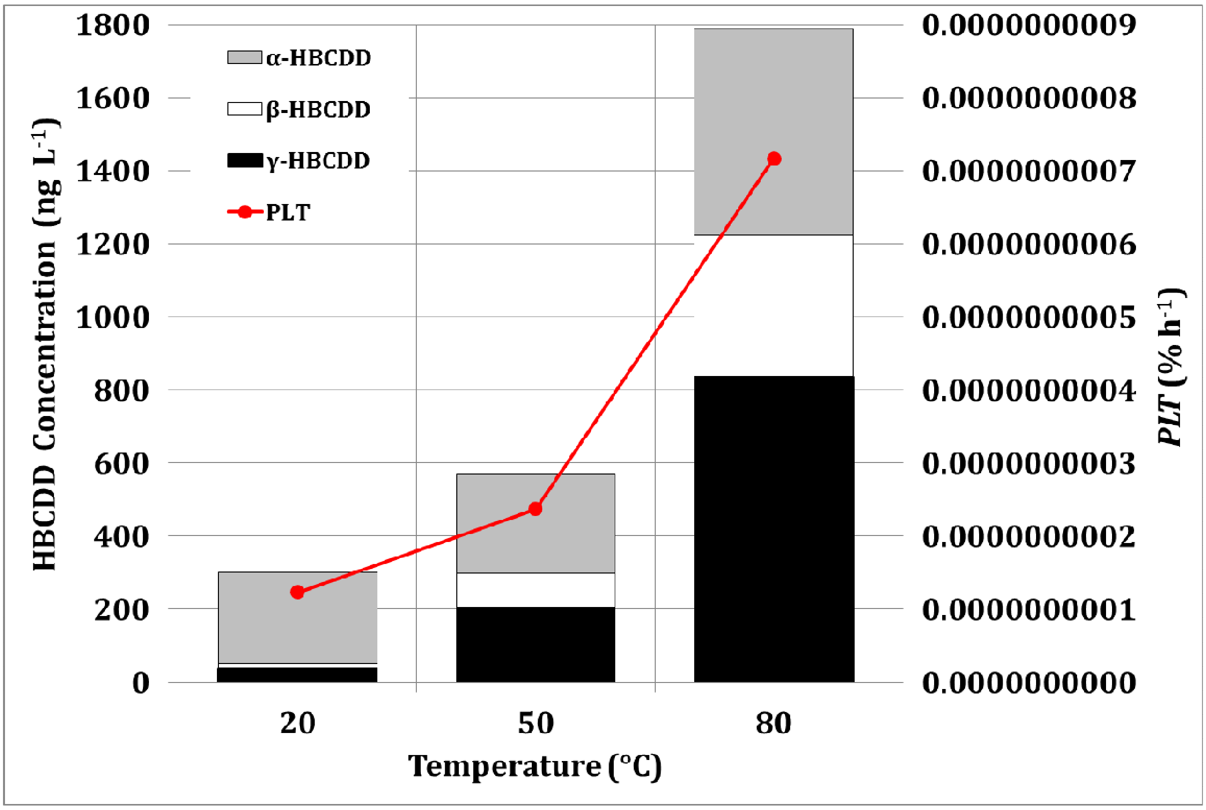

Figure 3.7: Mean (n=2) HBCDD concentrations (ng L^{-1}) (bars) and *PLT* values (% ΣHBCDD h^{-1}) (red circles) from Textile B at different temperatures during 24h single batch experiments.

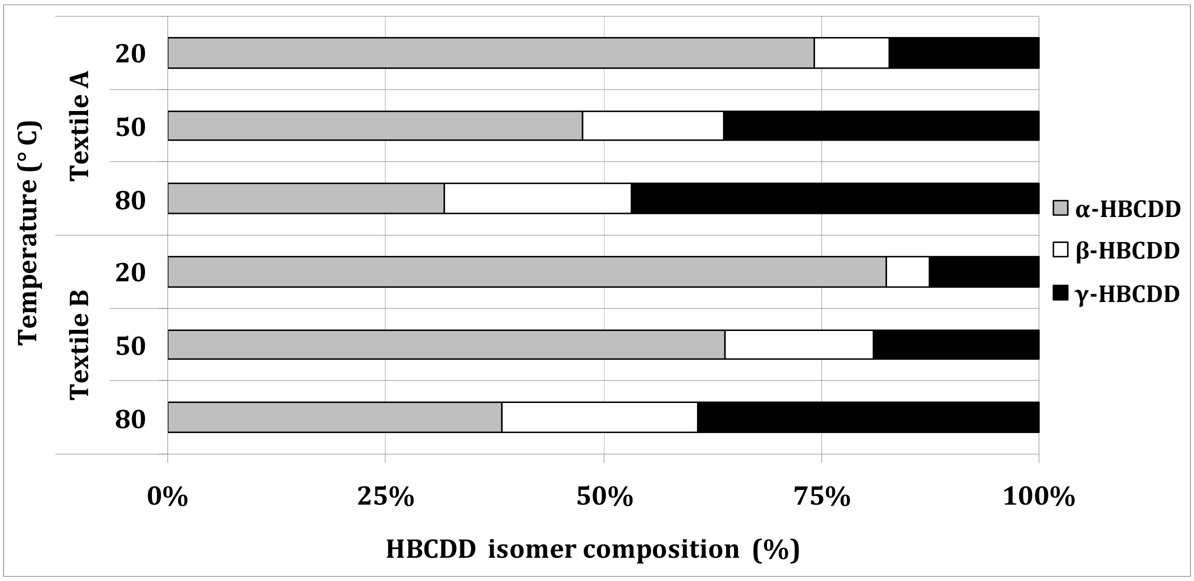

Figure 3.8: Influence of temperature on mean (n=2) HBCDD diastereomer profiles in leachate from Textile A and Textile B during 24h single batch experiments.

Table 3.10: HBCDD leachate concentrations in duplicate (ng L^{-1}), mean *PL* (%) and mean *PLT* values (% h^{-1}) from Textile A and B polyester curtains with different temperatures.

Material	Temperature (°C) /			20	
	Diastereomer	**Conc. (ng L^{-1})**	**Conc. (ng L^{-1})**	**PL (%)**	***PLT* (% h^{-1})**
Textile A	**α-HBCDD**	130	130	0.000031	0.0000013
	β-HBCDD	19	11	0.0000083	0.00000043
	γ-HBCDD	39	22	0.0000076	0.00000040
	ε-HBCDD	-	-	-	-
	ΣHBCDD	190	170	0.0000000017	0.0000000000072
Textile B	**α-HBCDD**	260	240	0.000063	0.0000023
	β-HBCDD	13	17	0.000011	0.00000045
	γ-HBCDD	43	32	0.0000090	0.00000037
	ε-HBCDD	-	-	-	-
	ΣHBCDD	310	290	0.0000000030	0.000000000012
Material	**Contact Time (h) /**			**50**	
	Diastereomer	**Conc. (ng L^{-1})**	**Conc. (ng L^{-1})**	**PL (%)**	***PLT* (% h^{-1})**
Textile A	**α-HBCDD**	280	260	0.000063	0.0000026
	β-HBCDD	100	85	0.000049	0.0000020
	γ-HBCDD	220	190	0.000050	0.0000021
	ε-HBCDD	-	-	-	-
	ΣHBCDD	610	530	0.0000000057	0.00000000024
Textile B	**α-HBCDD**	510	410	0.00011	0.0000047
	β-HBCDD	140	100	0.000086	0.0000036
	γ-HBCDD	160	110	0.000033	0.0000014
	ε-HBCDD	-	-	-	-
	ΣHBCDD	810	620	0.0000000071	0.00000000029
Material	**Contact Time (h) /**			**80**	
	Diastereomer	**Conc. (ng L^{-1})**	**Conc. (ng L^{-1})**	**PL (%)**	***PLT* (% h^{-1})**
Textile A	**α-HBCDD**	530	600	0.00014	0.0000057
	β-HBCDD	360	410	0.00021	0.0000088
	γ-HBCDD	810	860	0.00021	0.0000088
	ε-HBCDD	-	-	-	-
	ΣHBCDD	1,700	1,900	0.000000017	0.00000000072
Textile B	**α-HBCDD**	1,300	1,100	0.00030	0.000013
	β-HBCDD	810	580	0.00049	0.000020
	γ-HBCDD	1,400	1,000	0.00029	0.000012
	ε-HBCDD	-	-	-	-
	ΣHBCDD	3,500	2,700	0.000000031	0.0000000013

Table 3.11: Results of one-way analysis of variance with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in experiments examining the effects of temperature on leaching; performed both Textile A and Textile B polyester curtains.

Textile A

Diastereomer	Temperature (°C)	20	50
α-HBCDD	50	.035	
	80	.001	.004
β-HBCDD	50	.050	
	80	.001	.001
γ-HBCDD	50	.016	
	80	.000	.000

Textile B

Diastereomer	Temperature (°C)	20	50
α-HBCDD	50	.256	
	80	.006	.012
β-HBCDD	50	.566	
	80	.011	.018
γ-HBCDD	50	.821	
	80	.010	.013

p-values highlighted red = significant (p<0.05)

3.8. Effect of agitation on leaching.

By comparing the results of experiments conducted at 20 °C with contact times of 24 h in the contact time experiment and the temperature experiment, the effect of agitation on leaching of HBCDD from the textiles can be examined (Figure 3.9). The ΣHBCDD concentrations in the agitated leachate samples were 36 times greater than those in the corresponding unagitated samples for Textile A and 20 times greater for Textile B. This illustrates that agitation has a considerable role in enhancing HBCDD leachate concentrations from treated textiles. HBCDD concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) for the same experiments provided in Table 3.12. The results of paired sample t-tests are presented in Table 3.13 and indicate that agitation has a highly significant effect (p<0.05) on all diastereomers individually and summed.

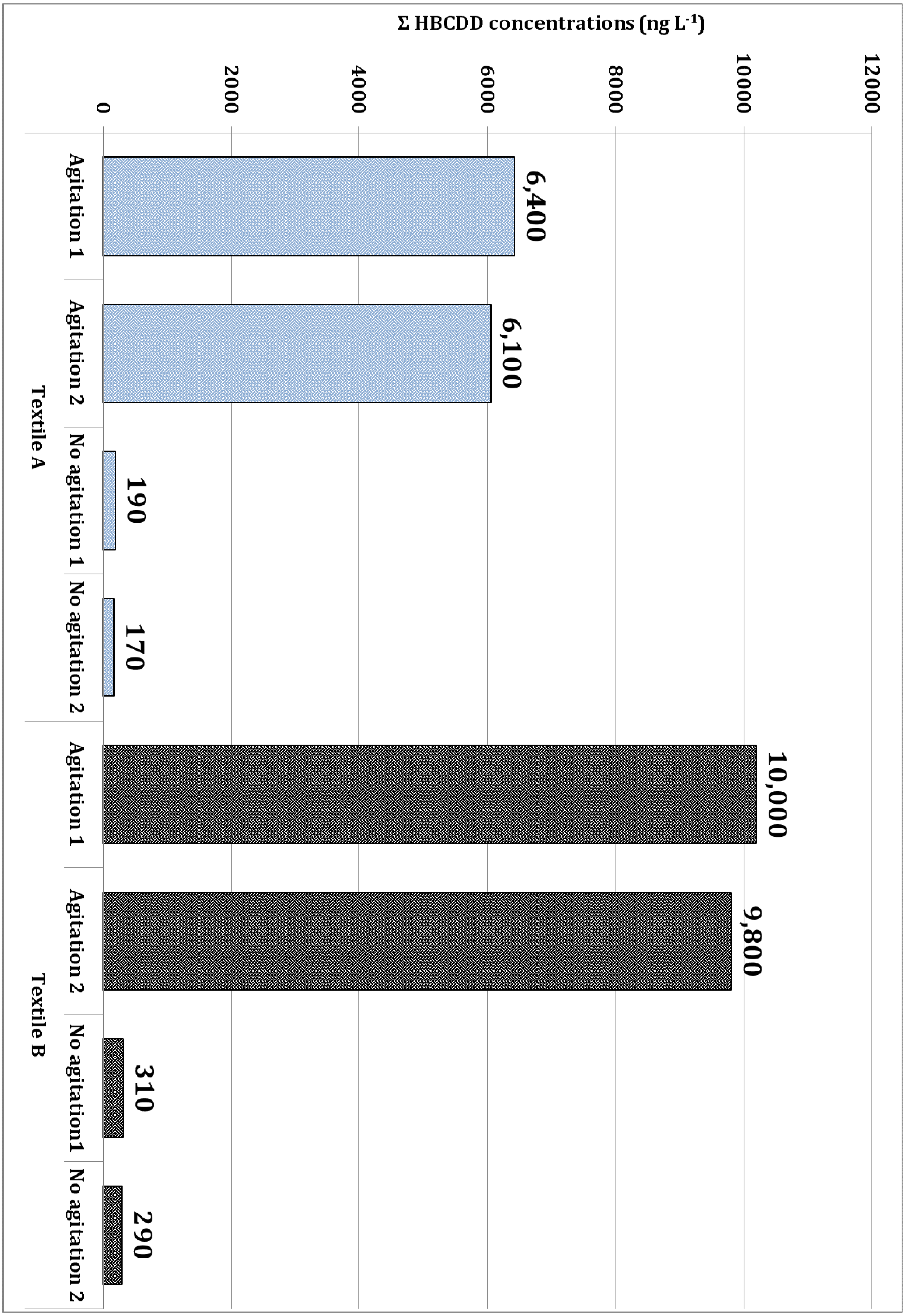

Figure 3.9: ΣHBCDD concentrations (ng L^{-1}) in leachate produced during duplicate 24 h single batch experiments examining the effects of agitation on leaching from Textile A and Textile B.

Table 3.12: HBCDD leachate concentrations in duplicate (ng L^{-1}), mean *PL* (%) and mean *PLT* values (% h^{-1}) from Textile A and B polyester curtains, comparing the effect of agitation (200 rpm) with no agitation during 24h single batch experiments.

Material			Agitation		
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
Textile A	α-HBCDD	6,000	5,600	0.0013	0.000055
	β-HBCDD	150	160	0.000084	0.0000035
	γ-HBCDD	150	180	0.000039	0.0000016
	ε-HBCDD	100	98	-	-
	ΣHBCDD	6,400	6,100	0.00060	0.000025
Textile B	α-HBCDD	9,600	9,300	0.0024	0.00010
	β-HBCDD	380	340	0.00025	0.000010
	γ-HBCDD	95	69	0.000019	0.00000081
	ε-HBCDD	120	130	-	-
	ΣHBCDD	10,000	9,800	0.0010	0.000043
Material			**No agitation**		
	Diastereomer	**Conc. (ng L^{-1})**	**Conc. (ng L^{-1})**	**PL (%)**	***PLT* (% h^{-1})**
Textile A	α-HBCDD	130	130	0.000031	0.0000013
	β-HBCDD	19	11	0.0000083	0.00000043
	γ-HBCDD	39	22	0.0000076	0.00000040
	ε-HBCDD	-	-	-	-
	ΣHBCDD	190	170	0.0000000017	0.0000000000072
Textile B	α-HBCDD	260	240	0.000063	0.0000023
	β-HBCDD	13	17	0.000011	0.00000045
	γ-HBCDD	43	32	0.0000090	0.00000037
	ε-HBCDD	-	-	-	-
	ΣHBCDD	310	290	0.0000000030	0.000000000012

Table 3.13: Results of paired sample t-tests for comparing differences in HBCDD concentrations between agitated and non-agitated leaching; performed for both Textile A and Textile B polyester curtains.

Diastereomer	Paired differences					*t*	df	*Sig.* (two-tailed)
	Mean (ng L^{-1})	Std. Dev.	Std. error mean	95 % confidence interval of the difference				
				Lower	Upper			
α-HBCDD	7,400	2000	1000	4,200	11,000	7.3	3	.005
β-HBCDD	240	120	61	50	440	4.0	3	.028
γ-HBCDD	89	56	28	-0.17	180	3.2	3	.050
ΣHBCDD	2,600	3,700	1,100	220	5,000	2.4	11	.035

3.9. Statistical analysis of the whole dataset.

The results of multiple linear regression analyses (MRLA) for both Textiles A and B are provided in Table 3.14, with independent variables for each HBCDD diastereomer ranked by relative importance and significance. The coefficients for each significant independent variable are also presented. The coefficient predicts how much the dependent variable is expected to increase when that independent variable increases by one, holding all the other independent variables constant.

Agitation of the sample during leaching (entered to the MLRA as a nominal category independent variable as: agitation = 1 and no agitation = 0) has a highly significant (*p*<0.05) positive effect on α-HBCDD concentrations for both textiles. Agitation also has a less important, yet highly significant effect on γ-HBCDD in Textile B. Increasing the leachate temperature has a highly significant effect on β-HBCDD and γ-HBCDD diastereomers in Textile A, but only for γ-HBCDD in Textile B. This supports the hypothesis of elevated leachate temperatures enhancing the leaching of the relatively less soluble β-HBCDD and γ-HBCDD diastereomers.

Table 3.14: Results for multiple linear regression analysis obtained for HBCDD diastereomers for leachate from both Textile A and Textile B polyester curtains[a].

Diastere-omer	Independent variable	*Coefficient (ng L^{-1} unit-^{1})*	Std. error	*Sig.*	95 % Confidence interval		Importance
					Lower	Upper	
Textile A							
α-HBCDD	Agitation	4,700	450	.000	3,800	5,700	0.964
β-HBCDD	Temperature (°C)	3.1	0.80	.001	1.4	4.7	1.000
γ-HBCDD	Temperature (°C)	9.0	1.5	.000	6.0	12	1.000
Textile B							
α-HBCDD	Agitation	8,700	1,300	.000	5,900	11,000	1.000
γ-HBCDD	Temperature (°C)	20	2.6	.000	14	25	0.923
	Agitation	230	110	.039	14	460	0.077

[a]Data only shown for effects with greater than 95 % significance.

3.10. Summary.

This study demonstrates that leaching of HBCDD from textiles using distilled deionised water as a leaching fluid is a second order process. Following an initial period of source:leaching fluid contact during which leaching is relatively facile, subsequent leaching is slower. Leaching is higher for the more water soluble diastereomers and is substantially greater at 80 ˚C compared to 20 ˚C. Our data, when combined with the plausibly enhanced solubility of BFRs in leaching fluid containing dissolved organic matter (Choi et al, 2009), and existing reports of measurable concentrations of HBCDD in landfill leachate (Morris et al., 2004; Remberger et al., 2004; Suzuki and Hasegawa, 2006), suggests that leaching of HBCDD from landfilled waste requires further study.

Chapter IV: Leaching behaviour of HBCDD from EPS and XPS building insulation foams.

4.1. Synopsis.

In this chapter, the leaching behaviour of HBCDD from treated EPS and XPS building insulation foam samples from Japan are investigated. Concentrations (ng L^{-1}), percentage leached (%) and *PLT* values (% h^{-1}), as well as leaching kinetics are presented for a range of landfill relevant leaching fluids. These are used to assess the contribution of this pathway to environmental contamination with HBCDD. Levels of HBCDD in leachate samples in this study will be compared to those reported previously for landfill leachates and aquatic environments. Additional information detailing the experimental set-up of these leaching experiments can be found in section 2.2.1 and extraction and clean up techniques are detailed in sections 2.3.1 and 2.4.1 respectively. A summary of the conditions explored are outlined in Table 4.1.

Table 4.1: Summary of conditions employed in leaching test protocols.

Experimental Scenario / Parameter	Single batch, variable contact time	Serial batch	Single batch, variable temperature	Single batch, variable pH
Extraction period (h)	6, 24, 48	6, 24, 48, 72, 96, 168	24	6
Agitation	200 rpm	200 rpm	None	200 rpm
Temperature (°C)	20	20	20, 50, 80	20
pH	6.5	6.5	6.5	5.8, 6.5, 8.5
DHM conc. (mg L^{-1})	0, 100, 1000	0	0, 100, 1000	0, 100, 1000

4.2. Initial HBCDD concentrations in building insulation foam samples.

Table 4.2 displays the initial concentrations of HBCDD and individual diastereomers in the treated foam samples used in this study. The EPS foam is close to the pattern of technical grade HBCDD with high γ-HBCDD and lower concentrations of α- and β-HBCDD (Becher, 2005; UNEP, 2011). The difference between the diastereomer patterns observed in these samples is explained by thermal isomerisation of γ-HBCDD to α-HBCDD diastereomer during the polymer extrusion process of XPS, which involves high temperatures of over 200 °C (Takigami et al., 2014). Concentrations of ΣHBCDD were a factor of 10 higher in XPS foams than EPS foams.

Table 4.2: Mean ± standard deviation concentrations (mg kg^{-1}) of HBCDD diastereomers in building insulation foams used in this study. (n=5)

Diastereomer / Sample	α-HBCDD	β-HBCDD	γ-HBCDD	ΣHBCDD
EPS	960 ± 22	720 ± 93	3,900 ± 190	5,600 ± 260
XPS	40,000 ± 5,500	9,500 ± 530	6,400 ± 870	56,000 ± 5,500

4.3. Effects of contact time and humic matter content of leaching fluid on HBCDD leaching (single batch experiments).

The influence of contact time on HBCDD concentrations and mean PLT values (% h^{-1}) in leachate in single batch experiments conducted for EPS and XPS foams at 20 ˚C are illustrated by Figures 4.1 and 4.3 respectively. The diastereomer pattern in leachate for EPS and XPS foams at different contact times are shown in Figures 4.2 and 4.4 respectively. Individual HBCDD diastereomer concentrations, mean PL (%) and mean PLT values (% h^{-1}) for the same experiments are provided in Table 4.3.

The results of one-way ANOVAs with post hoc Tukey tests are provided in Table 4.4. In EPS foam experiments with distilled deionised water as leaching fluid, the only significant differences ($p<0.05$) in concentrations were for β-HBCDD between 6 h and 48 h, and between 24 h and 48 h contact times. Similarly, in experiments on XPS foam with no DHM, only the β-HBCDD diastereomer exhibited significant differences in concentrations between 6 h and 24 h, and 6 h and 48 h.

When distilled deionised water is used as the leaching fluid, concentrations of α-HBCDD increase with increasing contact duration, for both EPS and XPS foams. This suggests that α-HBCDD is preferentially dissolved into solution in a secondary solubility-driven phase of leaching and supports a hypothesis of second-order kinetics.

With the addition of DHM to the leaching fluid there appears to be a distinct difference between the two insulation foams, with limited differences being observed for EPS foam contacted with a DHM concentration of 100 mg L^{-1}. The only significant differences ($p<0.05$) in concentrations were for β-HBCDD between 6 h and 24 h, and 6 h and 48 h. In experiments where 1000 mg L^{-1} DHM was contacted with EPS foam, significant differences ($p<0.05$) in α-HBCDD concentrations were observed between 6 h and 24 h, and 6 h and 48 h.

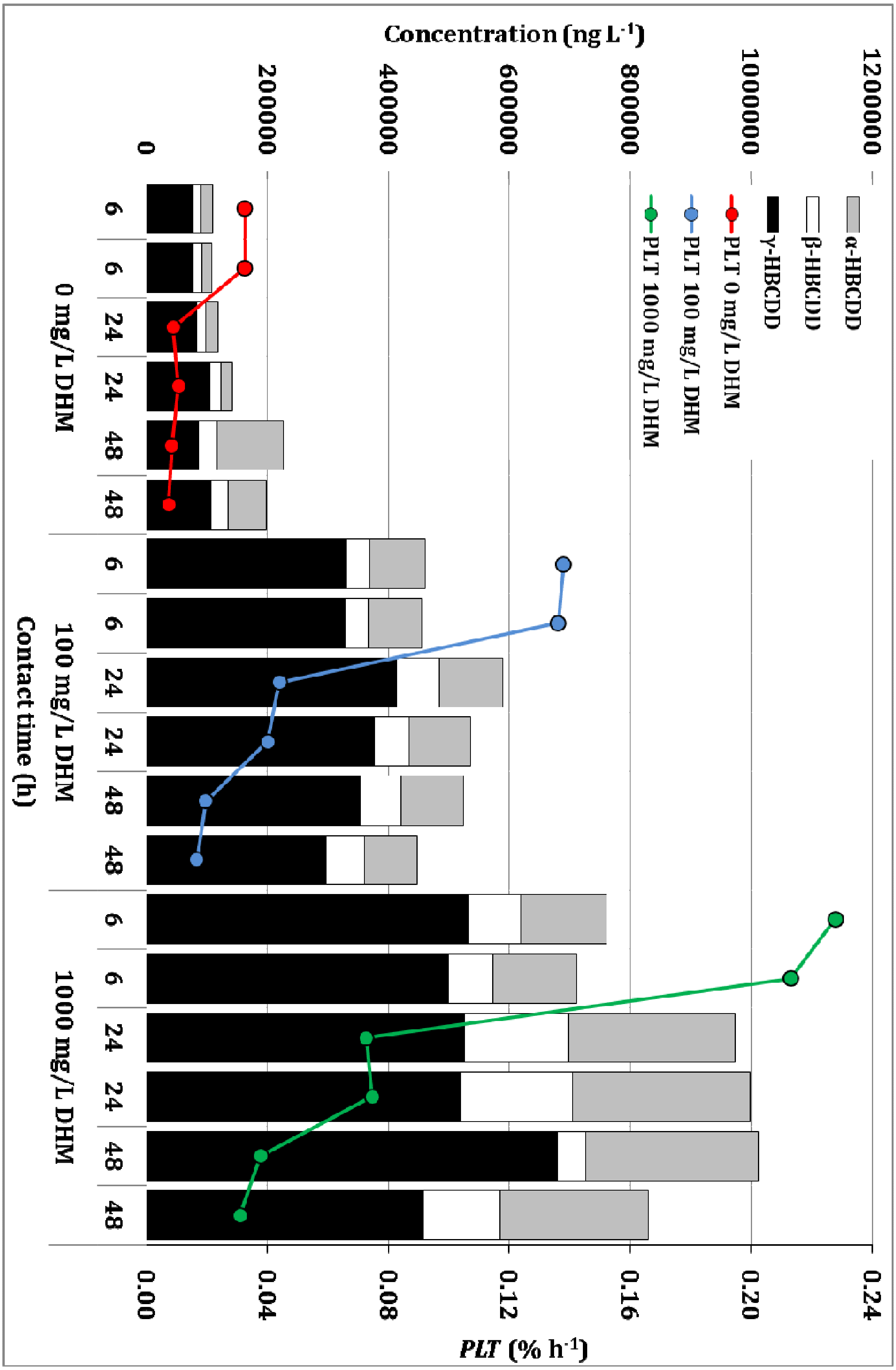

Figure 4.1: HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced during 24 h single batch experiments (run in duplicate) on EPS foam at different contact times with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

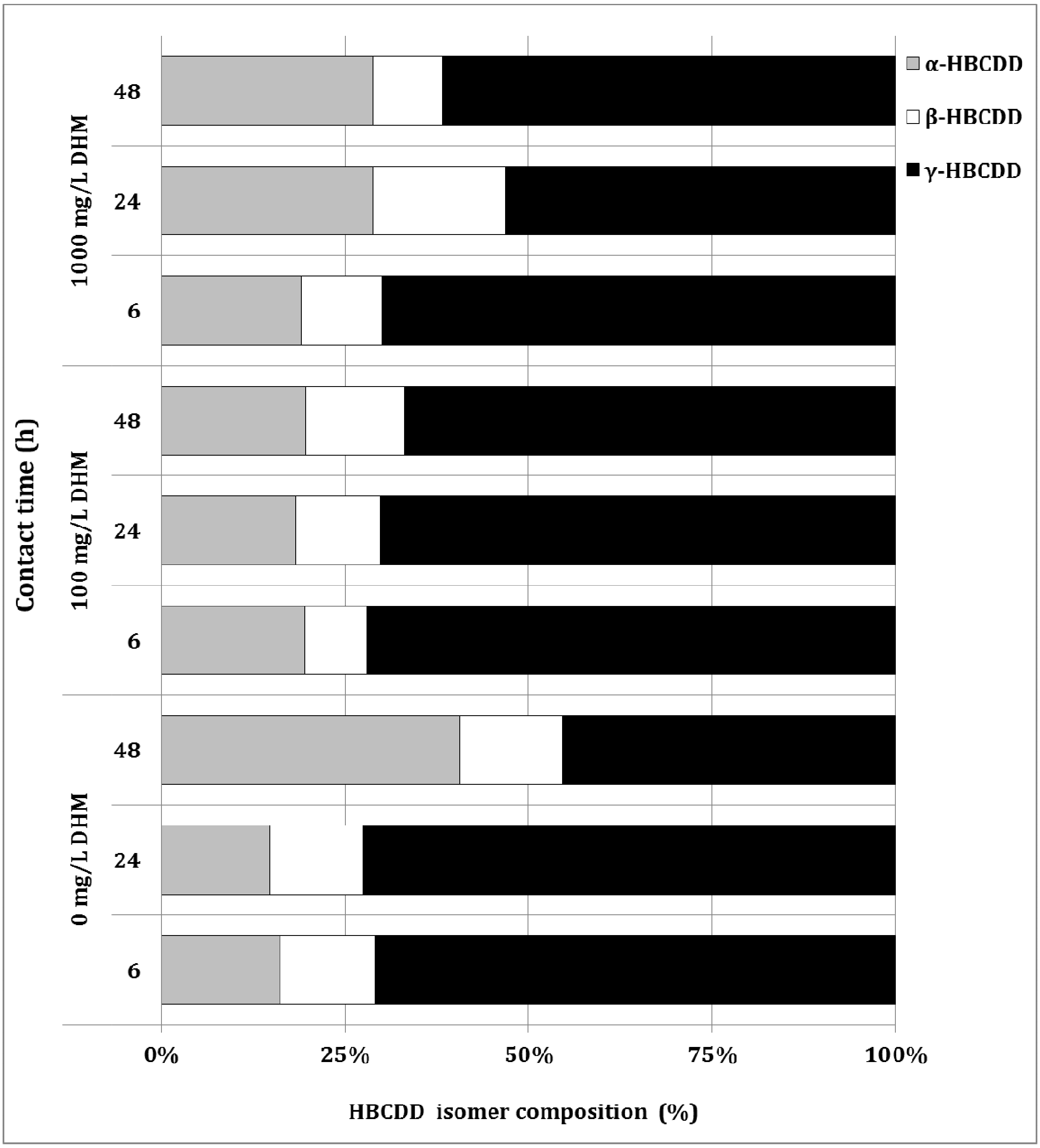

Figure 4.2: Influence of contact time on mean HBCDD diastereomer profiles in leachate for EPS foam from 24 h single batch experiments with leaching fluid containing 0, 100 and 1000 mg L^{-1} DHM concentrations.

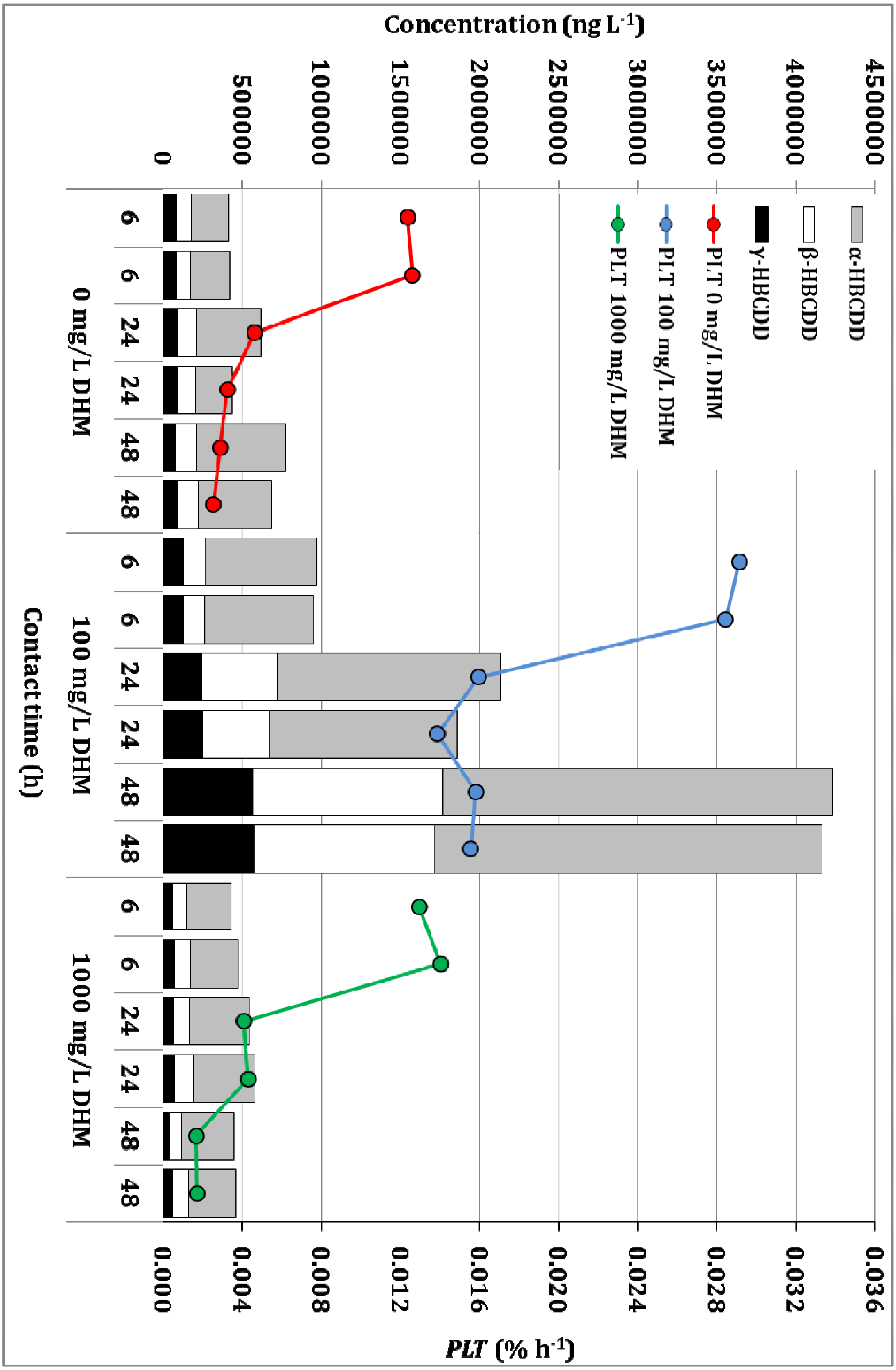

Figure 4.3: HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1})in leachate produced during 24 h single batch experiments (run in duplicate) on XPS foam at different contact times with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

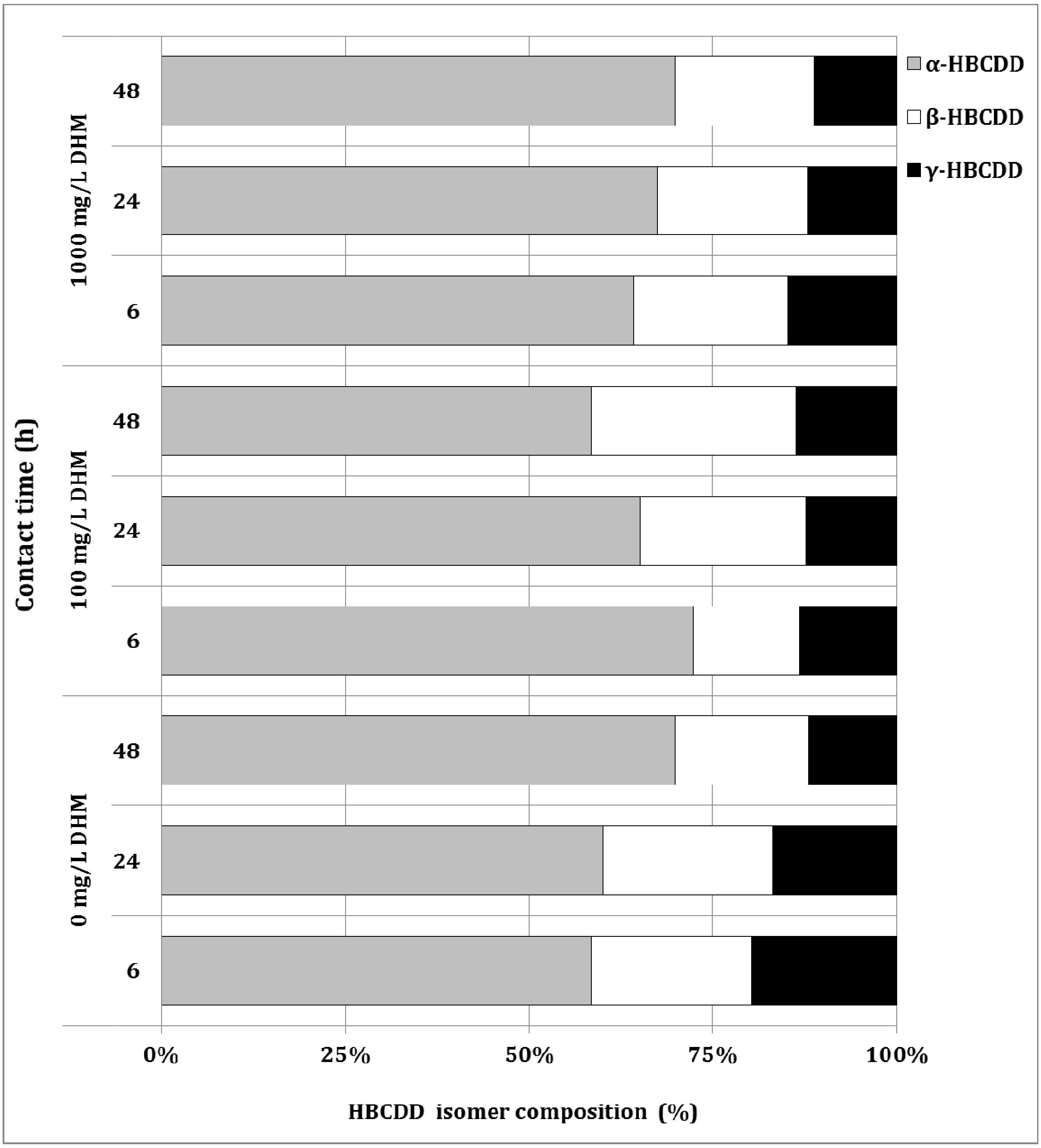

Figure 4.4: Influence of contact time on mean HBCDD diastereomer profiles in leachate for XPS foam from 24 h single batch experiments with leaching fluid containing 0, 100 and 1000 mg L^{-1} DHM concentrations.

In contrast, XPS foam experiments exhibited significant differences between all contact times for all three diastereomers at 100 mg L^{-1} DHM. In experiments where XPS foam was contacted with a DHM concentration of 1000 mg L^{-1}, highly significant differences between contact times were only observed for α-HBCDD concentrations in the leachate between 6 h and 24 h, and 24 h and 48 h, where concentrations are highest in the 24 h experiments.

It was observed that during 48 h single batch experiments involving XPS foam and the greatest DHM concentration, the XPS foam noticeably appeared to absorb the humic matter, trapping it within its pore spaces and the resulting leachate contained visibly less DHM when subsequently drained and filtered. Increasing the DHM concentration of the leaching fluid has a significantly positive effect on HBCDD concentrations for all three diastereomers (Table 4.3), therefore you would expect that the pattern of HBCDD concentrations would follow on from those observed for 100 mg L^{-1} DHM and increase linearly with increasing contact time. However, because the DHM was absorbed into the XPS foam, its resulting HBCDD concentrations were reduced. A possible reason for this would be that the additional HBCDD in the leachate associated with the DHM becomes sequestered inside the foam and was therefore not drained along with the rest of the leachate that was analysed. There is little difference in HBCDD concentrations between 6 h and 48 h contact duration at 1000 mg L^{-1} DHM and concentrations are only slightly greater than those observed for the leaching fluid with no DHM at 48 h contact duration.

Due to the weak physical properties of the insulation foam materials, it is likely that mechanical abrasion plays an important role in HBCDD leaching from both EPS and XPS foams. Longer periods of agitation result in greater abrasion of the foam material. Figure 4.5 demonstrates the abrasion of XPS foam that occurred within the leaching chamber during agitated experiments. When the resulting leachate was filtered there was a quantity of fine foam particles retained on the filter and the foam sample had been broken up and its edges smoothed like a pebble. Abrasion increases the overall surface area of the foam material, facilitating a greater leaching of HBCDD when compared to HBCDD treated textiles in the previous chapter. Another effect of abrasion on HBCDD leaching behaviour is to enable higher concentrations of the less soluble diastereomers to be present in the leachate associated with foam particles small enough to pass through the glass fibre filter (<0.45 μm). In general, longer contact times result in a larger contribution of α-HBCDD relative to β-HBCDD and γ-HBCDD diastereomers.

Figure 4.5: Abraded XPS foam after contact and foam particles filtered out of leachate after a contact period of 48 h in single batch experiments.

A strong indicator of this behaviour would be if the HBCDD concentrations present in the leachate are above the measured aqueous solubility values reported for each diastereomer and for the technical HBCDD mixture (α-HBCDD = 48,800 ng L^{-1}; β-HBCDD = 14,700 ng L^{-1}; γ-HBCDD = 2,100 ng L^{-1}; technical HBCDD = 66,000 ng L^{-1}). In all EPS foam contact time experiments, γ-HBCDD concentrations in the leachate are well above the aqueous solubility limit (77,000 - 680,000 ng L^{-1}). In experiments contacted for 6 h, γ-HBCDD is detected at concentrations between 37 and 252 times greater than its aqueous solubility. α-HBCDD is well below the aqueous solubility limit in 6 h experiments when no DHM or 100 mg L^{-1} DHM leaching fluid is contacted and also in 24 h experiments with no DHM. However in all other contact time experiments α-HBCDD concentrations are well above its aqueous solubility. β-HBCDD concentrations are just below the aqueous solubility limit (14,000 ng L^{-1}) in experiments where EPS foam was contacted for 6 h with distilled deionised water. However in all other contact time experiments on EPS foam it was well above this limit (15,000 - 180,000 ng L^{-1}). In all XPS foam contact time experiments all three diastereomers were well above the aqueous solubility limits, reflecting the weaker, more friable physical properties of the material.

Table 4.3: HBCDD leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on EPS and XPS foams with different contact times and DHM concentrations.

	DHM conc.	Agitation Time (h) /	6				24				48			
	(mg L^{-1})	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
EPS	0													
		α-HBCDD	18000	17000	0.18	0.030	20000	18000	0.20	0.0084	110000	63000	0.90	0.019
		β-HBCDD	14000	14000	0.20	0.033	15000	17000	0.23	0.0094	31000	28000	0.41	0.0086
		γ-HBCDD	77000	77000	0.20	0.033	83000	110000	0.24	0.010	86000	110000	0.25	0.0052
		ΣHBCDD	110000	110000	0.58	0.096	120000	140000	0.67	0.028	230000	200000	1.6	0.032
	100													
		α-HBCDD	92000	88000	0.93	0.16	100000	100000	1.1	0.044	100000	87000	0.99	0.021
		β-HBCDD	38000	39000	0.54	0.089	71000	59000	0.90	0.038	69000	62000	0.91	0.019
		γ-HBCDD	330000	330000	0.85	0.14	410000	380000	1.0	0.042	350000	300000	0.84	0.017
		ΣHBCDD	460000	450000	2.3	0.39	590000	540000	3.0	0.12	530000	450000	2.7	0.057
	1000													
		α-HBCDD	140000	140000	1.5	0.24	270000	290000	3.0	0.12	240000	290000	2.8	0.057
		β-HBCDD	86000	74000	1.1	0.18	170000	180000	2.5	0.10	130000	47000	1.2	0.025
		γ-HBCDD	530000	500000	1.3	0.22	530000	520000	1.3	0.056	460000	680000	1.5	0.030
		ΣHBCDD	760000	710000	3.9	0.65	970000	1000000	6.8	0.28	830000	1000000	5.4	0.11
XPS	0													
		α-HBCDD	240000	250000	0.061	0.010	400000	230000	0.079	0.0033	560000	460000	0.13	0.0027
		β-HBCDD	96000	87000	0.097	0.016	120000	120000	0.13	0.0054	140000	130000	0.14	0.0029
		γ-HBCDD	82000	83000	0.13	0.021	90000	88000	0.14	0.0058	79000	97000	0.14	0.0028
		ΣHBCDD	410000	420000	0.29	0.048	620000	440000	0.35	0.014	780000	690000	0.40	0.0084
	100													
		α-HBCDD	710000	690000	0.17	0.029	1400000	1200000	0.33	0.014	2500000	2400000	0.61	0.013
		β-HBCDD	140000	140000	0.15	0.024	480000	420000	0.47	0.020	1200000	1100000	1.2	0.026
		γ-HBCDD	130000	130000	0.20	0.033	240000	250000	0.38	0.016	570000	580000	0.90	0.019
		ΣHBCDD	980000	950000	0.52	0.087	2100000	1900000	1.2	0.049	4200000	4200000	2.7	0.057
	1000													
		α-HBCDD	280000	300000	0.073	0.012	380000	380000	0.095	0.0040	330000	300000	0.080	0.0017
		β-HBCDD	88000	100000	0.10	0.017	100000	120000	0.12	0.0050	73000	100000	0.091	0.0019
		γ-HBCDD	62000	72000	0.10	0.017	63000	74000	0.11	0.0044	43000	60000	0.080	0.0017
		ΣHBCDD	430000	470000	0.28	0.046	550000	580000	0.32	0.013	450000	460000	0.25	0.0052

Table 4.4: Results of one-way analysis of variance tests with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in experiments examining the effects of contact time on leaching; performed for each DHM concentration for both EPS and XPS foam.

EPS							
	DHM conc. (mg L^{-1})	**0**		**100**		**1000**	
Diastereomer	**Contact time (h)**	**6 h**	**24 h**	**6 h**	**24 h**	**6 h**	**24 h**
α-HBCDD	**24 h**	.995		.294		.009	
	48 h	.071	.076	.711	.614	.014	.614
β-HBCDD	**24 h**	.426		.038		.119	
	48 h	.004	.006	.037	.997	.974	.142
γ-HBCDD	**24 h**	.459		.184		.996	
	48 h	.410	.991	.985	.160	.841	.881
XPS							
	DHM conc. (mg L^{-1})	**0**		**100**		**1000**	
Diastereomer	**Contact time (h)**	**6 h**	**24 h**	**6 h**	**24 h**	**6 h**	**24 h**
α-HBCDD	**24 h**	.697		.014		.018	
	48 h	.096	.191	.001	.002	.273	.049
β-HBCDD	**24 h**	.017		.006		.478	
	48 h	.007	.226	.000	.000	.824	.275
γ-HBCDD	**24 h**	.705		.000		.986	
	48 h	.794	.984	.000	.000	.334	.289

p-values highlighted red = significant (p<0.05).

4.4. Effect of cyclical wetting and draining on HBCDD concentrations and leaching behaviour (serial batch experiments).

Mean concentrations of HBCDDs (ng L^{-1}) detected in leachate and mean *PLT* values (% h^{-1}) obtained from serial batch experiments on both EPS and XPS foams are displayed Figures 4.6 and 4.7, respectively. Concentrations of HBCDDs (ng L^{-1}) detected in leachate, mean PL (%) and mean *PLT* values (% h^{-1}) are provided in Table 4.5.

After 24 h cumulative contact time, concentrations of HBCDD leached from both insulation foams in these serial batch experiments plateau with increasing experimental duration, until the final 72 hour duration. The final contact duration 96-168 h elicited greater concentrations of α-HBCDD, possibly due to greater abrasion. Alternatively, the relatively longer contact duration enables the slower secondary phase of solubility-driven leaching to have more effect on preferentially dissolving the more soluble α-HBCDD. The decline in *PLT* values with each subsequent batch may be related to HBCDD aqueous solubility limits – i.e. HBCDD concentrations in leachate approach reported aqueous solubility values for these chemicals.

In serial batch experiments on EPS foams, the concentrations of α-HBCDD in the leachate were between 51 % and 65 % below the aqueous solubility limit, with the only exception being for the final batch in which α-HBCDD concentrations are between 74 % and 76% above the solubility limit. Concentrations of β-HBCDD and γ-HBCDD were well above the aqueous solubility limit in each of the batches with the exception of the initial batch in which β-HBCDD concentrations were ~700 ng L^{-1} below the solubility limit.

Concentrations of all three HBCDD diastereomers are well above the solubility limits in each batch in which XPS is the material tested. This suggests that abrasion plays an important role in leaching HBCDD from XPS foam in these leaching chamber experiments.

Overall – although longer term experiments are required to confirm this - this serial batch experiment indicates that replenishment of leaching fluid as would be expected in a landfill may facilitate HBCDD leaching from building insulation foams over long periods.

The results of one-way ANOVAs with post hoc Tukey tests are provided in Table 4.6 for both EPS and XPS foams. In experiments on EPS foam, there were highly significant differences ($p<0.05$) observed for α-HBCDD concentrations in the leachate between the first batch (0-6 h) and the second (6-24 h), fourth (48-72 h), fifth (72-96 h) and final sixth batch (96-168 h). The differences in α-HBCDD concentrations were less significant (93 % probability) between the first and third batch (24-48 h). Significant differences ($p<0.05$) were also observed between the second batch (6-24 h) and all other batches. There were highly significant differences ($p<0.05$) observed for α-HBCDD concentrations between the sixth batch (96-168 h) and all other batches, reflecting that the highest concentrations were observed in the last batch. There were highly significant differences in β-HBCDD concentrations in the leachate between the first batch (0-6 h) and all other batches, as β-HBCDD concentrations were lowest in the first batch. Significant differences ($p<0.05$) were also observed between the final batch (96-168 h) and all other batches, reflecting that β-HBCDD concentrations were greatest in the last batch. For γ-HBCDD concentrations, the only highly significant difference ($p<0.05$) observed was between the first batch (0-6 h) and the fourth batch; and weaker significant differences were observed between the first batch (0-6 h) and the third batch (24-48 h) (94.9 % probability) and the first batch and the fifth batch (72-96 h) (94.5 % probability).

For XPS foam, highly significant differences (p<0.05) were observed in α-HBCDD concentrations in leachate between the first batch (0-6 h) and all other batches; and the final batch (96-168 h) and all other batches. While for β-HBCDD concentrations, highly significant differences were observed between the final batch (96-168 h) and all other batches. No significant differences were observed for γ-HBCDD concentrations in the leachate between all batches.

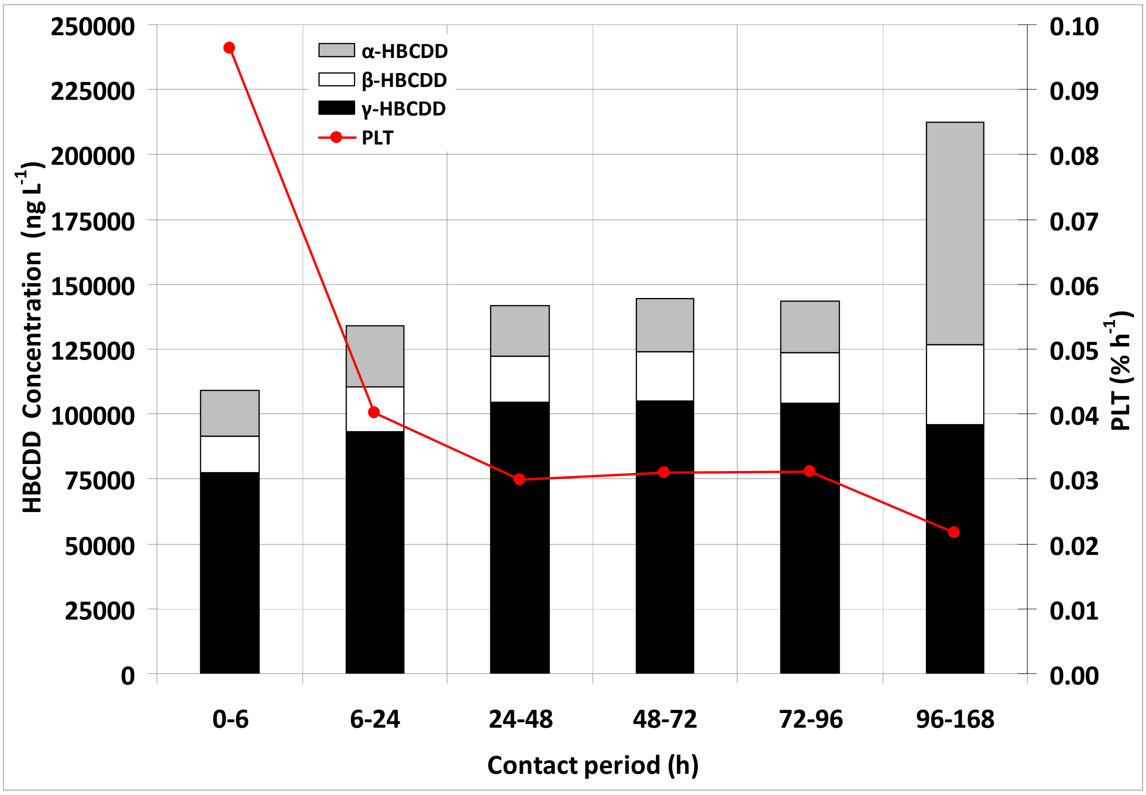

Figure 4.6: Average (n=2) HBCDD concentrations (ng L^{-1}) (bars) and *PLT* values (% ΣHBCDD h^{-1}) (red circles) in leachate produced during experiments on EPS foam examining the effect of cyclical wetting and draining.

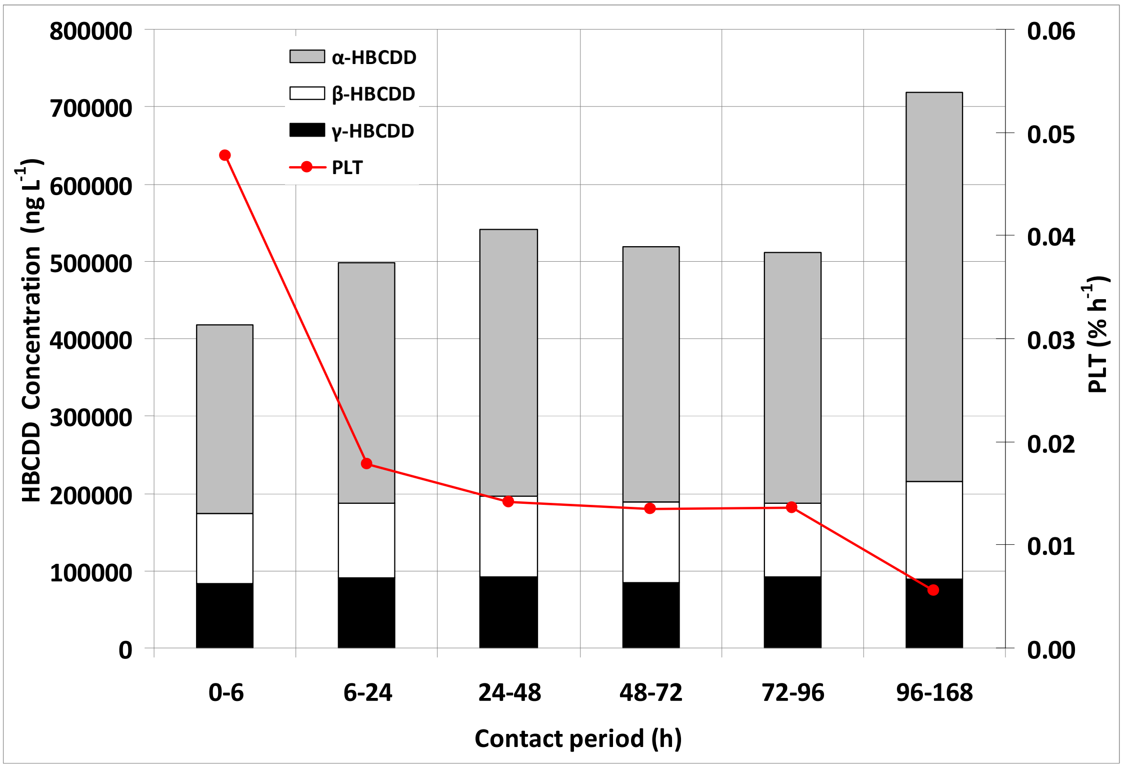

Figure 4.7: Average (n=2) HBCDD concentrations (ng L^{-1}) (bars) and *PLT* values (% ΣHBCDD h^{-1}) (red circles) in leachate produced during experiments on XPS foam examining the effect of cyclical wetting and draining.

Table 4.5: HBCDD leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on EPS and XPS foams from serial batch experiments.

Material	Contact duration (h) /	0-6				6-24				24-48			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
EPS													
	α-HBCDD	18000	17000	0.18	0.030	23000	24000	0.25	0.014	20000	19000	0.21	0.0085
	β-HBCDD	14000	14000	0.20	0.033	18000	16000	0.24	0.013	17000	18000	0.24	0.010
	γ-HBCDD	77000	77000	0.20	0.033	95000	91000	0.24	0.013	110000	100000	0.27	0.011
	ΣHBCDD	110000	110000	0.20	0.033	140000	130000	0.24	0.013	150000	140000	0.25	0.011
	Contact duration (h) /	48-72				72-96				96-168			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
	α-HBCDD	20000	21000	0.21	0.0088	20000	20000	0.21	0.0087	86000	85000	0.89	0.012
	β-HBCDD	19000	19000	0.26	0.011	19000	20000	0.27	0.011	31000	30000	0.43	0.0059
	γ-HBCDD	110000	110000	0.27	0.011	110000	94000	0.27	0.011	99000	93000	0.25	0.0034
	ΣHBCDD	140000	150000	0.26	0.011	150000	130000	0.26	0.011	220000	210000	0.38	0.0053
	Contact duration (h) /	0-6				6-24				24-48			
XPS	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
	α-HBCDD	240000	250000	0.061	0.010	310000	310000	0.078	0.0043	370000	320000	0.087	0.0036
	β-HBCDD	96000	87000	0.097	0.016	92000	100000	0.10	0.0057	110000	100000	0.11	0.0046
	γ-HBCDD	82000	83000	0.13	0.021	88000	93000	0.14	0.0078	90000	94000	0.14	0.0060
	ΣHBCDD	410000	420000	0.08	0.013	490000	510000	0.089	0.0050	560000	520000	0.097	0.0040
	Contact duration (h) /	48-72				72-96				96-168			
	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
	α-HBCDD	330000	330000	0.083	0.0034	330000	320000	0.081	0.0034	500000	500000	0.13	0.0018
	β-HBCDD	110000	100000	0.11	0.0046	92000	97000	0.10	0.0042	130000	120000	0.13	0.0019
	γ-HBCDD	86000	83000	0.13	0.0055	110000	79000	0.14	0.0060	83000	95000	0.14	0.0019
	ΣHBCDD	520000	520000	0.093	0.0039	530000	490000	0.092	0.0038	720000	720000	0.13	0.0018

Table 4.6: Results of one-way analysis of variance tests with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in serial batch experiments; performed for EPS and XPS foam.

EPS

Diastereomer	Batch number	1	2	3	4	5
α-HBCDD	2	.000				
	3	.070	.004			
	4	.021	.011	.839		
	5	.042	.006	.995	.978	
	6	.000	.000	.000	.000	.000
β-HBCDD	2	.046				
	3	.035	1.000			
	4	.006	.387	.501		
	5	.003	.133	.178	.912	
	6	.000	.000	.000	.000	.000
γ-HBCDD	2	.309				
	3	.051	.608			
	4	.046	.563	1.000		
	5	.055	.641	1.000	1.000	
	6	.197	.998	.811	.769	.840

XPS

Diastereomer	Batch number	1	2	3	4	5
α-HBCDD	2	.029				
	3	.004	.299			
	4	.009	.794	.868		
	5	.012	.936	.694	.999	
	6	.000	.000	.000	.000	.000
β-HBCDD	2	.874				
	3	.353	.856			
	4	.261	.725	1.000		
	5	.988	.995	.621	.483	
	6	.005	.012	.037	.049	.008
γ-HBCDD	2	.948				
	3	.893	1.000			
	4	1.000	.983	.951		
	5	.861	1.000	1.000	.930	
	6	.979	1.000	.999	.996	.997

Batch number: 1 = 0–6 h; 2 = 6–24 h; 3 = 24–48 h; 4 = 48–72 h; 5 = 72–96 h; 6 = 96–168 h.

p-values highlighted red = significant ($p<0.05$).

4.5. Leaching kinetics.

We generated plots of t/C_t against t for all single and serial batch experiments (18 data points) conducted at 20 ˚C and agitated at 200 RPM for distilled deionised water leaching fluids. Again, the same degrees of uncertainty outlined in chapter 3.6 are to be applied to these relationships and their constants. However, there is an additional degree of uncertainty with the kinetics for leaching fluids containing 100 and 1000 mg L^{-1} DHM because they only include the single batch experiments (6 data points).

The slope, Y-intercept, saturated leaching capacity, C_s, the leaching rate constant, k, two-tailed p values, and Pearson's correlation coefficients, r, are given for HBCDD diastereomers in Table 4.7. A positive and highly significant linear correlation between t/C_t and t was observed for all diastereomers in experiments with XPS foams with leaching fluids at 0 mg L^{-1} DHM. In the equivalent experiments on EPS foams, correlations were only observed for β-HBCDD and γ-HBCDD. For single batch experiments on EPS foam with leaching fluids containing 100 mg kg^{-1} DHM only β-HBCDD showed a significant correlation, while for XPS foams only α-HBCDD showed a weaker correlation. With EPS foam experiments with the 1000 mg kg^{-1} DHM leaching fluid, only α-HBCDD and γ-HBCDD are significantly correlated. The XPS foam y-intercepts were negative for all three diastereomers, and have therefore not been included.

EPS foam plots are provided for DHM concentrations 0, 100 and 1000 mg kg^{-1} as Figures 4.8, 4.9 and 4.10 respectively. XPS foam plots are provided for DHM concentrations 0, 100 mg kg^{-1} as Figures 4.11 and 4.12 respectively.

To further evaluate the hypothesis of second-order rate kinetics, the natural logarithm of the HBCDD leachate concentration data for both single and serial batch experiments conducted at 20 ˚C, were plotted against time to check for linearity and negative slope intercepts that would suggest first order kinetics. Plots of Ln Ct versus t were not consistent with first order kinetics. In all instances where slopes were negative, correlation coefficients r were insignificant and Pearson's two-tailed probability values also demonstrated no significance. This strongly supports the idea that leaching of HBCDD from building insulation foams in these experiments is predominantly governed by second-order leaching kinetics.

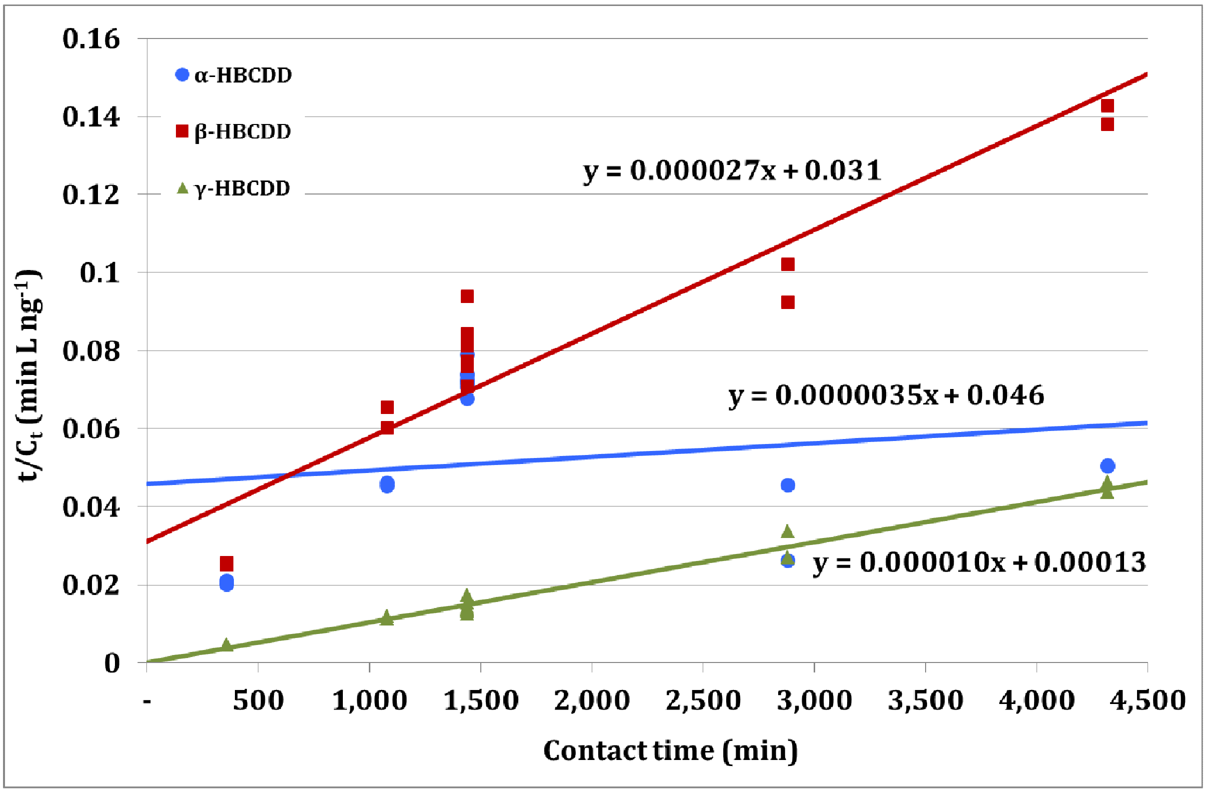

Figure 4.8: Plot of t/Ct versus t for leaching of HBCDD from EPS foam in single and serial batch experiments with Milli-Q leaching fluid. (n=18)

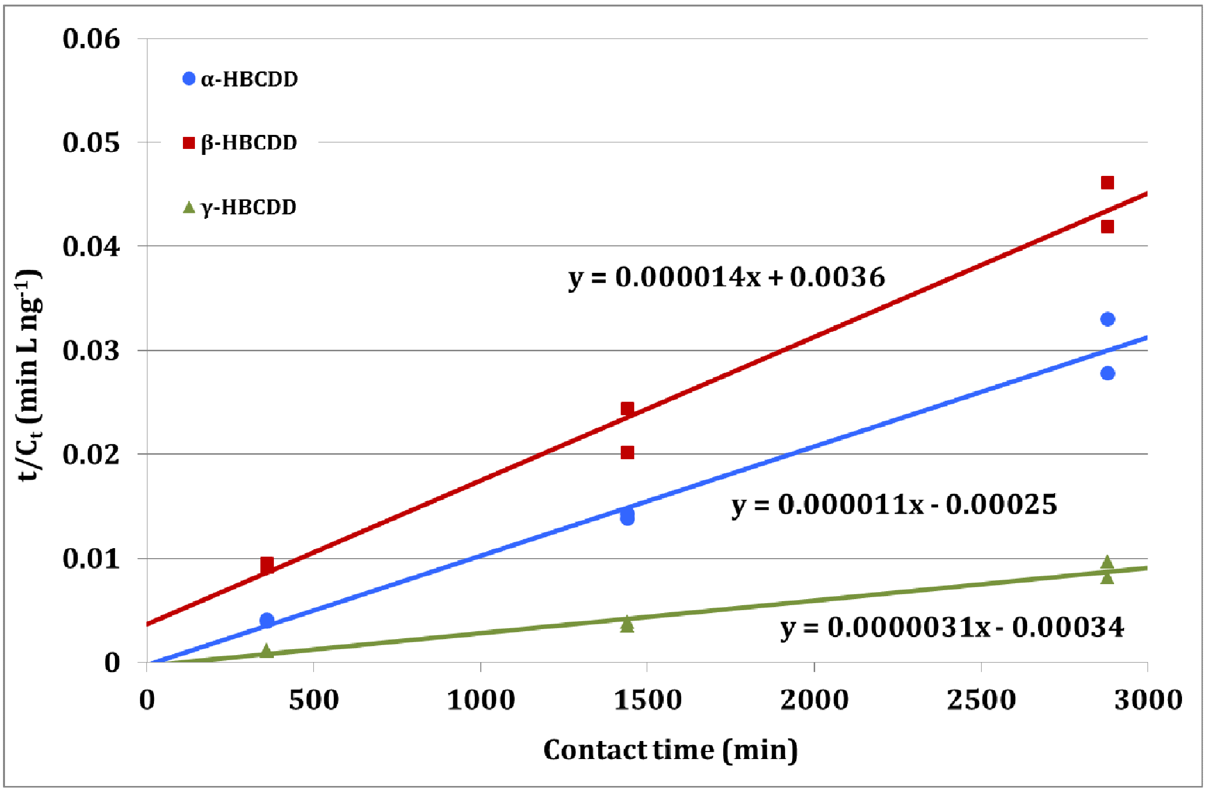

Figure 4.9: Plot of t/Ct versus t for leaching of HBCDD from EPS foam in single and serial batch experiments with 100 mg L^{-1} DHM leaching fluid. (n=6)

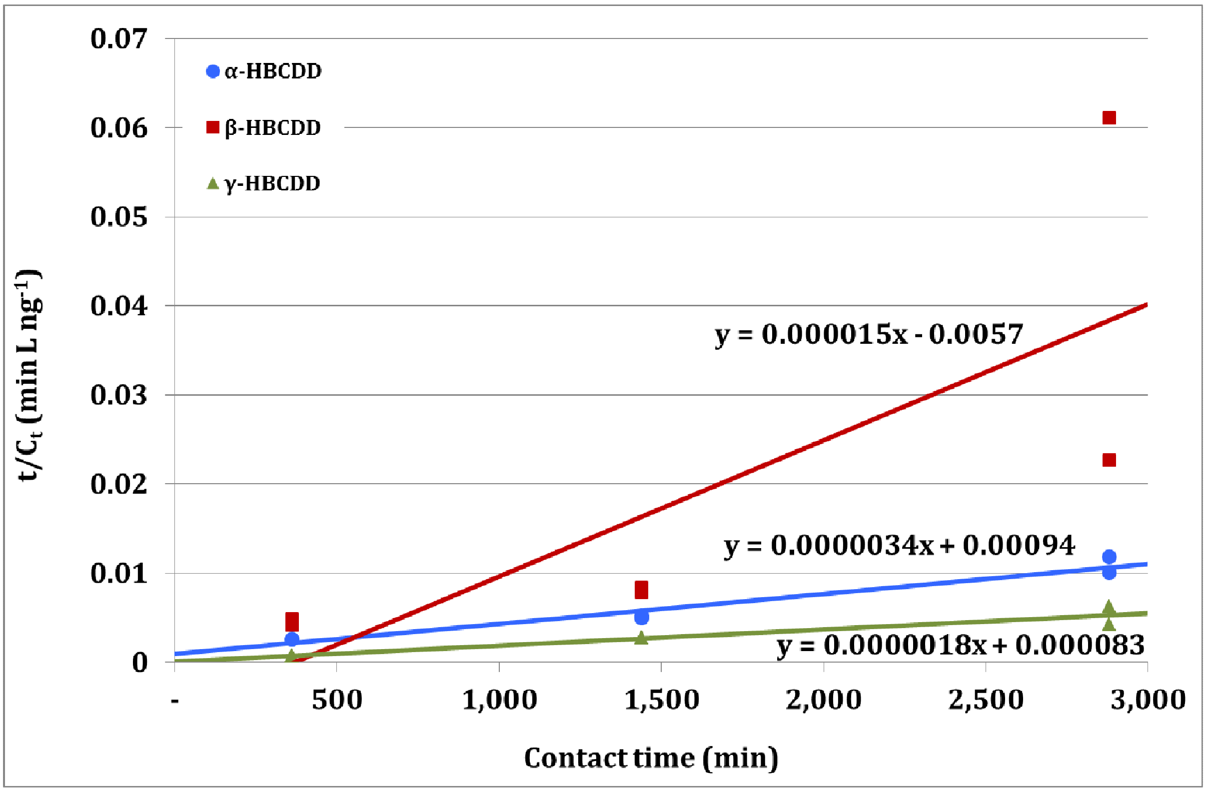

Figure 4.10: Plot of t/Ct versus t for leaching of HBCDD from EPS foam in single and serial batch experiments with 1000 mg L^{-1} DHM leaching fluid. (n=6)

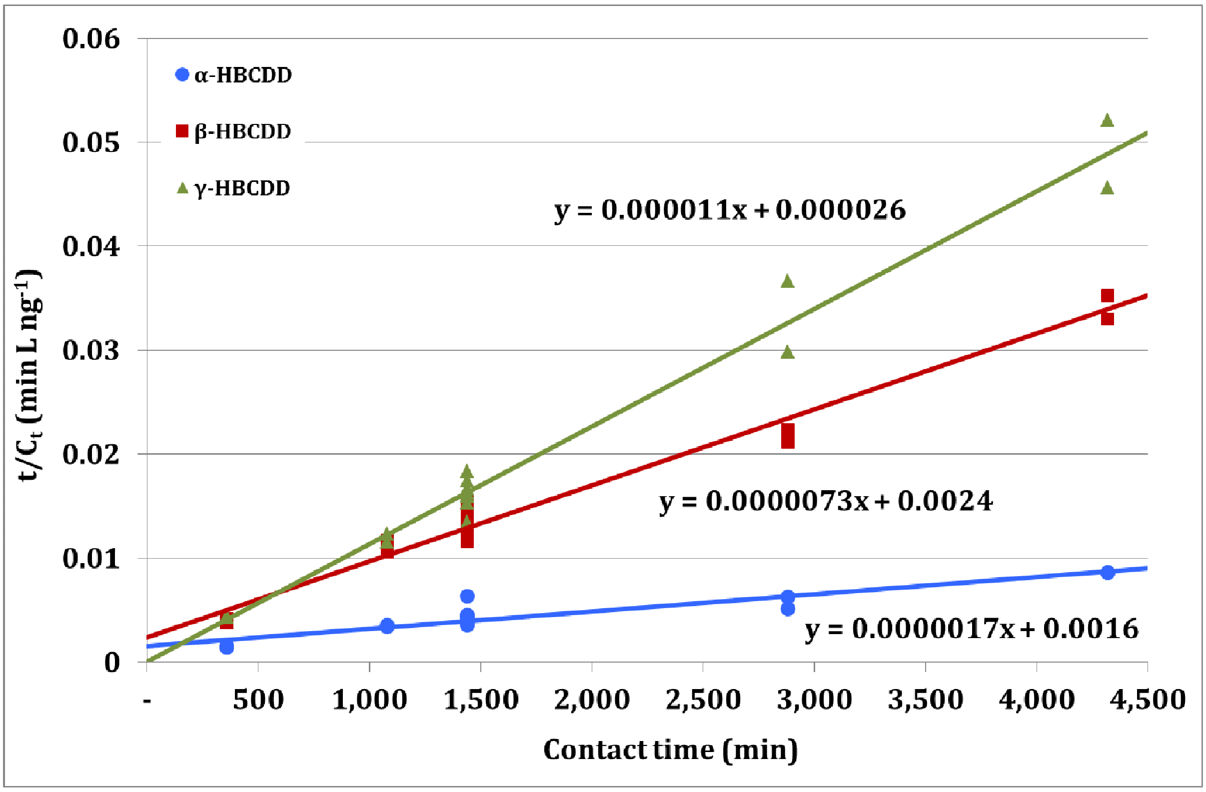

Figure 4.11: Plot of t/Ct versus t for leaching of HBCDD from XPS foam in single and serial batch experiments with Milli-Q leaching fluid. (n=18)

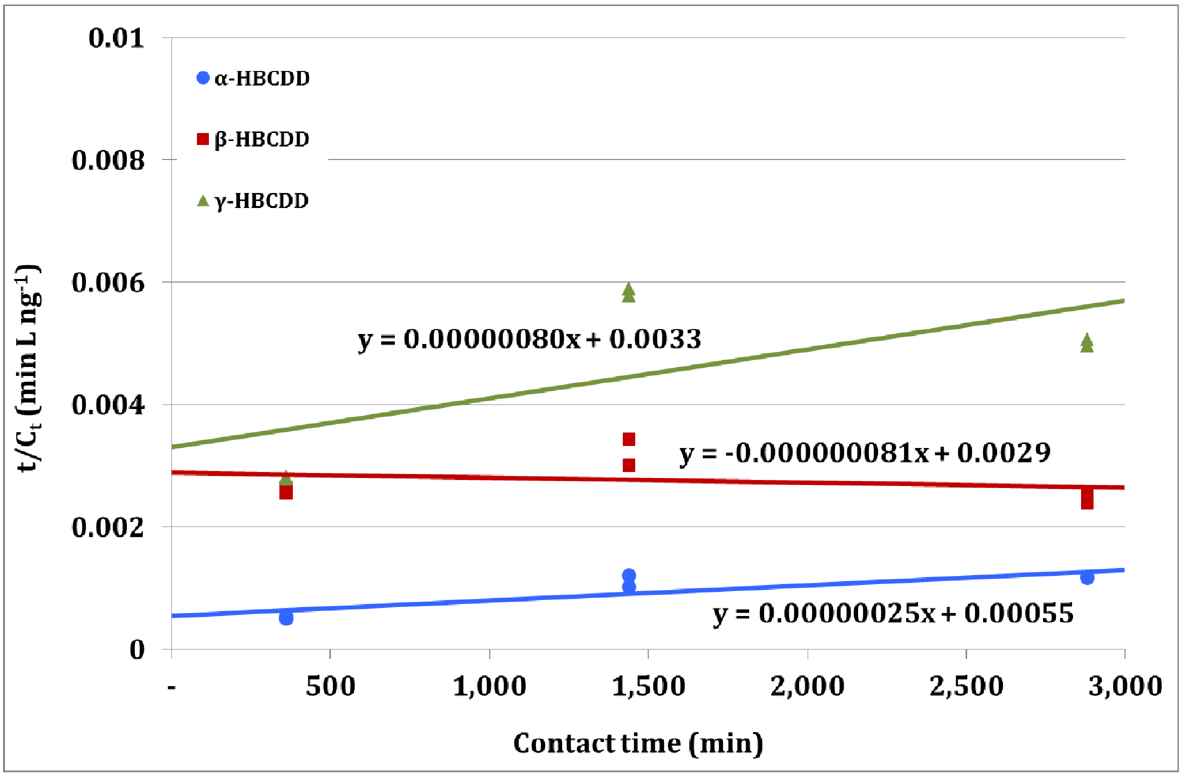

Figure 4.12: Plot of t/Ct versus t for leaching of HBCDD from XPS foam in single and serial batch experiments with 100 mg L^{-1} DHM leaching fluid. (n=6)

Table 4.7: Second order leaching rate constants (*k*) and saturated leaching capacities (C_s) obtained for HBCDD diastereomers from both EPS and XPS foam[a].

Constant / Compound	**Slope (min L ng^{-1} /min)**	**y-intercept (min L ng^{-1})**	***Cs* (ng L^{-1})**	***k* (L ng^{-1} min^{-1})**	***Two-tailed P value***	***Correlation coefficient: r***
0 mg L^{-1} DHM concentration.						
EPS						
β-HBCDD	0.000027	0.031	37,000	0.000000023	.000	0.933
γ-HBCDD	0.000010	0.00013	97,000	0.00000080	.000	0.991
XPS						
α-HBCDD	0.0000017	0.0016	600,000	0.0000000018	.000	0.933
β-HBCDD	0.0000073	0.0024	140,000	0.000000022	.000	0.988
γ-HBCDD	0.000011	0.000026	88,000	0.0000049	.000	0.991
100 mg L^{-1} DHM concentration.						
EPS						
β-HBCDD	0.000014	0.0036	72,000	0.000000053	.000	0.991
XPS						
α-HBCDD	0.00000025	0.00055	4,000,000	0.00000000011	.031	0.852
1000 mg L^{-1} DHM concentration.						
EPS						
α-HBCDD	0.0000034	0.00094	300,000	0.000000012	.000	0.980
γ-HBCDD	0.0000018	0.000083	550,000	0.000000039	.003	0.953

[a] Data not shown for plots for which y-intercept and thus k values were negative or for which Pearson's two tailed correlation coefficient (p value) exceeded 0.05.

4.6. Effects of temperature and humic matter content of leaching fluid on HBCDD leaching from EPS and XPS foams.

The influence of temperature on HBCDD concentrations and mean *PLT* values (% h^{-1}) in leachate in single batch experiments conducted at three different DHM contents for EPS foams and XPS foams are illustrated by Figure 4.13 and Figure 4.15, respectively. The diastereomer pattern in leachate for EPS foams and XPS foams at different contact times are shown in Figures 4.14 and 4.16, respectively. HBCDD concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) are provided in Table 4.8. The results of one-way ANOVAs with post hoc Tukey tests for the same experiments are provided in Table 4.9.

In experiments on both insulation foams, HBCDD leaching is enhanced by increasing leachate temperature, regardless of DHM concentration. However, this effect is less marked in XPS foam experiments with 100 mg L^{-1} DHM. The relative diastereomer pattern of HBCDD in leachate shifts pattern towards a greater relative abundance of a-HBCDD with increasing temperature. At 80 °C there is more α-HBCDD and less β-HBCDD and γ-HBCDD than at both 20 °C and 50 °C. XPS follows the same pattern of HBCDD diastereomer shift with increasing temperature as EPS but changes are less pronounced.

In experiments on EPS foam, there were highly significant differences ($p<0.05$) in α-HBCDD between 20 ºC and 80 ºC and between 50 ºC and 80 ºC across all DHM concentrations. α-HBCDD concentrations were greatest in experiments at 80 ºC. There are highly significant differences ($p<0.05$) in γ-HBCDD concentrations between 20 °C and 50 °C and between 20 ºC and 80 ºC when leaching fluids contained no DHM; between 20 ºC and 80 ºC and between 50 ºC and 80 ºC when leaching fluids contained 100 mg L^{-1} DHM; and between 20 ºC and 80 ºC only when leaching fluids contained 1000 mg L^{-1} DHM.

In experiments on XPS foam contacted with leaching fluids with no DHM, there were highly significant differences in α-HBCDD and γ-HBCDD concentrations between temperatures. Highly significant differences in β-HBCDD concentrations were detected only between 20 ºC and 80 ºC, with a weaker significance (94.6 % probability) in differences between 20 ºC and 50 ºC. In experiments where 100 mg L^{-1} DHM leaching fluid was contacted, there were no significant differences in any HBCDD diastereomer concentrations in the leachate between the temperatures. When 1000 mg L^{-1} DHM leaching fluid was contacted, there were highly significant differences in α-HBCDD and β-HBCDD concentrations in the leachate between 20 ºC and 80 ºC and between 50 ºC and 80 ºC. Highly significant differences in γ-HBCDD concentrations exist only between 20 ºC and 80 ºC.

In all temperature experiments on EPS foam, concentrations of γ-HBCDD in the leachates were well above the aqueous solubility limit at 20 ºC. In experiments on EPS foams contacted with leaching fluids at 20 ºC, concentrations of α-HBCDD and β-HBCDD were below the aqueous solubility limits for all three DHM concentrations explored.

In all temperature experiments on XPS foams, concentrations of all three diastereomers were well above the aqueous solubility limits at 20 ºC; with the only exception being for β-HBCDD concentrations in 20 ºC leaching fluids with no DHM, in which they are below the solubility limit (8,500 – 14,000 ng L^{-1}).

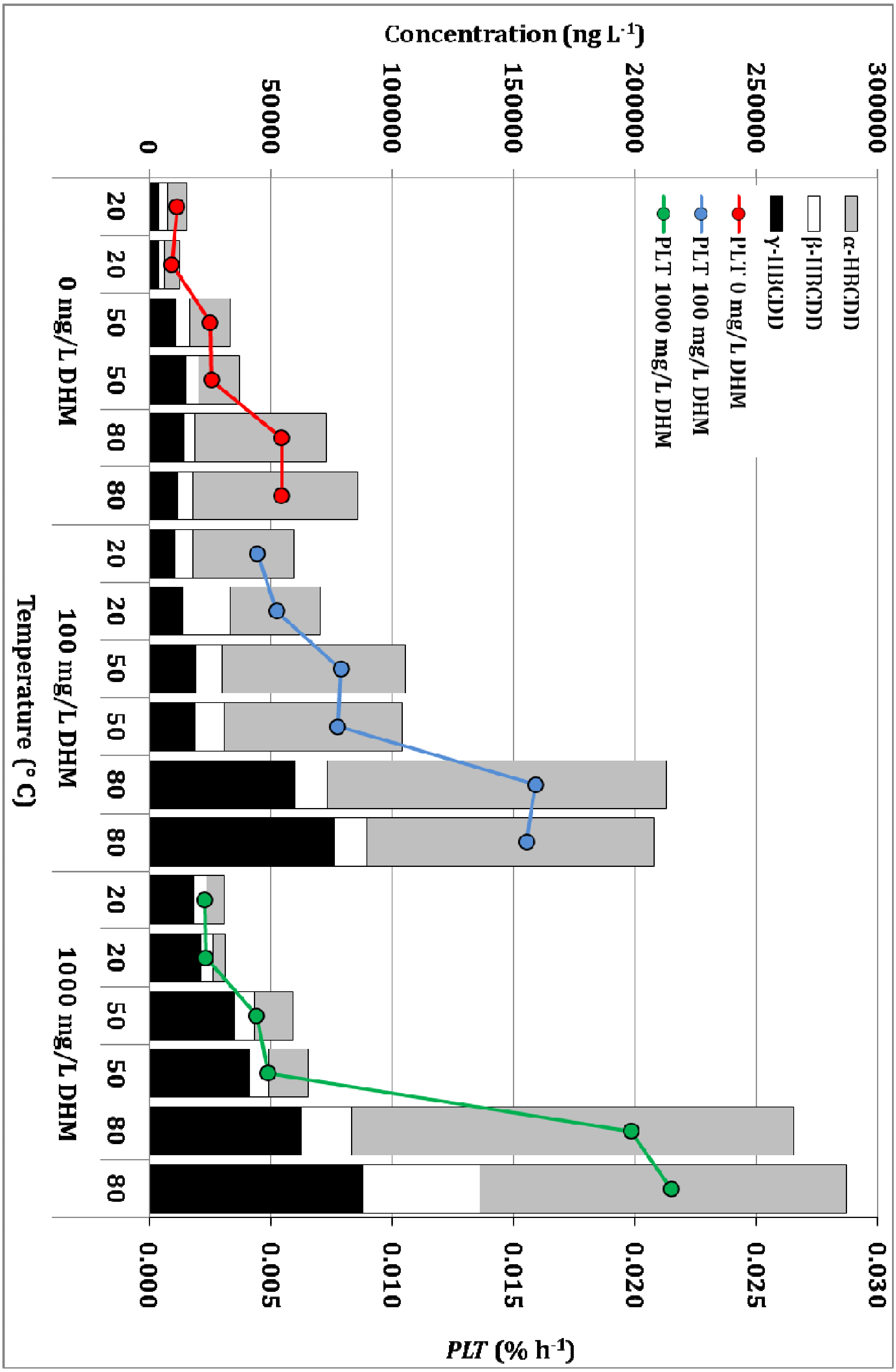

Figure 4.13: HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced during 24 h single batch experiments (run in duplicate) on EPS foam at different temperatures with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

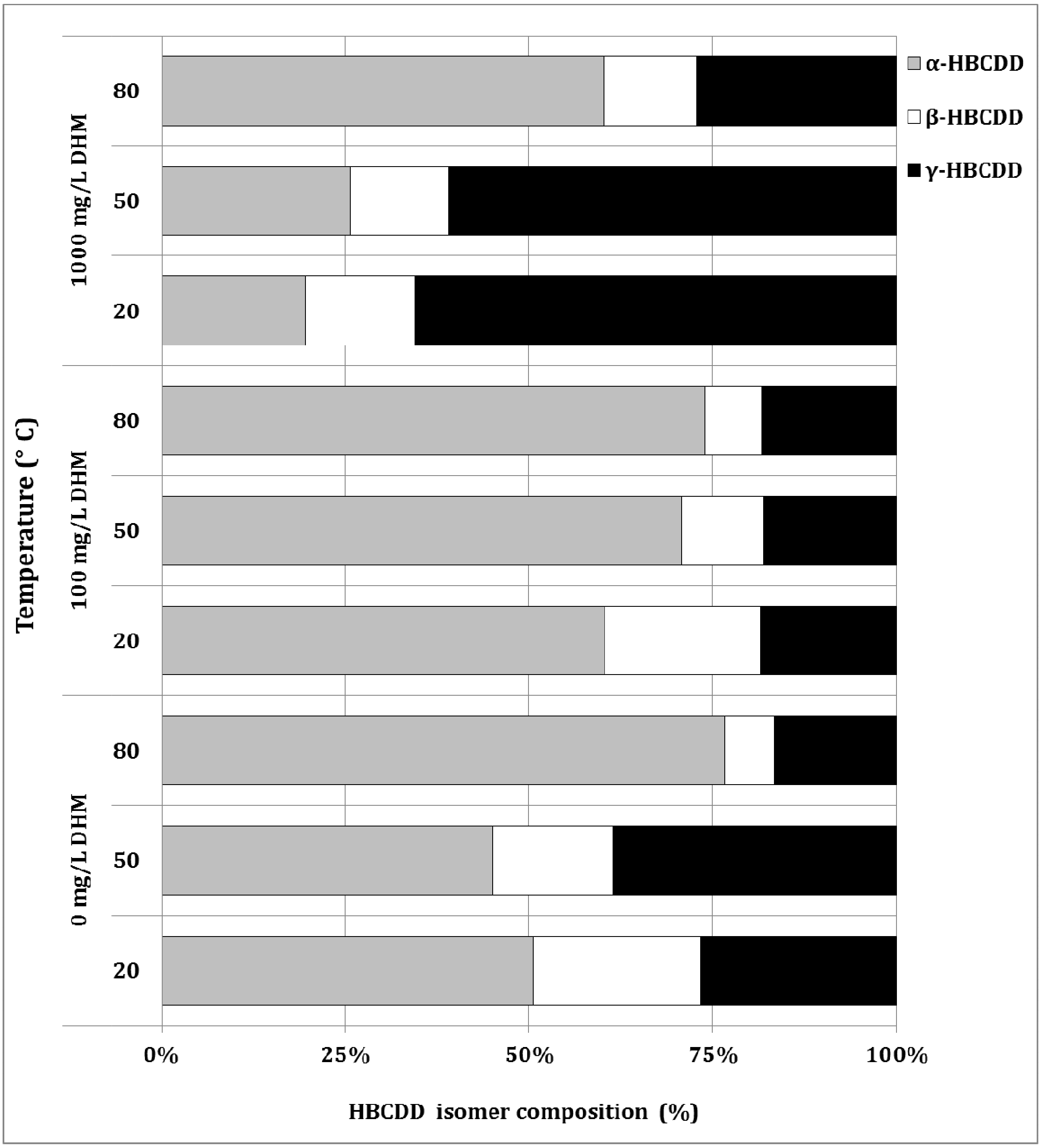

Figure 4.14: Influence of temperature on mean HBCDD diastereomer profiles in leachate for EPS foam from 24 h single batch experiments with leaching fluid containing 0, 100 and 1000 mg L^{-1} DHM concentrations.

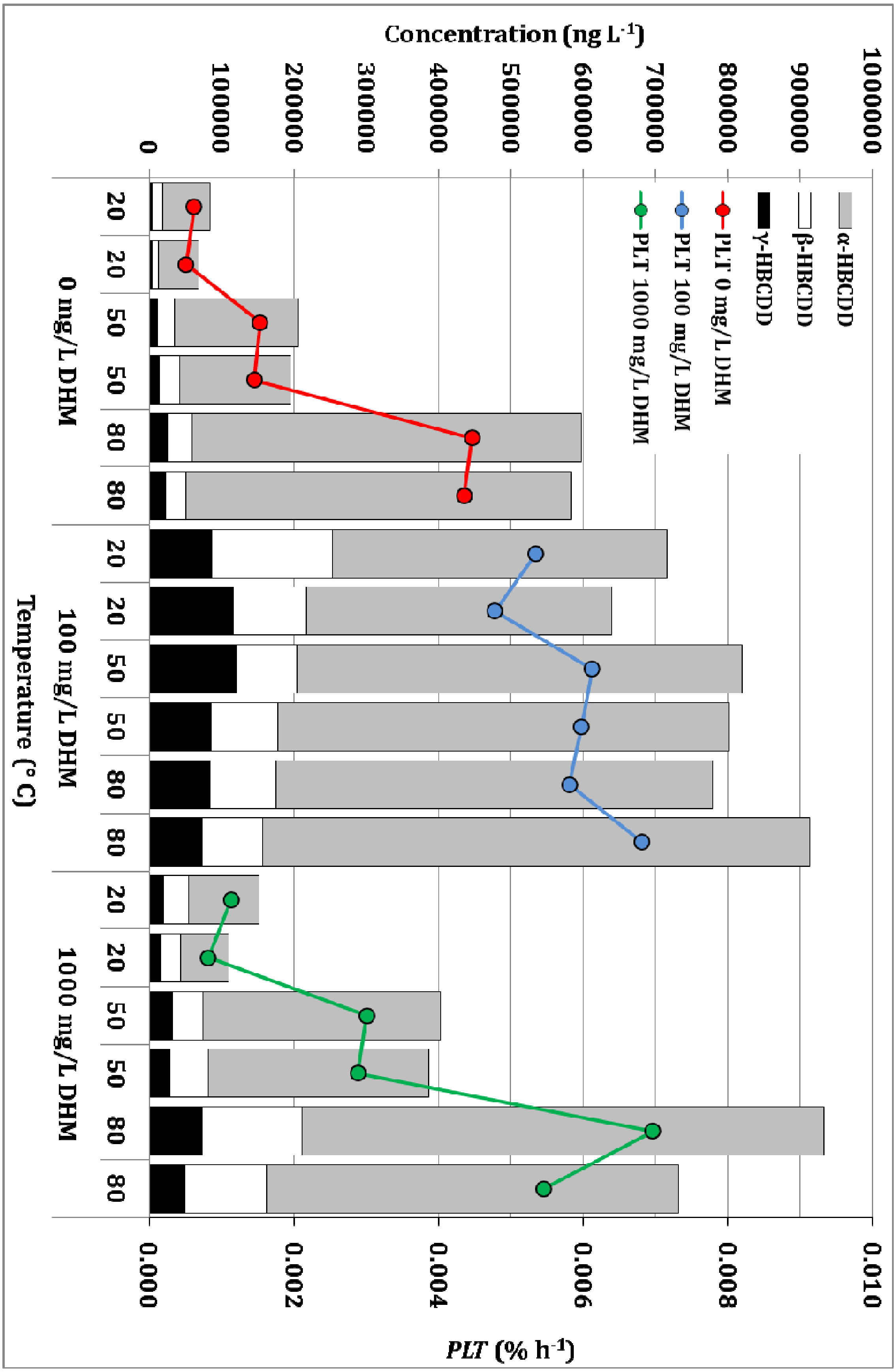

Figure 4.15: HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced during 24 h single batch experiments (run in duplicate) on XPS foam at different temperatures with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

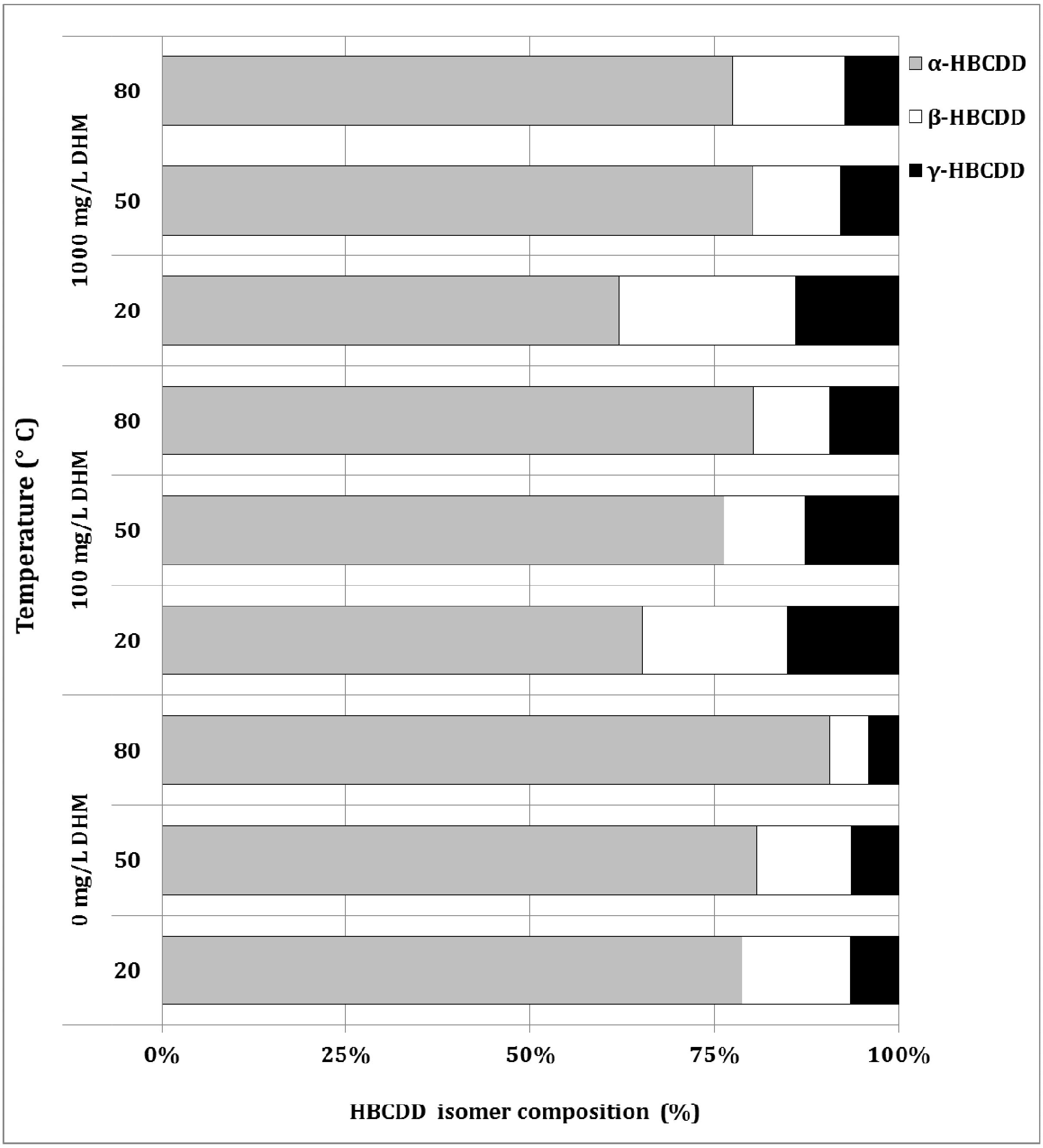

Figure 4.16: Influence of temperature on mean HBCDD diastereomer profiles in leachate for XPS foam from 24 h single batch experiments with leaching fluid containing 0, 100 and 1000 mg L^{-1} DHM concentrations.

Table 4.8: HBCDD leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on EPS and XPS foams with different temperatures and DHM concentrations.

	DHM conc.	Temperature (°C) /	20				50				80			
	(mg L^{-1})	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
EPS	0													
		α-HBCDD	8100	6200	0.0031	0.074	17000	14000	0.0066	0.1594	67000	54000	0.026	0.63
		β-HBCDD	3800	2700	0.0019	0.045	5800	5300	0.0032	0.0766	6200	4600	0.0031	0.075
		γ-HBCDD	3700	3800	0.00040	0.0097	11000	15000	0.0014	0.0337	12000	14000	0.0014	0.034
		ΣHBCDD	16000	13000	0.025	0.0011	34000	34000	0.061	0.0025	86000	73000	0.14	0.0059
	100													
		α-HBCDD	42000	37000	0.017	0.41	75000	73000	0.032	0.7714	140000	120000	0.056	1.3
		β-HBCDD	7700	20000	0.0079	0.19	11000	12000	0.0067	0.1609	13000	14000	0.0078	0.19
		γ-HBCDD	10000	14000	0.0013	0.031	19000	19000	0.0020	0.0491	60000	4100	0.0034	0.082
		ΣHBCDD	60000	70000	0.12	0.0049	110000	100000	0.19	0.0078	210000	140000	0.31	0.013
	1000													
		α-HBCDD	7300	5100	0.0027	0.064	16000	16000	0.0069	0.1665	180000	150000	0.072	1.7
		β-HBCDD	4900	4500	0.0027	0.066	8500	8200	0.0048	0.1160	21000	48000	0.020	0.48
		γ-HBCDD	19000	22000	0.0022	0.052	35000	41000	0.0041	0.0979	63000	88000	0.0081	0.19
		ΣHBCDD	31000	31000	0.056	0.0023	59000	66000	0.11	0.0047	270000	290000	0.50	0.021
XPS	0													
		α-HBCDD	65000	56000	0.015	0.00063	170000	150000	0.041	0.0017	540000	530000	0.13	0.0056
		β-HBCDD	14000	8500	0.012	0.00049	23000	28000	0.027	0.0011	34000	29000	0.033	0.0014
		γ-HBCDD	5000	4900	0.0077	0.00032	12000	14000	0.020	0.0008	26000	22000	0.038	0.0016
		ΣHBCDD	84000	69000	0.014	0.00057	210000	190000	0.036	0.0015	600000	580000	0.11	0.0044
	100													
		α-HBCDD	460000	420000	0.11	0.0046	620000	620000	0.16	0.0065	760000	600000	0.17	0.0071
		β-HBCDD	170000	100000	0.14	0.0059	84000	93000	0.093	0.0039	84000	91000	0.092	0.0038
		γ-HBCDD	87000	120000	0.16	0.0066	120000	86000	0.16	0.0067	73000	85000	0.12	0.0051
		ΣHBCDD	720000	640000	0.12	0.0051	820000	800000	0.15	0.0061	910000	780000	0.15	0.0063
	1000													
		α-HBCDD	97000	66000	0.020	0.00085	330000	300000	0.079	0.0033	720000	570000	0.16	0.0067
		β-HBCDD	35000	29000	0.033	0.0014	42000	53000	0.050	0.0021	140000	110000	0.13	0.0055
		γ-HBCDD	21000	15000	0.028	0.0012	33000	29000	0.048	0.0020	73000	50000	0.10	0.0040
		ΣHBCDD	150000	110000	0.024	0.0010	400000	390000	0.071	0.0029	930000	730000	0.15	0.0062

Table 4.9: Results of one-way analysis of variance with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in experiments examining the effects of temperature on leaching; performed for each DHM concentration for both EPS and XPS foam.

EPS

	DHM conc. (mg L^{-1})	0		100		1000	
Diastereomer	**Temperature (°C)**	**20**	**50**	**20**	**50**	**20**	**50**
α-HBCDD	**50**	.330		.065		.736	
	80	.005	.009	.005	.020	.002	.003
β-HBCDD	**50**	.132		.906		.945	
	80	.145	.992	1.000	.917	.145	.190
γ-HBCDD	**50**	.032		.612		.343	
	80	.031	.999	.008	.011	.028	.078

XPS

	DHM conc. (mg L^{-1})	0		100		1000	
Diastereomer	**Temperature (°C)**	**20**	**50**	**20**	**50**	**20**	**50**
α-HBCDD	**50**	.003		.139		.070	
	80	.000	.000	.070	.659	.006	.029
β-HBCDD	**50**	.054		.343		.480	
	80	.022	.374	.332	.999	.009	.014
γ-HBCDD	**50**	.030		.998		.485	
	80	.002	.011	.530	.502	.044	.106

p-values highlighted red = significant ($p<0.05$).

4.7. Effects of pH and humic matter content of leaching fluid on HBCDD leaching.

The influence of pH on HBCDD concentrations and mean *PLT* values (% h^{-1}) in leachate in single batch experiments conducted at 20 ˚C for EPS foams and XPS foams are illustrated by Figure 4.17 and Figure 4.19, respectively. The diastereomer pattern in leachate for EPS foams and XPS foams at different contact times are illustrated by Figures 4.18 and 4.20, respectively. HBCDD concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) are provided in Table 4.10. The results of one-way ANOVAs with post hoc Tukey tests are provided for the same experiments in Table 4.11.

In experiments on EPS foam, there are highly significant differences in α-HBCDD concentrations in the leachate between pH 6.5 and pH 5.8, and between pH 6.5 and pH 8.5 in leaching fluids with no DHM. In experiments where 100 mg L^{-1} DHM leaching fluid was contacted, there were highly significant differences in α-HBCDD concentrations in the leachate between the pH levels tested, with the only exceptions being no significant differences between pH 6.5 and pH 5.8. When 1000 mg L^{-1} DHM leaching fluid was contacted, there were no significant differences between the pH levels. There are no significant differences in β-HBCDD concentrations in the leachate between pH levels when either no DHM or 1000 mg L^{-1} DHM leaching fluid was contacted. However in leaching fluids containing 100 mg L^{-1} DHM, there were highly significant differences in β-HBCDD concentrations in the leachate between pH 8.5 and pH 5.8, and between pH 8.5 and pH 6.5. There are highly significant differences in γ-HBCDD concentrations between pH 8.5 and pH 5.8, and between pH 8.5 and pH 6.5 when leaching fluids contained no DHM; and between pH 6.5 and pH 5.8, and between pH 6.5 and pH 8.5 when leaching fluids contained 1000 mg L^{-1} DHM. There were highly significant differences between all pH levels when the leaching fluid contained 100 mg L^{-1} DHM.

In experiments on XPS foam contacted with leaching fluids with no DHM, there were weakly significant differences in α-HBCDD and β-HBCDD concentrations between pH 6.5 and pH 8.5 (94.7 % and 94 % probability, respectively); and highly significant differences between all other pH levels. In experiments where 100 mg L^{-1} DHM leaching fluid was contacted, there were no significant differences in α-HBCDD concentrations in the leachate between pH 6.5 and pH 8.5 and no significant differences in β-HBCDD concentrations between pH 6.5 and pH 5.8. When 1000 mg L^{-1} DHM leaching fluid was contacted, there were no significant differences in α-HBCDD and β-HBCDD concentrations in the leachate between pH 6.5 and pH 5.8 and highly significant differences between all other pH levels. There were highly significant differences in γ-HBCDD concentrations between all pH levels at all DHM concentrations, with one exception being no significant differences between pH 5.8 and pH 6.5 when 1000 mg L^{-1} DHM leaching fluid was contacted.

In experiments on EPS foams contacted with leaching fluids of pH 5.8 and pH 8.5, concentrations of all three diastereomers were well above the aqueous solubility limits for all three DHM concentrations explored; with the only exception being for β-HBCDD concentrations in leaching fluids with no DHM and pH 8.5, in which they are at the solubility limit (13,000 – 15,000 ng L^{-1}).

In experiments on XPS foams contacted with leaching fluids of pH 5.8 and pH 8.5, concentrations of all three diastereomers were well above the aqueous solubility limits for all three DHM concentrations explored.

In general, more HBCDD is leached under acidic (5.8) and alkaline (8.5) conditions when the leaching fluid contained no DHM. More HBCDD is leached under alkaline (8.5) conditions with DHM solutions and less under acidic (5.8) conditions. α-HBCDD appears to be more readily leached when contacted with alkaline (8.5) leaching fluids. There is relatively more α-HBCDD and γ-HBCDD in acidic and alkaline leaching fluids than at the slightly acidic pH 6.5. The effect of pH appears to be smallest for the β-HBCDD diastereomer.

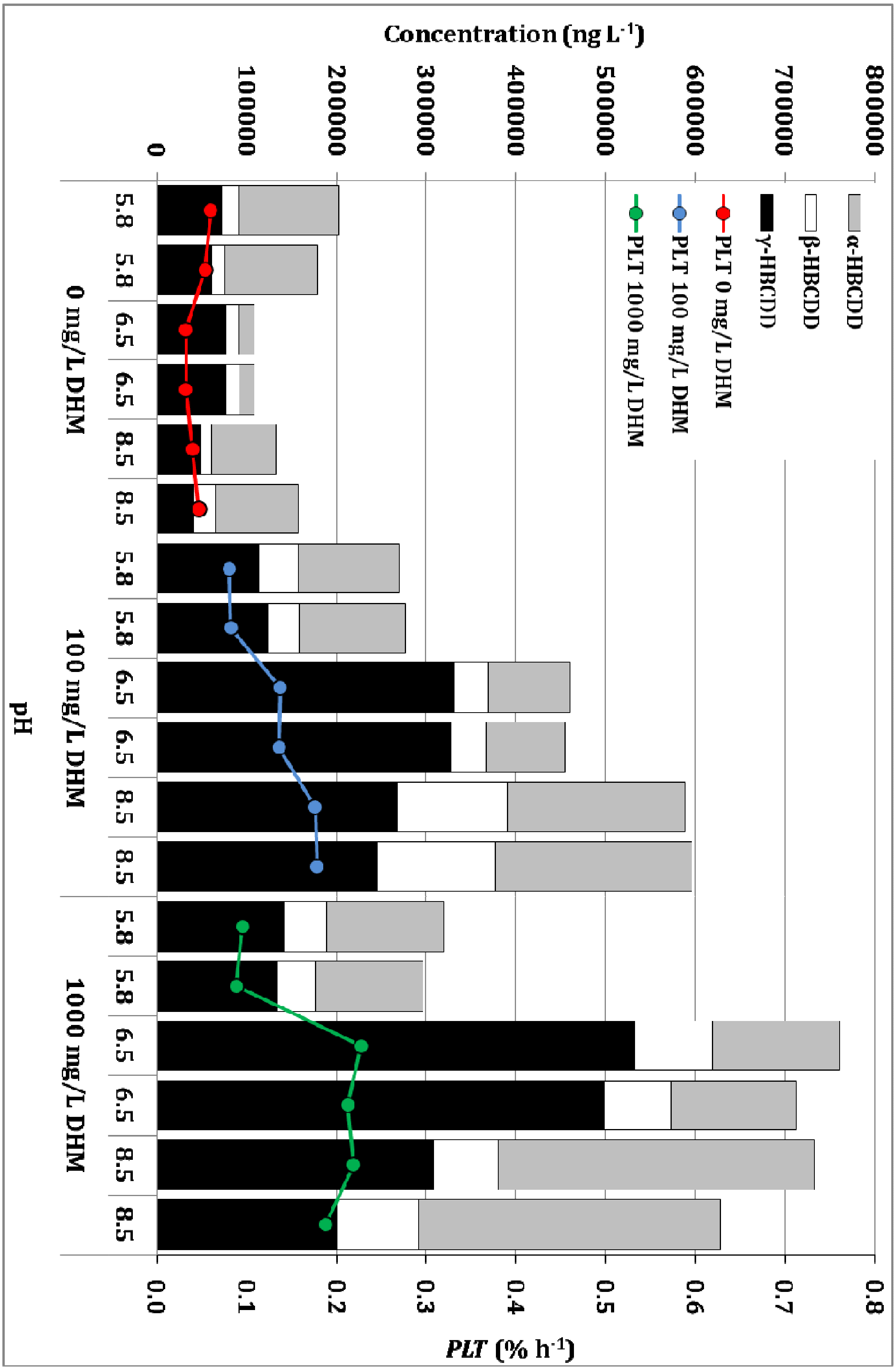

Figure 4.17: HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced during 24 h single batch experiments (run in duplicate) on EPS foam at different pH levels with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

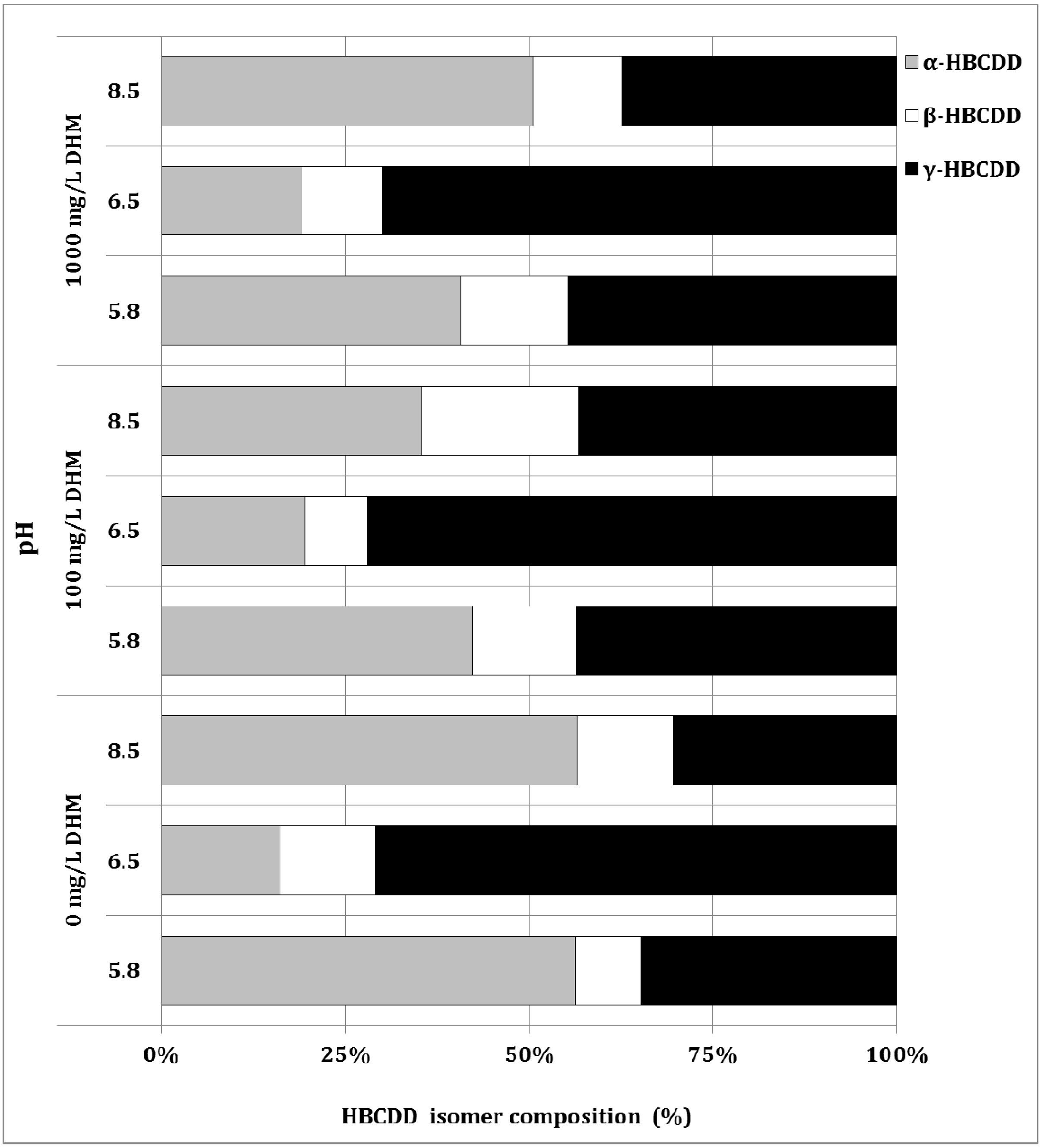

Figure 4.18: Influence of pH on mean HBCDD diastereomer profiles in leachate for EPS foam from 24 h single batch experiments with leaching fluid containing 0, 100 and 1000 mg L^{-1} DHM concentrations.

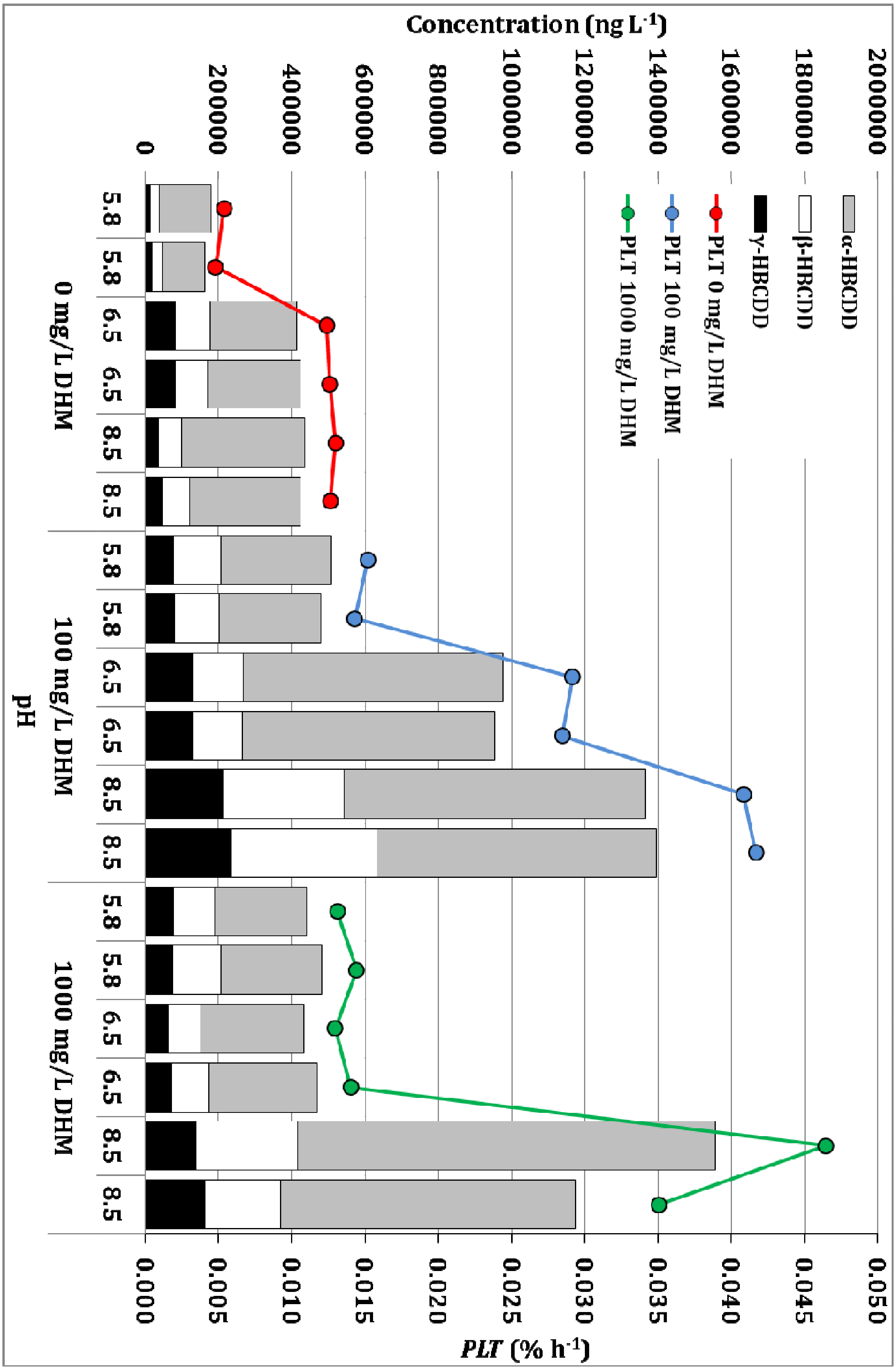

Figure 4.19: HBCDD concentrations (ng L^{-1}) and *PLT* values (% ΣHBCDD h^{-1}) in leachate produced during 24 h single batch experiments (run in duplicate) on XPS foam at different pH levels with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

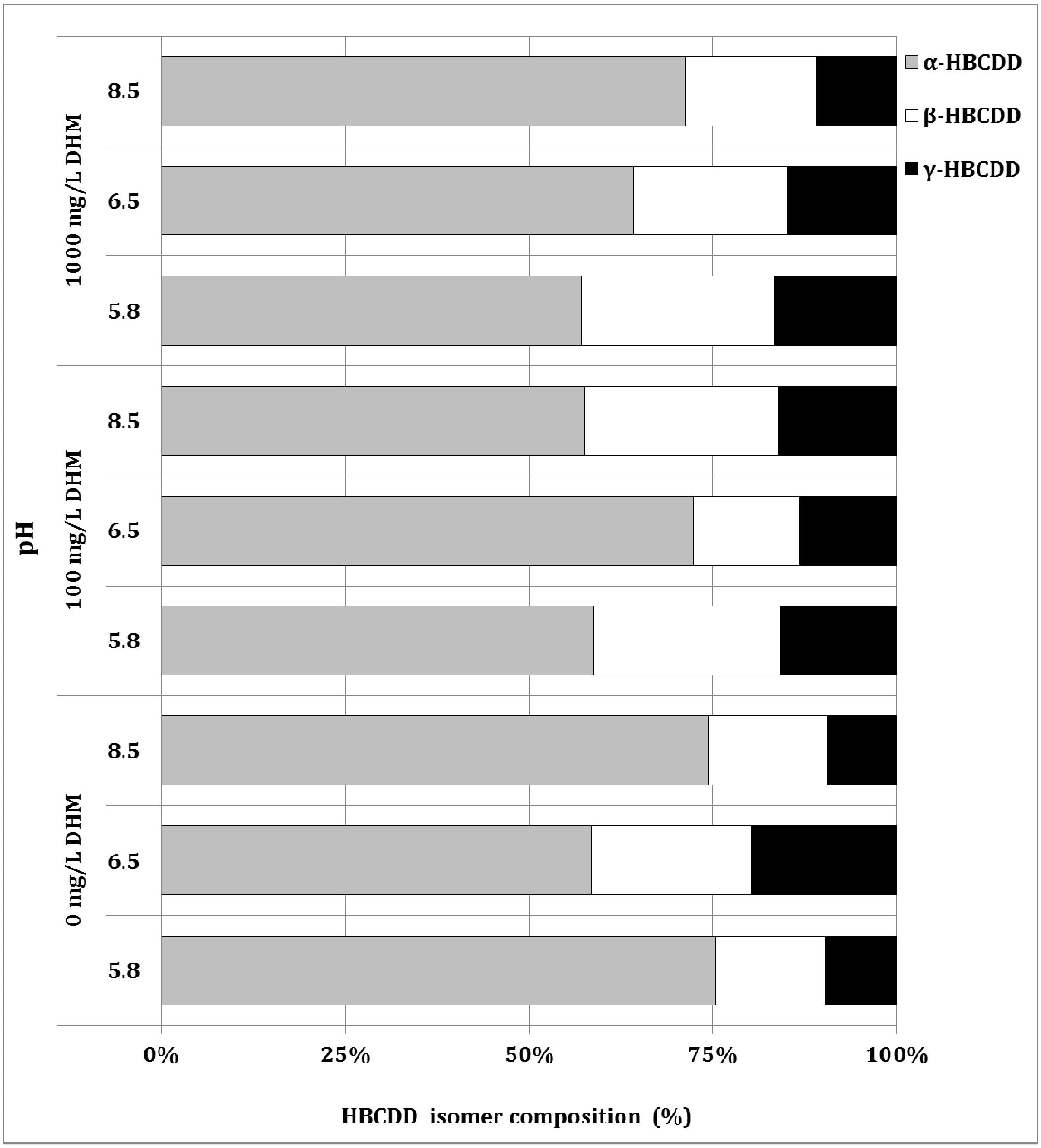

Figure 4.20: Influence of pH on mean HBCDD diastereomer profiles in leachate for XPS foam from 24 h single batch experiments with leaching fluid containing 0, 100 and 1000 mg L^{-1} DHM concentrations.

Table 4.11: HBCDD leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on EPS and XPS foams with different pH values and DHM concentrations.

	DHM conc.	pH /	5.8				6.5				8.5			
	(mg L^{-1})	Diastereomer	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
EPS	0													
		α-HBCDD	110000	100000	1.1	0.19	18000	17000	0.18	0.030	72000	100000	0.85	0.14
		β-HBCDD	19000	15000	0.23	0.039	14000	14000	0.20	0.033	13000	15000	0.26	0.044
		γ-HBCDD	72000	61000	0.17	0.028	77000	77000	0.20	0.033	48000	61000	0.11	0.019
		ΣHBCDD	200000	180000	0.34	0.057	110000	110000	0.20	0.033	130000	180000	0.26	0.043
	100													
		α-HBCDD	110000	120000	1.2	0.20	92000	88000	0.93	0.16	200000	220000	2.2	0.36
		β-HBCDD	43000	34000	0.54	0.089	38000	39000	0.54	0.089	120000	130000	1.8	0.29
		γ-HBCDD	110000	120000	0.31	0.051	330000	330000	0.85	0.14	270000	240000	0.66	0.11
		ΣHBCDD	270000	280000	0.49	0.082	460000	450000	0.82	0.14	590000	600000	1.1	0.18
	1000													
		α-HBCDD	130000	120000	1.3	0.22	140000	140000	1.5	0.24	350000	340000	3.6	0.60
		β-HBCDD	48000	42000	0.62	0.10	86000	74000	1.1	0.18	71000	92000	1.1	0.19
		γ-HBCDD	140000	130000	0.36	0.059	530000	500000	1.3	0.22	310000	200000	0.66	0.11
		ΣHBCDD	320000	300000	1.1	0.18	760000	710000	0.55	0.092	730000	630000	1.2	0.20
XPS	0													
		α-HBCDD	140000	120000	0.032	0.0054	240000	250000	0.061	0.010	330000	300000	0.080	0.013
		β-HBCDD	24000	27000	0.027	0.0045	96000	87000	0.097	0.016	65000	75000	0.074	0.012
		γ-HBCDD	15000	19000	0.026	0.0043	82000	83000	0.13	0.021	35000	45000	0.063	0.010
		ΣHBCDD	180000	160000	0.085	0.014	410000	420000	0.29	0.048	430000	420000	0.22	0.036
	100													
		α-HBCDD	300000	280000	0.073	0.012	710000	690000	0.17	0.029	820000	760000	0.20	0.033
		β-HBCDD	130000	120000	0.13	0.022	140000	140000	0.15	0.024	330000	400000	0.39	0.064
		γ-HBCDD	79000	79000	0.12	0.020	130000	130000	0.20	0.033	210000	230000	0.35	0.058
		ΣHBCDD	510000	480000	0.33	0.055	980000	950000	0.52	0.087	1400000	1400000	0.93	0.16
	1000													
		α-HBCDD	250000	280000	0.066	0.011	280000	300000	0.073	0.012	1100000	810000	0.24	0.041
		β-HBCDD	110000	130000	0.13	0.021	88000	100000	0.10	0.017	280000	210000	0.26	0.043
		γ-HBCDD	79000	75000	0.12	0.020	62000	72000	0.10	0.017	140000	160000	0.23	0.039
		ΣHBCDD	440000	480000	0.31	0.052	430000	470000	0.28	0.046	1600000	1200000	0.73	0.12

Table 4.11: Results of one-way analysis of variance with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in experiments examining the effects of different pH levels on leaching; performed for each DHM concentration for both EPS and XPS foam.

EPS

	DHM conc. (mg L^{-1})	0		100		1000	
Diastereomer	**pH**	**5.8**	**6.5**	**5.8**	**6.5**	**5.8**	**6.5**
α-HBCDD	**6.5**	.004		.105		.992	
	8.5	.114	.010	.003	.002	.919	.959
β-HBCDD	**6.5**	.860		1.000		.581	
	8.5	.918	.658	.001	.001	.968	.705
γ-HBCDD	**6.5**	.244		.001		.011	
	8.5	.048	.016	.002	.013	1.000	.011

XPS

	DHM conc. (mg L^{-1})	0		100		1000	
Diastereomer	**pH**	**5.8**	**6.5**	**5.8**	**6.5**	**5.8**	**6.5**
α-HBCDD	**6.5**	.016		.002		.979	
	8.5	.004	.053	.001	.086	.028	.031
β-HBCDD	**6.5**	.003		.887		.707	
	8.5	.008	.060	.007	.008	.057	.034
γ-HBCDD	**6.5**	.001		.024		.641	
	8.5	.029	.005	.001	.004	.012	.009

p-values highlighted red = significant ($p<0.05$).

4.8. Effects of agitation on HBCDD leaching.

By comparing the results of experiments conducted at 20 °C with contact times of 24 h in the agitated contact time experiments and the non-agitated temperature experiments; the effect of agitation on leaching of HBCDD from the both EPS and XPS foams can be examined (Figures 4.21 and 4.22).

The results of paired sample t-tests are presented in Table 4.12 and indicate that agitation has a large role to play in HBCDD leaching from building insulation foams. In experiments on EPS foam, highly significant differences ($p<0.05$) are observed in β-HBCDD and γ-HBCDD leachate concentrations between agitated and non-agitated samples. There is also a weaker significant difference (92.9 % probability) between α-HBCDD concentrations in leachate in agitated and non-agitated samples.

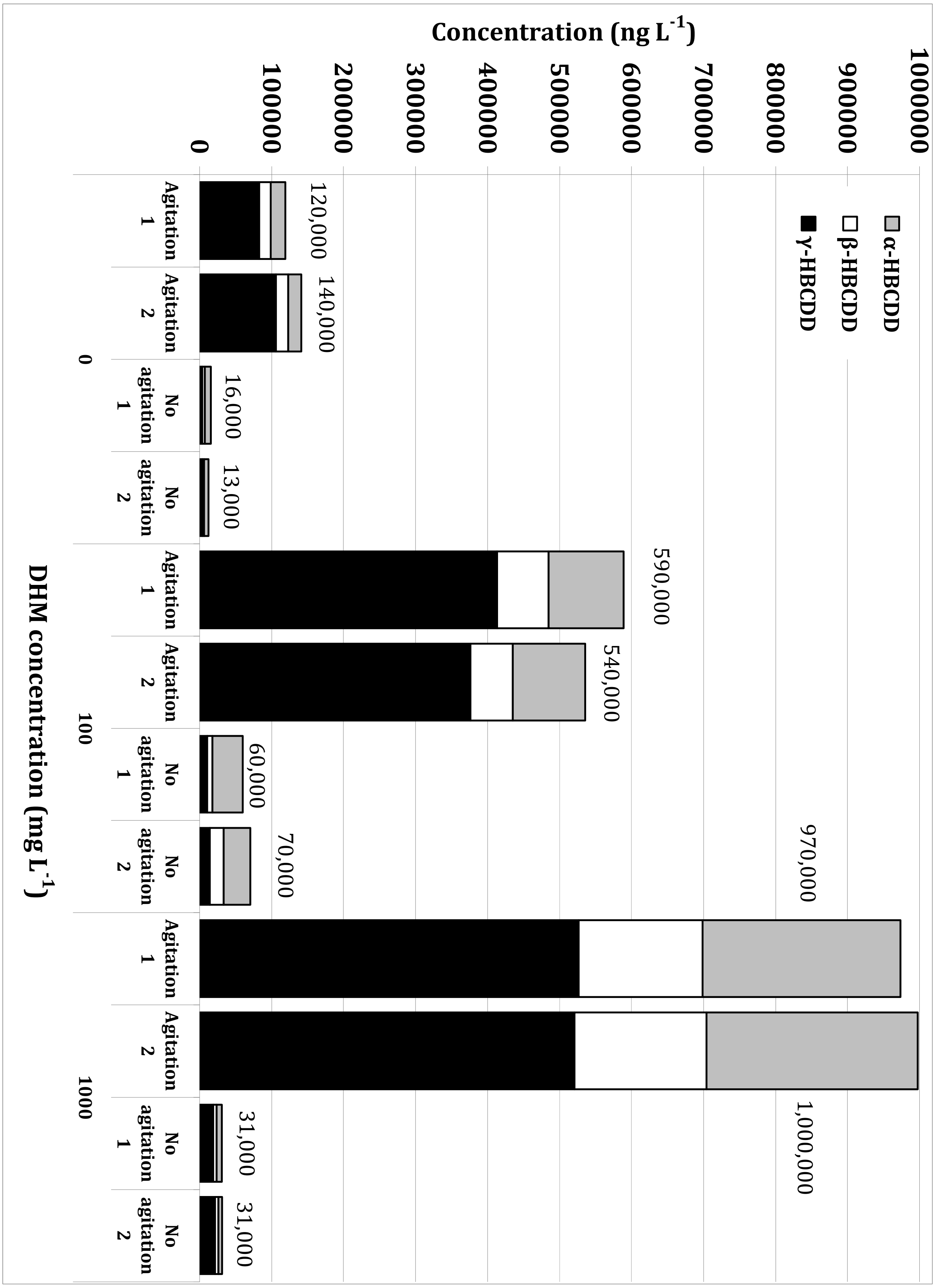

Figure 4.21: HBCDD concentrations (ng L^{-1}) in leachate produced during duplicate experiments examining the effects of agitation on leaching from EPS foam from 24 h single batch experiments using 0, 100 and 1000 mg L^{-1} DHM as leaching fluid. Data labels on bars are for ΣHBCDD and rounded to two significant figures.

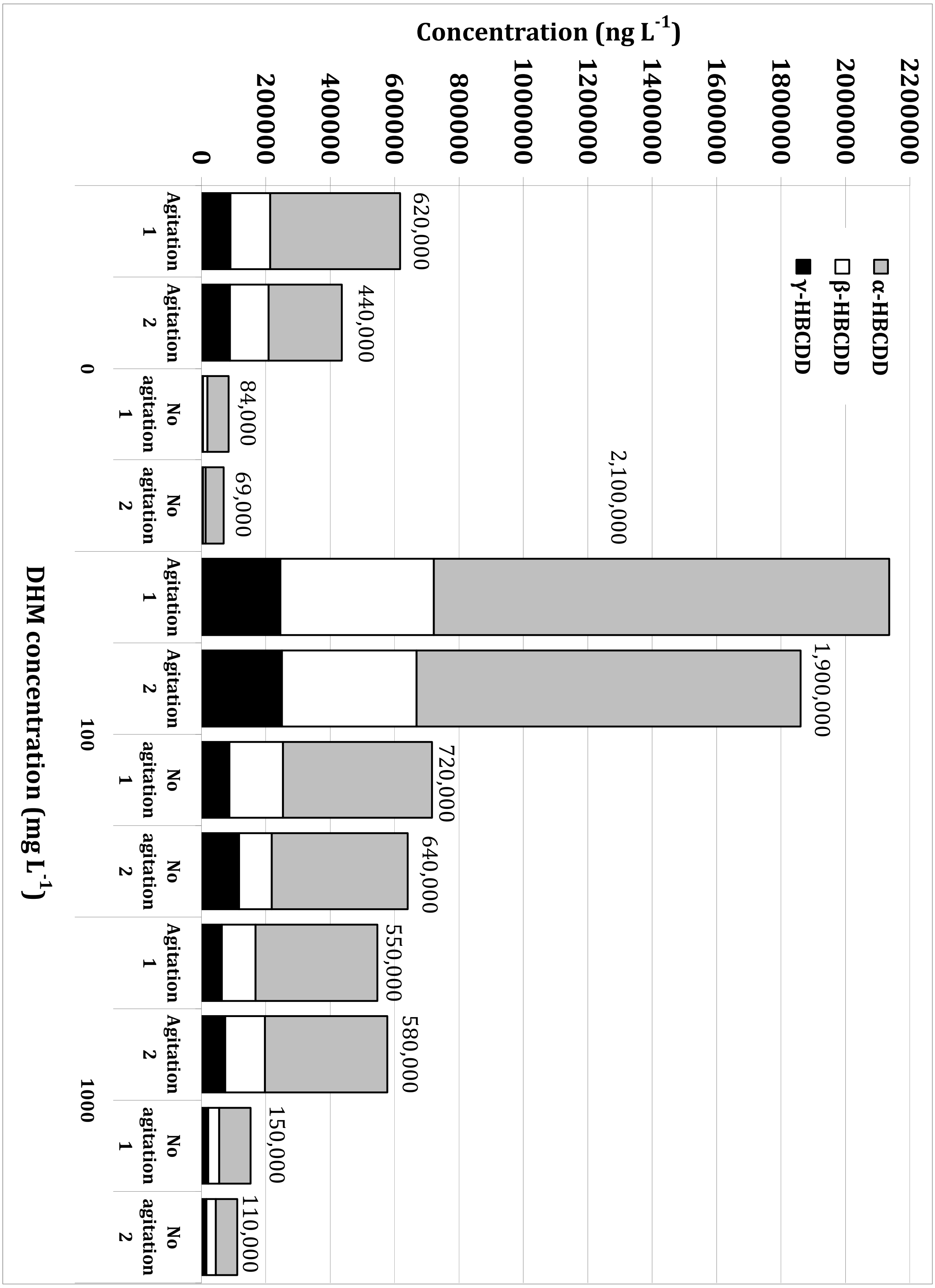

Figure 4.22: HBCDD concentrations (ng L^{-1}) in leachate produced during duplicate experiments examining the effects of agitation on leaching from XPS foam from 24 h single batch experiments using 0, 100 and 1000 mg L^{-1} DHM as leaching fluid. Data labels on bars are for ΣHBCDD and rounded to two significant figures.

In XPS foam experiments, highly significant differences ($p<0.05$) are observed for all HBCDD diastereomer concentrations between agitated and non agitated experiments. Agitation of leaching fluids from XPS experiments containing no DHM and DHM concentrations of 100 mg L^{-1} generated increases of total HBCDD concentrations in the leachate by 590 % and 195 % respectively. As previously detailed, XPS foam leaching experiments contacted with leaching fluids containing DHM concentrations of 1000 mg L^{-1} DHM yielded lower than expected concentrations of HBCDD due to anomalous behaviour in which the humic matter was absorbed into the XPS material. Despite this behaviour, HBCDD concentrations in the leachate for experiments where XPS foams were contacted with DHM concentrations of 1000 mg L^{-1}, agitation yielded increases of total HBCDD concentrations of 303 %.

Table 4.12: Results of paired sample t-tests for comparing differences in HBCDD diastereomer concentrations between agitated and non-agitated leaching; performed both EPS and XPS building insulation foams.

Material	Diastereomer	Paired differences					*t*	df	*Sig.* (two-tailed)
		Mean	Std. Dev.	Std. error mean	95 % confidence interval of the difference				
					Lower	Upper			
EPS	α-HBCDD	120,000	130,000	52,000	-15,000	250,000	2.3	5	.071
	β-HBCDD	80,000	75,000	31,000	300	160,000	2.6	5	.049
	γ-HBCDD	330,000	190,000	78,000	130,000	530,000	4.2	5	.009
XPS	α-HBCDD	470,000	310,000	130,000	140,000	800,000	3.7	5	.014
	β-HBCDD	170,000	110,000	46,000	50,000	290,000	3.7	5	.015
	γ-HBCDD	93,000	44,000	18,000	47,000	140,000	5.2	5	.003

4.9. Effects of DHM on HBCDD leaching.

In general, HBCDD concentrations and *PLT* values increase with increasing DHM concentrations. DHM enhances HBCDD solubility in the leachate by enabling more HBCDD to be suspended in water associated with DHM particles. The results of one-way ANOVAs with post hoc Tukey tests are provided in Table 4.14.

For EPS foams, there were highly significant differences ($p<0.05$) in all HBCDD diastereomer concentrations between all three DHM concentrations examined after both 6 h and 24 h contact time. After 48 h contact time, there were significant differences ($p<0.05$) in α-HBCDD between 0 and 1000 mg L^{-1} DHM, and between 100 and 1000 mg L^{-1} DHM. There were no significant differences in β-HBCDD concentrations in the leachate between the different DHM concentrations explored after 48 h. The only significant differences (*p*<0.05) in γ-HBCDD concentrations in the leachate after 48 h contact duration were between 0 and 1000 mg L^{-1} DHM.

For XPS foams, there were highly significant differences (*p*<0.05) in all diastereomer concentrations in the leachate between different DHM concentrations after 24 h contact duration. There were highly significant differences (*p*<0.05) observed for all diastereomer concentrations between 0 and 100 mg L^{-1} DHM, and between 100 and 1000 mg L^{-1} DHM after 6 h and 48 h contact durations.

Table 4.13: HBCDD leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on EPS and XPS foams with different DHM concentrations and contact times.

	Contact time (h)	DHM conc. (mg L^{-1}) / Diastereomer	0				100				1000			
			Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
EPS	6													
		α-HBCDD	18000	17000	0.18	0.030	92000	88000	0.93	0.16	140000	140000	1.5	0.24
		β-HBCDD	14000	14000	0.20	0.033	38000	39000	0.54	0.089	86000	74000	1.1	0.18
		γ-HBCDD	77000	77000	0.20	0.033	330000	330000	0.85	0.14	530000	500000	1.3	0.22
		ΣHBCDD	110000	110000	0.58	0.096	460000	450000	2.3	0.39	760000	710000	3.9	0.65
	24													
		α-HBCDD	20000	18000	0.20	0.0084	100000	100000	1.1	0.044	270000	290000	3.0	0.12
		β-HBCDD	15000	17000	0.23	0.0094	71000	59000	0.90	0.038	170000	180000	2.5	0.10
		γ-HBCDD	83000	110000	0.24	0.010	410000	380000	1.0	0.042	530000	520000	1.3	0.056
		ΣHBCDD	120000	140000	0.67	0.028	590000	540000	3.0	0.12	970000	1000000	6.8	0.28
	48													
		α-HBCDD	110000	63000	0.90	0.019	100000	87000	0.99	0.021	240000	290000	2.8	0.057
		β-HBCDD	31000	28000	0.41	0.0086	69000	62000	0.91	0.019	130000	47000	1.2	0.025
		γ-HBCDD	86000	110000	0.25	0.0052	350000	300000	0.84	0.017	460000	680000	1.5	0.030
		ΣHBCDD	230000	200000	1.6	0.032	530000	450000	2.7	0.057	830000	1000000	5.4	0.11
XPS	6													
		α-HBCDD	240000	250000	0.061	0.010	710000	690000	0.17	0.029	280000	300000	0.073	0.012
		β-HBCDD	96000	87000	0.097	0.016	140000	140000	0.15	0.024	88000	100000	0.10	0.017
		γ-HBCDD	82000	83000	0.13	0.021	130000	130000	0.20	0.033	62000	72000	0.10	0.017
		ΣHBCDD	410000	420000	0.29	0.048	980000	950000	0.52	0.087	430000	470000	0.28	0.046
	24													
		α-HBCDD	400000	230000	0.079	0.0033	1400000	1200000	0.33	0.014	380000	380000	0.095	0.0040
		β-HBCDD	120000	120000	0.13	0.0054	480000	420000	0.47	0.020	100000	120000	0.12	0.0050
		γ-HBCDD	90000	88000	0.14	0.0058	240000	250000	0.38	0.016	63000	74000	0.11	0.0044
		ΣHBCDD	620000	440000	0.35	0.014	2100000	1900000	1.2	0.049	550000	580000	0.32	0.013
	48													
		α-HBCDD	560000	460000	0.13	0.0027	2500000	2400000	0.61	0.013	330000	300000	0.080	0.0017
		β-HBCDD	140000	130000	0.14	0.0029	1200000	1100000	1.2	0.026	73000	100000	0.091	0.0019
		γ-HBCDD	79000	97000	0.14	0.0028	570000	580000	0.90	0.019	43000	60000	0.080	0.0017
		ΣHBCDD	780000	690000	0.40	0.0084	4200000	4200000	2.7	0.057	450000	460000	0.25	0.0052

Table 4.14: Results of one-way analysis of variance with post hoc Tukey tests comparing HBCDD diastereomer concentrations determined in experiments examining the effects of DHM concentration on leaching; performed for each contact time for both EPS and XPS foam.

EPS

	Contact time (h)	6		24		48	
Diastereomer	**DHM conc. (mg L^{-1})**	**0**	**100**	**0**	**100**	**0**	**100**
α-HBCDD	**100**	.000		.003		.938	
	1000	.000	.000	.000	.000	.013	.015
β-HBCDD	**100**	.035		.012		.581	
	1000	.002	.008	.000	.001	.324	.801
γ-HBCDD	**100**	.001		.001		.175	
	1000	.000	.002	.000	.011	.030	.154

XPS

	DHM conc. (mg L^{-1})	6		24		48	
Diastereomer	**pH**	**0**	**100**	**0**	**100**	**0**	**100**
α-HBCDD	**100**	.000		.007		.000	
	1000	.057	.000	.001	.004	.101	.000
β-HBCDD	**100**	.014		.005		.000	
	1000	.859	.017	.000	.000	.782	.000
γ-HBCDD	**100**	.003		.000		.000	
	1000	.058	.001	.000	.000	.264	.000

p-values highlighted red = significant ($p<0.05$).

4.10. Statistical analysis of the whole data set.

The results of MLRA for both EPS and XPS foams are provided in Table 4.15. Agitation of the sample during leaching has a highly significant ($p<0.05$) positive effect on β-HBCDD and γ-HBCDD diastereomers for both EPS and XPS foams. Agitation has the largest effect on γ-HBCDD in EPS foams (200,000 ng L^{-1}), while it has the largest effect on β-HBCDD in XPS foams (140,000 ng L^{-1}) suggesting that agitation enhances the leaching of relatively less soluble diastereomers, most likely due to increased abrasion. A highly significant ($p<0.05$) positive effect was also observed for α-HBCDD in agitated experiments on EPS foam. Elevating leaching fluid temperatures had a highly significant ($p<0.05$) positive effect on α-HBCDD concentrations in experiments on EPS foam. DHM also has a highly significant positive effect on all diastereomers for EPS foam. This effect is not observed in the MRLA for

XPS foam because of the aforementioned anomalous behaviour of DHM in XPS foam experiments.

In experiments on XPS foams, the length of contact time in experiments has a significant positive effect on all diastereomers, but only for γ-HBCDD in EPS foam experiments. The pH of the leaching fluid has a highly significant effect on α-HBCDD in XPS foam experiments, with the alkaline 8.5 pH leaching fluids eliciting the greatest concentrations.

Table 4.15: Results for multiple linear regression analysis obtained for HBCDD diastereomers for leachate from both EPS and XPS foam[a].

Diaster-eomer	**Independent variable (Model term)**	***Coefficient (ng L^{-1} unit^{-1})***	**Std. error**	**Sig.**	**95 % Confidence interval**		**Importance**
					Lower	**Upper**	
			EPS				
α-HBCDD	DHM concentration (mg L^{-1})	95	19	.000	57	130	0.492
	Agitation	100,000	26,000	.006	49,000	150,000	0.301
	Temperature (°C)	1,700	610	.024	470	2,900	0.153
β-HBCDD	DHM concentration (mg L^{-1})	42	9.8	.000	22	61	0.479
	Agitation	39,000	9,200	.000	20,000	57,000	0.459
γ-HBCDD	Agitation	200,000	34,000	.000	130,000	270,000	0.490
	DHM concentration (mg L^{-1})	181	36	.000	110	250	0.444
	Contact time (h)	2,300	1,100	.010	42	4,500	0.066
			XPS				
α-HBCDD	Contact time (h)	12,000	4,000	.005	3,600	20,000	0.632
	pH	190,000	85,000	.031	18,000	360,000	0.368
β-HBCDD	Contact time (h)	4,700	1,800	.012	1,100	8,300	0.509
	Agitation	140,000	56,000	.013	31,000	250,000	0.491
γ-HBCDD	Agitation	75,000	27,000	.001	21,000	130,000	0.455
	Contact time (h)	2,300	900	.000	550	4,100	0.410

[a] Data only shown for effects with greater than 95 % significance.

4.11. Summary.

This study demonstrates that leaching of HBCDD from EPS and XPS building insulation foams using distilled deionised water and DHM solutions as leaching fluid is a second order process. Following an initial period of source:leaching fluid contact during which leaching is relatively facile, subsequent leaching is slower.

HBCDD concentrations in leachate almost all exceed the aqueous solubilities for each diastereomer and the technical HBCDD formulation. This is important because it means that agitation and abrasion play a large role in leaching from building insulation foam materials. Agitation had a significant positive effect on HBCDD leaching from both EPS and XPS foams. It also means that the aqueous solubility limit does not necessarily limit the viable amount of HBCDD present in leachates as the HBCDD is associated with fine abraded particles of the foam. In a landfill environment, deposited wastes are subjected to size reduction, compaction and percolation of waters, resulting in abrasion and degradation of the foam materials. Potentially building insulation foams could be a large source of HBCDD in landfill leachates.

Further supporting this, the length of contact time had a significant positive effect on the leaching of all HBCDD diastereomers from XPS foams and γ-HBCDD from EPS foams. Enhanced abrasion from longer contact times enables more HBCDD to be present in leachates and this is particularly highlighted for the least soluble diastereomer γ-HBCDD.

The presence of DHM had significant positive effects on HBCDD leaching from EPS foams. In leaching fluids containing 1000 mg L^{-1} DHM the XPS absorbed the humic matter and resulting HBCDD concentrations in leachate were reduced. This difference in behaviour between the two foams is likely to be because the XPS foam is more porous and permeable than the relatively more rigid and tough EPS foam.

Temperature was identified as having a significant positive effect on the leaching of α-HBCDD from EPS foams in MRLA. In general, elevated temperatures did elicit greater concentrations of HBCDD in leachates from both foams.

Overall pH has only a small effect on the leaching of HBCDD from building insulation foams. Leaching fluids with an alkaline pH 8.5 had a significant positive effect on α-HBCDD leaching from EPS foams only.

The concentrations of HBCDD in leachates produced in these experiments are massively greater than those reported in the limited number of studies measuring HBCDD in landfill leachates (Morris et al., 2004; Remberger et al., 2004; Suzuki and Hasegawa, 2006). However, although not directly comparable, Morris et al., (2004) report maximum concentrations of HBCDD in leachates from a MSW landfill in The Netherlands as 36 mg kg^{-1} (dry weight) and γ-HBCDD concentrations were at least four times greater than α-HBCDD concentrations. HBCDD concentrations were reported for suspended solids in the leachate. They are also vastly greater than HBCDD concentrations reported in other aqueous environments, e.g. in UK lakes ΣHBCDD was 0.08 - 0.27 ng L^{-1}, and Japanese rivers ΣHBCDD was 2.5 - 2100 ng L^{-1} (Oh et al., 2014; Harrad et al., 2009b) (see Table 1.8, Chapter I).

The data presented here are preliminary and to the author's knowledge, there are no comparable studies examining HBCDD leaching from waste materials in the literature. Further work is required to bridge knowledge gaps and develop a greater understanding of HBCDD leaching behaviour from HBCDD treated materials in order to accurately gauge the magnitude of the problem. Both concentrations of HBCDD and PLT values were greater in leaching from EPS and XPS foam when compared to leaching from the treated curtain textiles in the previous chapter. ΣHBCDD concentrations ranged between 170 ng L^{-1} and 13,000 ng L^{-1} in textile leaching experiments with ΣHBCDD *PLT* values between 0.0000000000072 % h^{-1} and 0.000026 % h^{-1}. Contrary to what was observed in building insulation foams experiments, concentrations of HBCDD in leachate were constrained by HBCDD solubility limits in textile leaching experiments.

Chapter V: Leaching behaviour of PBDEs from cathode ray tube (CRT) plastics.

5.1. Synopsis.

In this chapter, the leaching behaviour of PBDEs from treated CRT plastic samples collected from a WEEE recycling stream is investigated. Concentrations (ng L^{-1}), percentage leached (%), percentage leached per unit time values (*PLT*; % h^{-1}) and leaching kinetics are presented for a range of landfill relevant leaching fluids. These will be then be used to assess the magnitude of this pathway in contributing PBDE contamination to the environment. Levels of target PBDEs will be compared to those reported in landfill leachates and aquatic environments from previous studies. Additional information detailing the experimental set-up of these leaching experiments can be found in section 2.2.1 and leachate extraction, filter extraction and clean up techniques are detailed in sections 2.3.1, 2.3.2 and 2.4.1 respectively. A summary of the conditions explored are outlined in Table 5.1.

Table 5.1: Summary of conditions employed in leaching test protocols.

Experimental Scenario/ Parameter	Single batch, variable contact time	Single batch, variable temperature	Single batch, variable pH
Extraction period (h)	6, 24, 48	24	6
Agitation	200 rpm	None	200 rpm
Temperature (°C)	20	20, 50, 80	20
pH	6.5	6.5	5.8, 6.5, 8.5
DHM conc. (mg L^{-1})	0, 100, 1000	0, 100, 1000	0, 100, 1000

5.2. Initial PBDE concentrations in CRT plastic samples.

CRT housings were conventionally produced using either ABS or HIPS. ABS was predominantly treated with Octa-BDE typically added at concentrations between 10-18 % by weight, while HIPS were predominantly treated with Deca-BDE typically added at concentrations between 13-15 % by weight (EC, 2011; BSEF, 2014).

Table 5.2 displays the mean initial concentrations and aqueous solubilities of individual PBDE congeners in the CRT plastics used in this study. The pulverised homogenised plastics samples were analysed for BDEs-47, -85, -99, -100, -153, -154, -183, and -209. Concentrations of BDE-47, BDE-85 and BDE-100 were below the LOQ. The LOQ values for BDE-47, BDE-85 and BDE-100 were 217 ng g^{-1}, 13 ng g^{-1} and 12 ng g^{-1}, respectively.

The range of PBDE concentrations present in the plastics is not for each individual CRT chip but a representative homogenised pulverised mixture of multiple chips (see section 2.3.4). Deca-BDE was the predominant congener found in the samples followed by Octa-BDE. This may be due to HIPS being more prevalent in the grab sample of CRT chips, or because Deca-BDE, to some extent, replaced Octa-BDE in ABS plastics after the EU ban on Octa-BDE. Concentrations of ΣPBDE congeners are <1 % by weight suggesting that some dilution has occurred, meaning that some plastic chips within the CRT waste stream sample were likely not treated with PBDEs. It is likely that some of the chips were treated with Deca-BDE, a smaller fraction with Octa-BDE and some were not treated at all. Hand-held XRF analysis of these chips revealed a heterogenous distribution of Br (pers. comm., Antonella Guzzonato).

Table 5.2: Mean Concentrations (mg kg^{-1}) of PBDEs in CRT plastics used in this study.

Congener	Concentration (mg kg^{-1})	% RSD	Aqueous Solubility (mg L^{-1})
BDE-99	0.36 ± 0.025	7.1	0.077[a]
BDE-153	14 ± 2.0	14	0.031[a]
BDE-154	0.73 ± 0.065	9.0	-
BDE-183	220 ± 19	8.7	-
BDE-209	2600 ± 120	4.5	0.002[a]
(n=5)			[a] Yue & Li (2013)

5.3. Effects of contact time and humic matter content of leaching fluid on PBDE leaching (single batch experiments).

Aliquots of CRT plastic chips (used as received and not pulverised – i.e. in the state in which they would be landfilled) were contacted with 125 mL leaching fluid for 6 h, 24 h and 48 h respectively at 20 ˚C. Fresh plastic samples were used for each time period (i.e. single batch experiments). The effects of different landfill relevant leaching fluids were explored and dissolved organic matter contents of 0, 100 and 1000 mg L^{-1} were contacted with the plastics for each contact time.

Table 5.3 presents PBDE congener concentrations in duplicate samples, as well as mean PL (%) and mean PLT values (% h^{-1}) in leachate from the single batch contact time experiments. Relatively little change in PBDE concentrations in leachate are observed with increasing contact time for leaching fluids containing 0 and 100 mg L^{-1} DHM. This suggests that the bulk of the transfer to the leaching fluid is occurring within the first 6 hours, during which time the most easily available PBDEs are “washed” off the surface of the CRT plastics. Therefore, serial batch experiments were not considered. However, the concentrations of ΣPBDEs in the leachate did increase slightly with longer contact times in the presence of the 1000 mg L^{-1} DHM leaching fluid.

Contacting the CRT plastics with Milli-Q water alone as the leaching fluid resulted in surprisingly high PBDE concentrations when considering the hydrophobicity of the higher brominated congeners (Table 5.1). It appears likely that dislodgement of fine dust from the surface of the CRT plastics was an important leaching mechanism for the more hydrophobic BDEs-153, -154, -183 and -209. Any dust that was present on the surface of the chips may be “washed” off when the leaching fluid was added to the chamber. If PBDEs had partitioned into this dust they would be more readily leached. An alternative mechanism would be abrasion of the CRT chips during agitation of the leaching chamber resulting in ultrafine particles of the FR plastics being present in the leachate. Solubility is likely to be more important for the relatively more soluble lower brominated PBDE congeners. These more soluble congeners are more readily dissolved in the aqueous phase resulting in higher PLT values than observed for the higher brominated PBDEs. While BDE-47, BDE-85 and BDE-100 were not present at substantial concentrations in the CRT chips, they were detected in some of the leaching fluids and were found in the highest concentrations for the experiments with the longest contact times. This suggests either some debromination of the heavier PBDE congeners has occurred or demonstrates their relatively higher aqueous solubility. This is similar to what was found in Chapter 3, where ε-HBCDD was present in quantifiable concentrations in the leachates after being contacted with HBCDD treated textiles, despite being <LOQ in the curtain material leached.

The results of a one-way ANOVA with post hoc Tukey tests are presented in Table 5.4. This revealed no significant differences between BDE-209 concentrations at different contact times, this supports the hypothesis that the heaviest PBDE congeners are simply “washed off” when the leaching fluid is initially contacted. At 1000 mg L^{-1} DHM concentration there were no significant differences between concentrations at different contact times for congeners BDE-100 upwards. There were significant differences between 6 h and 24 h contact times but not between 24 h and 48 h for BDEs-153, -154 and -183.

Table 5.3: PBDE leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on CRT plastics with different contact times and DHM concentrations.

DHM conc.	Contact Time (h) /	6				24				48			
(mg L^{-1})	Congener	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
0													
	BDE-47	140	150			81	31			380	380		
	BDE-85					9.4				26	29		
	BDE-99	430	410	3.0	0.021	150	160	1.1	0.045	690	820	5.3	0.11
	BDE-100	730	650			440	460			660	830		
	BDE-153	7700	7600	7.4	0.0034	370	400	0.24	0.010	890	920	0.64	0.013
	BDE-154	2200	2100	1.3	0.0012	65	74	0.066	0.0028	190	180	0.16	0.0033
	BDE-183	28000	25000	0.30	0.00048	2300	2200	0.026	0.0011	5000	5300	0.059	0.0012
	BDE-209	44000	46000	0.043	0.0015	110000	63000	0.084	0.0035	79000	76000	0.073	0.0015
	ΣPBDEs	83000	81000	0.072	0.012	120000	66000	0.080	0.0033	86000	84000	0.074	0.0015
100													
	BDE-47	290	340			350	340			180	550		
	BDE-85	11	12								18		
	BDE-99	650	760	5.0	0.83	430	500	3.3	0.14	210	410	2.2	0.046
	BDE-100	1000	1300			640	630			740	540		
	BDE-153	1200	1400	2.3	0.38	410	410	0.34	0.014	1200	760	0.58	0.012
	BDE-154	660	660	0.23	0.039	99	99	0.071	0.0030	200	140	0.17	0.0035
	BDE-183	5600	5700	0.065	0.011	2200	2000	0.024	0.0010	6100	5100	0.064	0.0013
	BDE-209	64000	62000	0.060	0.010	58000	63000	0.058	0.0024	48000	63000	0.053	0.0011
	ΣPBDEs	73000	73000	0.064	0.011	63000	67000	0.056	0.0024	56000	71000	0.055	0.0012
1000													
	BDE-47	130	130			120	120			760	690		
	BDE-85									31			
	BDE-99	410	470	3.1	0.52	640	300	3.3	0.14	940	1000	6.8	0.14
	BDE-100	920	760			1200	790			930	1100		
	BDE-153	1200	1600	1.0	0.17	1000	1200	1.2	0.049	1100	1400	1.6	0.034
	BDE-154	430	150	0.24	0.040	92	580	0.19	0.0079	250	710	0.22	0.0046
	BDE-183	4500	4700	0.052	0.0087	4800	6500	0.065	0.0027	6500	7200	0.079	0.0016
	BDE-209	60000	62000	0.058	0.010	74000	84000	0.075	0.0031	80000	190000	0.13	0.0027
	ΣPBDEs	68000	70000	0.060	0.010	81000	93000	0.076	0.0032	91000	200000	0.13	0.0027

Table 5.4: Results of one-way analysis of variance with post hoc Tukey tests comparing PBDE congener concentrations determined in experiments examining the effects of contact time on leaching; performed for each DHM concentration.

	DHM conc. (mg L^{-1})	0		100		1000	
Congener	**Contact time (h)**	**6 h**	**24 h**	**6 h**	**24 h**	**6 h**	**24 h**
BDE-47	**24 h**	.044		.971		.949	
	48 h	.003	.001	.940	.993	.001	.000
BDE-85	**24 h**	.541		.355		1.000	
	48 h	.013	.021	.908	.519	.518	.518
BDE-99	**24 h**	.028		.166		.984	
	48 h	.016	.003	.054	.392	.072	.081
BDE-100	**24 h**	.113		.062		.747	
	48 h	.786	.069	.065	.998	.668	.987
BDE-153	**24 h**	.000		.034		.482	
	48 h	.000	.187	.284	.120	.864	.739
BDE-154	**24 h**	.000		.000		.987	
	48 h	.000	.187	.001	.146	.819	.891
BDE-183	**24 h**	.001		.006		.414	
	48 h	.001	.217	.985	.007	.105	.366
BDE-209	**24 h**	.241		.929		.921	
	48 h	.394	.856	.545	.730	.357	.506

p-values highlighted red = significant ($p<0.05$)

5.4. Leaching kinetics.

In section 3.6 we generated plots of *t*/*Ct* against *t* for all experiments conducted at 20 ˚C and agitated at 200 RPM to explore the plausibility for second order kinetics. The same rationale was applied to the single batch experiment data presented in this chapter. The slope, Y-intercept, saturated leaching capacity, Cs, the leaching rate constant, k, two-tailed p values, and Pearson's correlation coefficients, r, are given for selected PBDE congeners in Table 5.5. A positive and highly significant ($p<0.05$) linear correlation between t/Ct and t was observed for BDE-100 and BDE-209 with leaching fluids at 0 mg L^{-1}, while weaker correlations are observed for BDE-153 (90 % probability), -154 (84 % probability) and -183 (91 % probability). At 100 mg L^{-1} DHM only BDE-154 shows a highly significant correlation, while BDE-153 (90 % probability) and BDE-183 (82 % probability) show weaker correlations. With the 1000 mg L^{-1} DHM leaching fluid, BDE- 100, 153 and 183 are significantly correlated ($p<0.05$) and BDE-209 shows a weaker significance (93 % probability). Plots are provided for DHM concentrations 0, 100 and 1000 mg L^{-1} as Figures 5.1, 5.2 and 5.3 respectively.

This apparent fit with second order kinetics suggests initial rapid leaching followed by a slower second phase. This is consistent with our hypothesis that the most readily available PBDEs are “washed” off the CRT polymer surface early in the experiment. A second, slower stage follows, which corresponds primarily to external diffusion and is related to the soluble remainder within the polymer matrix. This kinetics model seems especially relevant to the higher brominated PBDE congeners and perhaps supports the idea that some debromination may have taken place resulting in lower brominated PBDEs being present in the leachate.

To further evaluate the hypothesis of second-order rate kinetics, the natural logarithm of the same PBDE leachate concentration data for single batch experiments conducted at 20 ˚C, were plotted against time to check for linearity and negative slope intercepts that would suggest first order kinetics. The results are presented in Table 5.6 and the only congener to satisfy all first-order criteria was BDE-99 when the leaching fluid contained 100 mg L^{-1} DHM. A weaker correlation (92.2 % probability) was observed for BDE-100 at the same DHM concentration. This strongly supports of the idea that leaching of PBDEs from CRT plastics in these experiments is predominantly governed by second-order leaching kinetics.

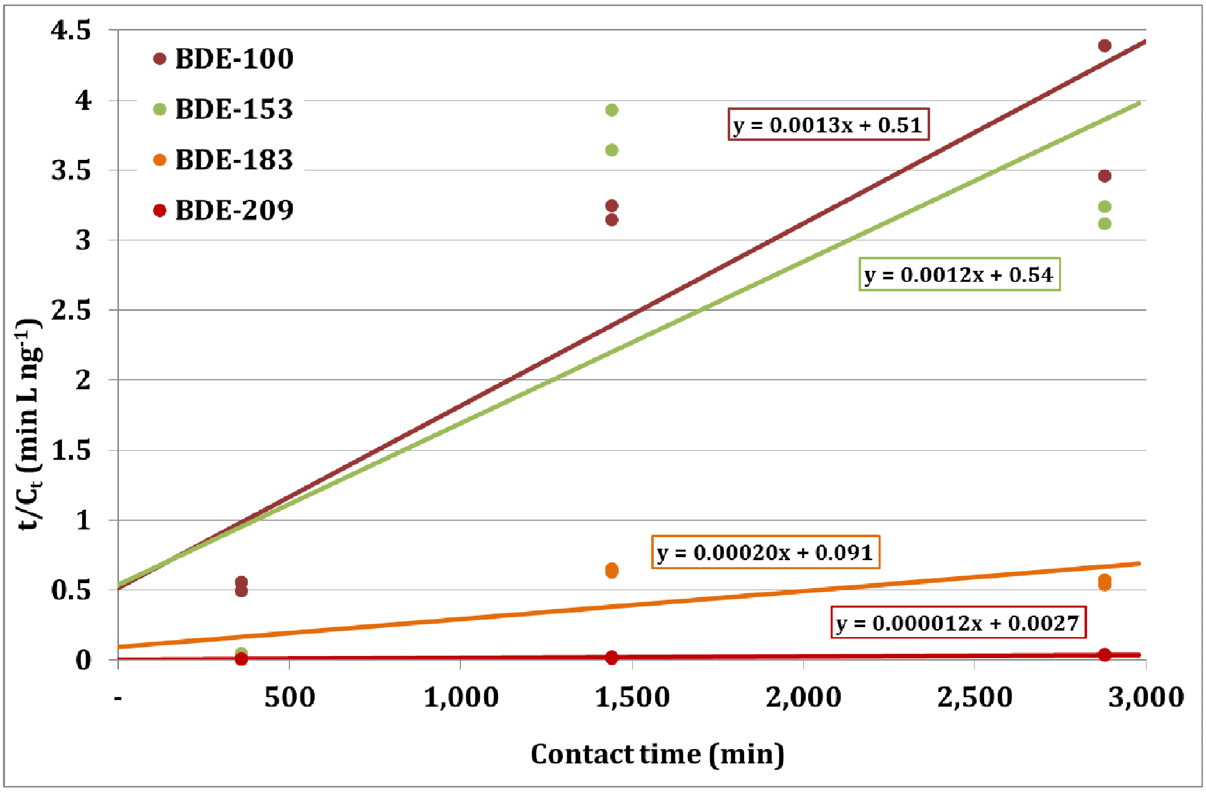

Figure 5.1 Plot of *t/Ct* versus *t* for leaching of selected PBDE congeners in single batch experiments with Milli-Q leaching fluid conducted on CRT plastics. (n=6)

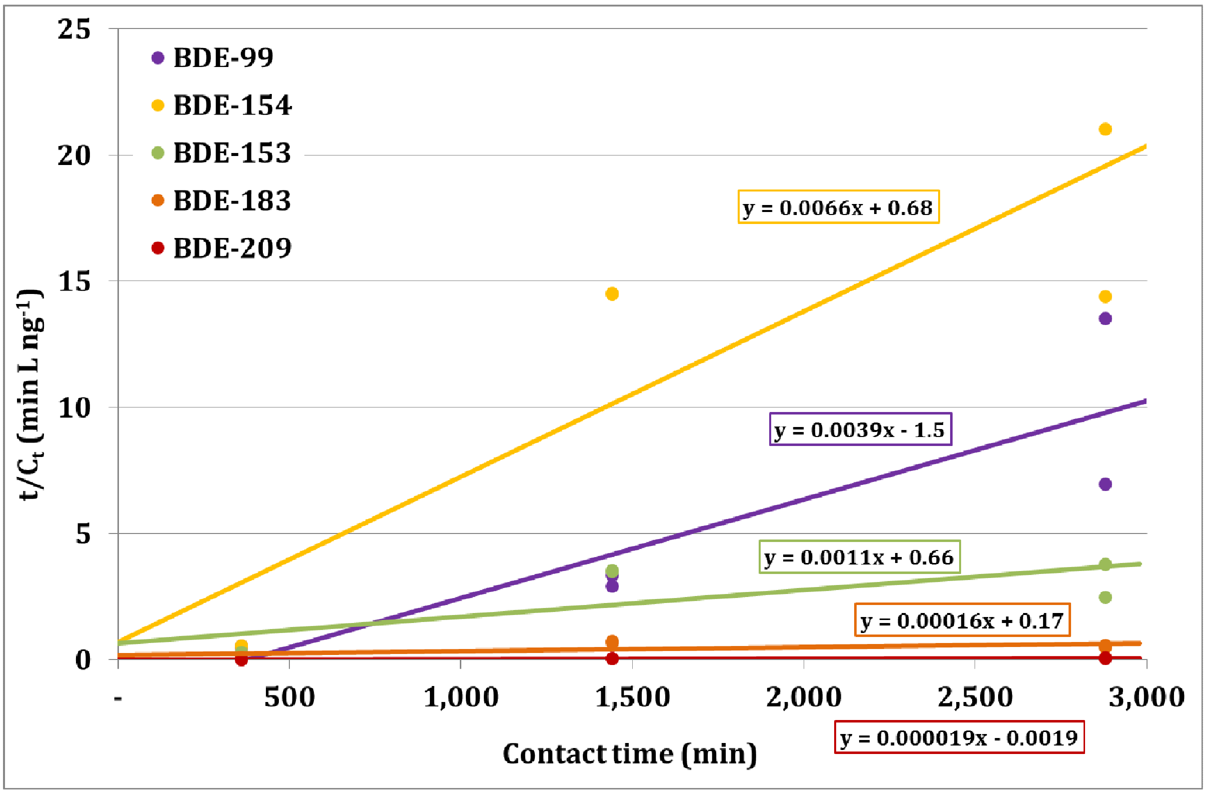

Figure 5.2 Plot of *t/Ct* versus *t* for leaching of selected PBDE congeners in single batch experiments with 100 mg kg^{-1} DHM leaching fluid conducted on CRT plastics. (n=6)

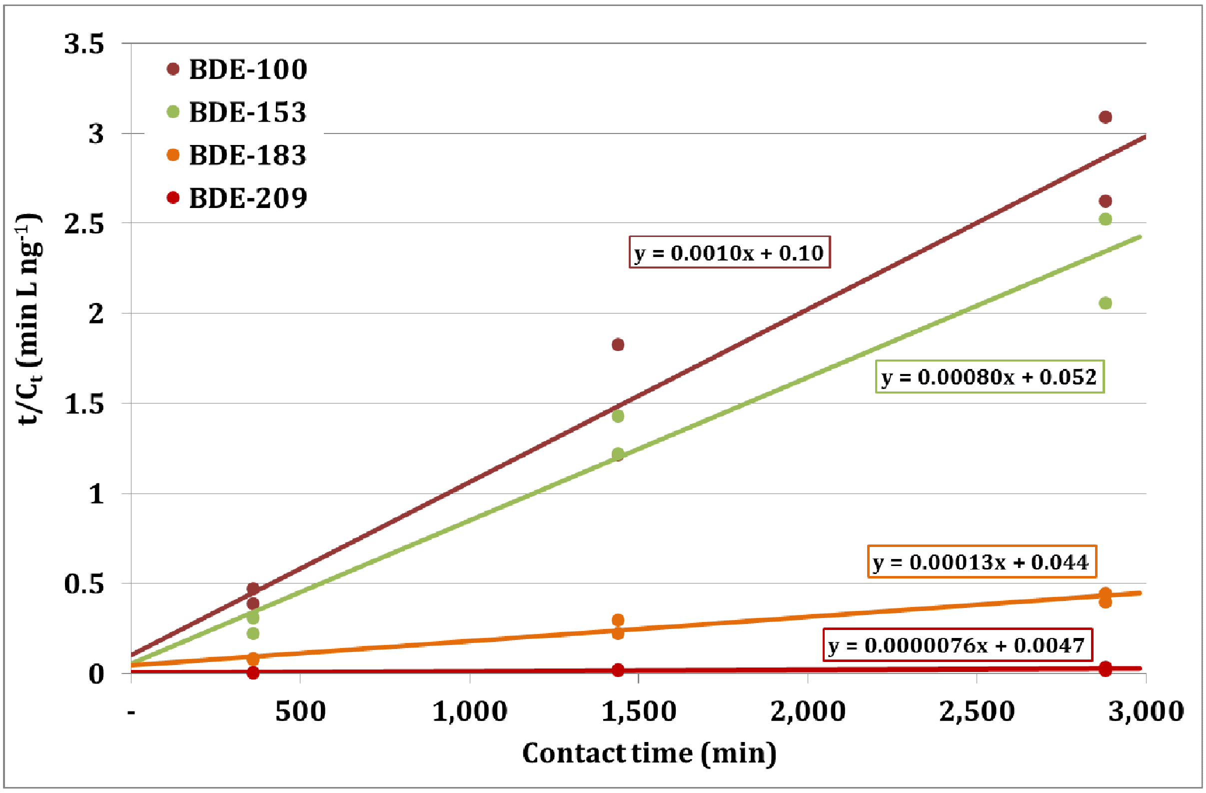

Figure 5.3 Plot of *t/Ct* versus *t* for leaching of selected PBDE congeners in single batch experiments with 1000 mg kg^{-1} DHM leaching fluid conducted on CRT plastics. (n=6)

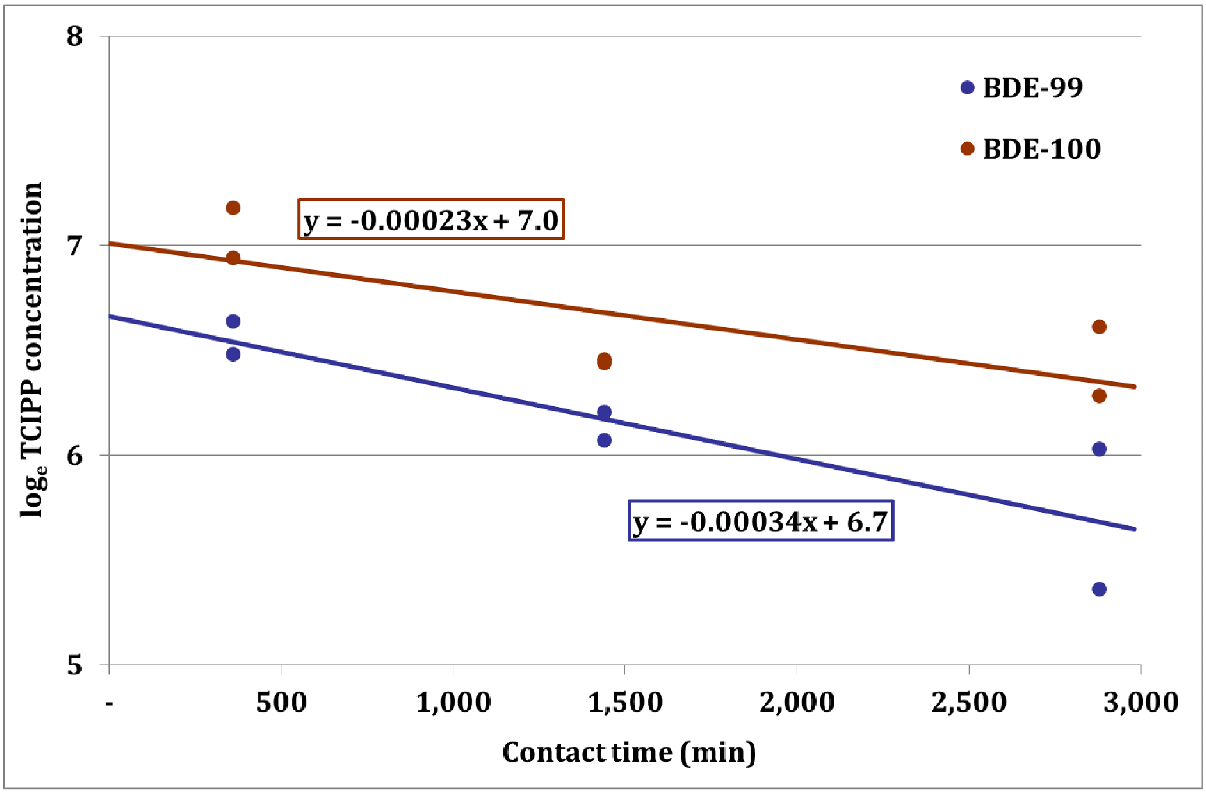

Figure 5.4: Plot of natural logarithm of selected PBDE congener concentrations versus *t* for single batch leaching experiments with 100 mg L^{-1} DHM concentration conducted on CRT plastics. (n=6)

Table 5.5: Second order leaching rate constants (*k*) and saturated leaching capacities (C_s) obtained for PBDE congeners from CRT plastics[a].

Constant / Compound	Slope (min L ng^{-1} /min)	y-intercept (min L ng^{-1})	*Cs* (ng L^{-1})	*k* (L ng^{-1} min^{-1})	*Two-tailed P value*	*Correlation Coefficient: r*
0 mg L^{-1} DHM concentration.						
BDE-47	0.0010	13	1014	0.000000078	.901	0.066
BDE-99	0.00092	3.3	1091	0.00000026	.114	0.267
BDE-100	0.0013	0.51	767	0.0000033	.013	0.905
BDE-153	0.0012	0.54	867	0.0000025	.096	0.725
BDE-154	0.0055	3.6	181	0.0000086	.103	0.648
BDE-183	0.00020	0.092	4989	0.00000044	.164	0.743
BDE-209	0.000012	0.0027	85046	0.000000051	.091	0.965
100 mg L^{-1} DHM concentration.						
BDE-153	0.0011	0.66	949	0.0000017	.100	0.729
BDE-154	0.0066	0.68	152	0.000063	.020	0.881
BDE-183	0.00016	0.17	6085	0.00000016	.177	0.634
1000 mg L^{-1} DHM concentration.						
BDE-47	0.00011	6.2	8925	0.0000000020	.959	0.028
BDE-99	0.00079	1.2	1266	0.00000051	.224	0.584
BDE-100	0.0010	0.10	1040	0.0000089	.001	0.976
BDE-153	0.00080	0.052	1256	0.000012	.001	0.978
BDE-154	0.0023	2.6	434	0.0000020	.394	0.431
BDE-183	0.00013	0.044	7420	0.00000042	.001	0.977
BDE-209	0.0000076	0.0047	131122	0.000000012	.068	0.779

[a] Data not shown for plots for which y-intercept and thus k values were negative.
p-values highlighted red = significant ($p<0.10$).

Table 5.6: First order leaching rate slopes, y-intercepts, constants (*k*), and *r* values obtained for PBDE congeners from CRT plastics[a].

Constant / Compound	Slope ($\log_e$ ng L^{-1} /min)	y-intercept ($\log_e$ ng L^{-1})	*k* (min^{-1})	*Two-tailed P value*	*Correlation Coefficient: r*
100 mg L^{-1} DHM concentration.					
BDE-99	-0.00034	6.7	0.000000018	.025	-0.867
BDE-100	-0.00023	7.0	0.0000000075	.078	-0.762

[a] Data only shown for plots for which the slope was negative and significance $p<0.10$.

5.5. Effects of temperature and humic matter content of leaching fluid on PBDE leaching from CRT plastics.

The influence of the temperature of the leaching fluid on PBDE leaching from CRT plastics was examined. The only other study the author is aware of examining the effects of temperature on PBDE leaching only examined differences between low temperatures of 10 °C, 20 °C and 25 °C (Danon-Schaffer et al., 2013b).

Table 5.7 presents PBDE congener concentrations in duplicate experiments as well as mean PL (%) and mean PLT values (% h^{-1}) in leachate from single batch temperature experiments. The highest concentrations of PBDEs were when Milli-Q water was used as leaching fluid and contacted at 50 °C and 80 °C. Potential reasons for this could be related to reduced PBDE extraction efficiencies from DHM solutions or from the filters in which DHM had passed through. This result is different from the findings of similar studies contacting WEEE plastics with deionised water by Danon-Schaffer et al., (2013b) and Choi et al., (2009), in which PBDE concentrations were always significantly higher in leachate/DHM solutions, than those detected when deionised water was the leaching fluid.

No agitation was used in these temperature experiments and this resulted in lower overall concentrations of PBDEs when compared with the agitated contact time experiments at 20 °C. Because no agitation occurred in these temperature experiments it is very unlikely that abrasion of particles contributed to the concentrations of PBDEs in the leachate. BDE-85 was not detected in the leachates in these temperature experiments.

The results of a one-way ANOVA with post hoc Tukey tests are presented in Table 5.8. There were significant differences in BDE-209 leachate concentrations between 20 °C and 80 °C for all DHM concentrations. There were no significant differences observed when the DHM concentration was 100 mg L^{-1}.

There were significant differences in BDE-99 leachate concentrations between 20 °C and 50 °C and between 20 °C and 80 °C for all DHM concentrations, with one exception of no significant difference in concentrations between 20 °C and 80 °C in 1000 mg L^{-1} DHM leaching fluid.

There were no significant differences in BDE-47 concentrations observed between temperatures when no DHM was present in the leaching fluid, however significant differences were observed between 20 ºC and 50 ºC and 50 ºC and 80 ºC at 100 mg L^{-1} DHM and between all temperatures at 1000 mg L^{-1} DHM leaching fluid.

Concentrations of PBDEs were consistently higher in the 1000 mg L^{-1} DHM leaching fluid when compared to the concentrations found in the 100 mg L^{-1} DHM leaching fluid which supports the hypothesis that greater DHM concentrations in the leaching fluid would enable more PBDEs to be present in leachate.

Table 5.7: PBDE leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on CRT plastics with different temperatures and DHM concentrations.

DHM conc.	Temperature (°C) /	20				50				80			
(mg L^{-1})	Congener	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
0													
	BDE-47	76				93				160	120		
	BDE-85												
	BDE-99	78	65	0.51	0.021	81	75	0.55	0.023	290	260	1.9	0.080
	BDE-100	380				270	230			550	520		
	BDE-153	160	160	0.082	0.0034	290	440	0.13	0.0053	320	380	0.29	0.012
	BDE-154	25	22	0.028	0.0012	32	42	0.063	0.0026	83	86	0.061	0.0026
	BDE-183	1000	980	0.012	0.00048	2200	2700	0.028	0.0012	2100	2100	0.024	0.0010
	BDE-209	32000	47000	0.037	0.0015	94000	110000	0.095	0.0040	140000	120000	0.12	0.0052
	ΣPBDEs	33000	48000	0.035	0.0015	97000	110000	0.090	0.0038	140000	130000	0.12	0.0049
100													
	BDE-47					280	190			42	72		
	BDE-85												
	BDE-99	25	21	0.16	0.0062	160	150	1.09	0.045	81	87	0.59	0.025
	BDE-100	340	310			530	520			940	1000		
	BDE-153	130	98	0.066	0.0079	1200	690	1.70	0.071	240	250	0.12	0.0049
	BDE-154	22	17	0.020	0.0024	870	110	0.16	0.0069	32	37	0.043	0.0018
	BDE-183	720	1200	0.011	0.0013	8600	4200	0.073	0.0030	2000	21000	0.13	0.0054
	BDE-209	13000	12000	0.012	0.00049	16000	19000	0.017	0.00071	63000	39000	0.048	0.0020
	ΣPBDEs	15000	14000	0.012	0.00052	28000	25000	0.023	0.0010	66000	61000	0.055	0.0023
1000													
	BDE-47	170	170			210	200				5.4		
	BDE-85												
	BDE-99	130	130	0.94	0.039	330	320	2.3	0.096	140	150	1.0	0.042
	BDE-100	440	440			630	620			480	220		
	BDE-153	630	600	0.33	0.014	550	580	0.42	0.018	410	410	0.24	0.0099
	BDE-154	98	95	0.11	0.0044	120	120	0.099	0.0041	68	71	0.072	0.0030
	BDE-183	3900	3800	0.044	0.0018	3100	3300	0.037	0.0015	6900	23000	0.17	0.0071
	BDE-209	35000	33000	0.032	0.0013	36000	38000	0.035	0.0014	68000	59000	0.060	0.0025
	ΣPBDEs	40000	38000	0.034	0.0014	41000	43000	0.036	0.0015	76000	83000	0.069	0.0029

Table 5.8: Results of one-way analysis of variance with post hoc Tukey tests comparing PBDE congener concentrations determined in experiments examining the effects of temperature on leaching; performed for each DHM concentration.

	DHM conc. (mg L^{-1})	**0**		**100**		**1000**	
Congener	**Temperature (°C)**	**20**	**50**	**20**	**50**	**20**	**50**
BDE-47	**50**	.985		.023		.003	
	80	.248	.288	.462	.048	.000	.000
BDE-99	**50**	.874		.000		.000	
	80	.001	.001	.001	.000	.069	.000
BDE-100	**50**	.926		.012		.303	
	80	.220	.308	.000	.001	.714	.148
BDE-153	**50**	.101		.056		.177	
	80	.115	.983	.813	.086	.003	.007
BDE-154	**50**	.109		.396		.001	
	80	.002	.338	.999	.817	.001	.313
BDE-183	**50**	.012		.784		.995	
	80	.025	.338	.477	.817	.343	.313
BDE-209	**50**	.020		.869		.733	
	80	.006	.117	.062	.088	.008	.011

p-values highlighted red = significant ($p<0.05$)

5.6. Effects of pH and humic matter content of leaching fluid on PBDE leaching from CRT plastics.

The influence of three pH levels representing an acidic leachate (5.8), an alkaline leachate (8.5) and a mildly acidic leachate (6.5) on PBDE concentrations and *PLT* values in leachate were explored in a series of 6 h single batch experiments with 0, 100 and 1000 mg L^{-1} DHM leaching fluid. PBDE congener concentrations in duplicate samples, as well as mean PL (%) and mean *PLT* values (% h^{-1}) in leachate from these pH experiments are illustrated in Table 5.9.

There is very little variation in total PBDE concentrations at the different pH levels examined. Experiments with acidic pH (5.8) leaching fluids yield the lowest total PBDE concentrations of the three pH levels examined but this difference is not statistically significant. The pH of the leaching fluid has a highly significant effect on the leachability of BDE-85, -99, -100 and -154 (Table 5.2). The concentration and PLT value of BDE-154 was significantly increased at pH 5.8 and 8.5 when compared to the slightly acidic value (6.5) for both the 100 and 1000 mg L^{-1} DHM leaching fluid experiments, while for the Milli-Q leaching fluid only pH 8.5 had this effect. This contradicts what was reported by Danon-Schaffer et al. (2013b) in which acidic leaching fluids of pH 4-5 facilitated a greater transfer of PBDEs to the leachate than pH 7 and 9 with the effect being greatest with decreasing number of bromines.

The results of a one-way ANOVA with post hoc Tukey tests are presented in Table 5.10. There are significant differences in BDE-209 concentrations in the leachate between all pH levels explored and this is true for all three DHM concentrations; with the only exception being between 6.5 and 8.5 at 1000 mg L^{-1} DHM.

There are no significant differences in BDE-154 concentrations in the leachate between pH levels at all DHM concentrations, strongly suggesting that pH has no effect on the leaching of this congener.

Significant differences in BDE-99 and BDE-100 concentrations in the leachate were only observed between 5.8 and 8.5 and 6.5 and 8.5 when the DHM concentration of the leachate was 1000 mg L^{-1}.

Table 5.10: PBDE leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on CRT plastics with different pH levels and DHM concentrations.

DHM conc. (mg L^{-1})	pH / Congener	5.8				6.5				8.5			
		Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
0													
	BDE-47	190	190			140	150			140	140		
	BDE-85	9.0	22							11	11		
	BDE-99	220	350	2.0	0.34	430	410	3.0	0.49	250	250	1.8	0.29
	BDE-100	350	630			730	650			1700	820		
	BDE-153	680	860	0.41	0.068	7700	7600	7.4	1.23	3300	6000	25	4.2
	BDE-154	110	120	0.13	0.022	2200	2100	1.3	0.22	3300	11000	0.81	0.14
	BDE-183	4300	4800	0.052	0.0086	28000	25000	0.30	0.051	4100	5200	0.053	0.0089
	BDE-209	49000	52000	0.048	0.0080	44000	46000	0.043	0.0071	77000	78000	0.074	0.012
	ΣPBDEs	55000	59000	0.050	0.01	83000	81000	0.072	0.012	90000	100000	0.083	0.014
100													
	BDE-47	160	99			290	340			610	220		
	BDE-85					11	12			11	11		
	BDE-99	520	560	3.8	0.63	650	760	5.0	0.83	760	670	5.1	0.84
	BDE-100	880	1400			1000	1300			1100	890		
	BDE-153	940	1000	5.5	0.92	1200	1400	2.3	0.38	1500	2600	5.6	0.93
	BDE-154	1900	1300	0.17	0.028	660	660	0.23	0.039	350	2900	0.36	0.059
	BDE-183	4300	4400	0.050	0.0083	5600	5700	0.065	0.011	4000	3800	0.044	0.0074
	BDE-209	44000	45000	0.042	0.0070	64000	62000	0.060	0.010	54000	55000	0.052	0.0086
	ΣPBDEs	52000	53000	0.046	0.0077	73000	73000	0.064	0.011	63000	66000	0.056	0.0093
1000													
	BDE-47	98	100			130	130			390	260		
	BDE-85									23	20		
	BDE-99	240	300	1.9	0.32	410	470	3.1	0.52	1400	1200	9.2	1.4
	BDE-100	960	900			920	760			1900	1600		
	BDE-153	820	1400	4.6	0.77	1200	1600	1.0	0.17	2300	1900	3.8	0.97
	BDE-154	1200	1500	0.19	0.032	430	150	0.24	0.040	510	1700	0.36	0.055
	BDE-183	2400	2900	0.030	0.0050	4500	4700	0.052	0.0087	5400	4700	0.058	0.0089
	BDE-209	40000	43000	0.039	0.0066	60000	62000	0.058	0.0096	60000	59000	0.056	0.0093
	ΣPBDEs	46000	50000	0.042	0.0070	68000	70000	0.060	0.010	72000	70000	0.062	0.010

Table 5.10: Results of one-way analysis of variance with post hoc Tukey tests comparing PBDE congener concentrations determined in experiments examining the effects of different pH levels on leaching; performed for each DHM concentration.

	DHM conc. (mg L^{-1})	0		100		1000	
Congener	**pH**	**5.8**	**6.5**	**5.8**	**6.5**	**5.8**	**6.5**
BDE-47	**6.5**	.005		.551		.878	
	8.5	.003	.420	.317	.821	.048	.067
BDE-85	**6.5**	.120		.000		1.000	
	8.5	.733	.232	.000	.127	.001	.001
BDE-99	**6.5**	.174		.134		.380	
	8.5	.793	.102	.118	.987	.005	.009
BDE-100	**6.5**	.870		.993		.772	
	8.5	.256	.407	.827	.770	.016	.011
BDE-153	**6.5**	.017		.748		.669	
	8.5	.077	.141	.192	.377	.112	.238
BDE-154	**6.5**	.816		.684		.248	
	8.5	.215	.378	1.000	.676	.888	.379
BDE-183	**6.5**	.001		.002		.026	
	8.5	.995	.001	.034	.001	.014	.479
BDE-209	**6.5**	.045		.000		.002	
	8.5	.001	.000	.002	.004	.003	.605

p-values highlighted red = significant ($p<0.05$)

5.7. Effects of agitation on PBDE leaching from CRT plastics.

By comparing the results of experiments conducted at 20 °C with contact times of 24 h in the agitated contact time experiment and the non-agitated temperature experiment the effect of agitation on leaching of PBDEs from the CRT plastics can be examined (Figure 5.5).

The ΣPBDE concentrations in the agitated leachate samples were 178 % greater at 0 mg L^{-1} DHM, 353 % greater at 100 mg L^{-1} DHM and 124 % greater at 1000 mg L^{-1} DHM. This illustrates that agitation has a considerable role in enhancing PBDE leachate concentrations from CRT plastics. The results of paired samples t-tests are presented in Table 5.11. There are highly significant differences in BDE-153, BDE-183 and BDE-209 concentrations in the leachate between agitated and non-agitated samples and a weaker significant difference in BDE-100 concentrations (90 % probability).

Table 5.11: Results of paired sample t-tests for comparing differences in PBDE congener concentrations determined in experiments examining the effects of agitation on leaching; performed for CRT plastics.

Congener	Paired differences					*t*	df	*Sig.* (two-tailed)
	Mean	Std. Dev.	Std. error mean	95 % confidence interval of the difference				
				Lower	Upper			
BDE-47	100	190	78	-97	310	1.3	5	.241
BDE-99	290	200	81	77	500	3.5	5	.017
BDE-100	370	230	92	140	610	4.0	5	.010
BDE-153	330	140	56	190	480	5.9	5	.002
BDE-154	120	180	75	-69	310	1.6	5	.161
BDE-183	1,400	660	270	690	2,100	5.1	5	.004
BDE-209	47,000	22,000	8,800	25,000	70,000	5.4	5	.003

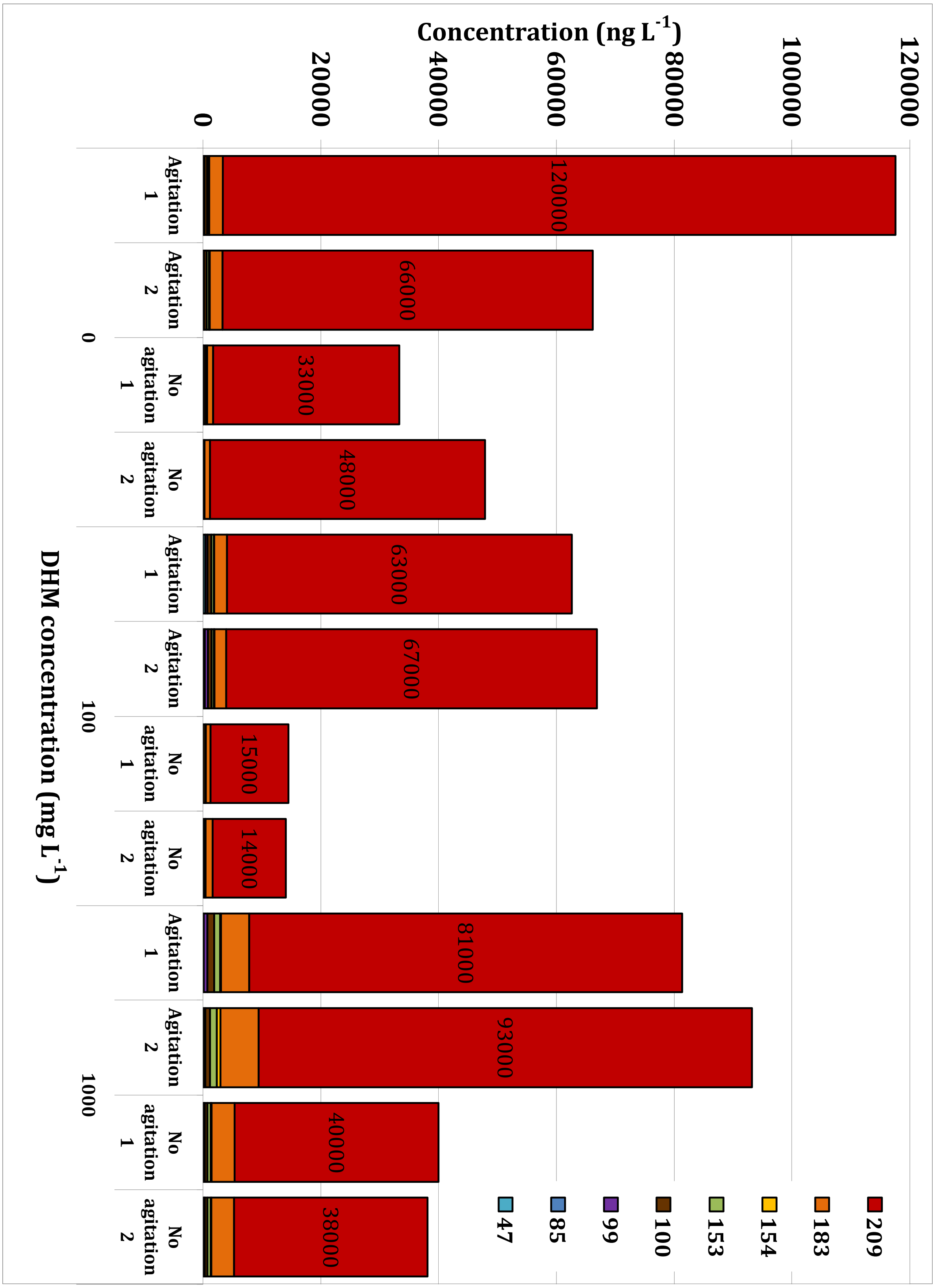

Figure 5.5: PBDE concentrations (ng L^{-1}) in leachate produced during duplicate 24 h single batch experiments examining the effects of agitation on leaching from CRT plastics using 0, 100 and 1000 mg L^{-1} DHM as leaching fluid. Data labels on bars are for ΣPBDEs and rounded to two significant figures.

5.8. Effects of DHM on PBDE leaching from CRT plastics.

There is some evidence in the literature that PBDE concentrations and *PLT* values increase with increasing DHM concentrations. It has been recognized that the presence of DHM in leaching fluids enhances the leachability of PBDEs suspended in water (Choi et al., 2009). However, there are multiple instances in this study in which leachates from experiments in which the leaching fluid contained no DHM actually have higher concentrations and *PLT* values (% h^{-1}) than in leachates obtained when the leaching fluid contained DHM.

Duplicate PBDE congener concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) in leachate from these pH experiments are illustrated in Table 5.12.

The results of one-way ANOVAs with post-hoc Tukey tests are presented in Table 5.13. After 6 h contact duration, there were significant differences ($p<0.05$) observed in BDE-153, -154, -183 and -209 concentrations in the leachate between 0 and 100 mg L^{-1} DHM, and between 0 and 1000 mg L^{-1} DHM. For the lower brominated congeners, significant differences were observed in BDE-47, -85 and -99 between 0 and 100 mg L^{-1} DHM, and between 100 and 1000 mg L^{-1} DHM.

When the leaching fluid was contacted for 24 h, significant differences were observed in BDE-153 and -183 concentrations between 0 and 1000 mg L^{-1} DHM, and between 100 and 1000 mg L^{-1} DHM. Significant differences ($p<0.05$) were also observed in in BDE-47 concentrations in the leachate between 0 and 100 mg L^{-1} DHM, and between 0 and 1000 mg L^{-1} DHM.

Significant differences were only observed for BDE-99 concentrations between 0 and 1000 mg L^{-1} DHM, and between 100 and 1000 mg L^{-1} DHM after 48 h contact duration.

Table 5.12: PBDE leachate concentrations (ng L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on CRT plastics with different DHM concentrations and contact times.

Contact time	DHM conc. (mg L^{-1}) /	0				100				1000			
(h)	Congener	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
6													
	BDE-47	140	150			290	340			130	130		
	BDE-85					11.0	12.0						
	BDE-99	430	410	3.0	0.021	650	760	4.99	0.831	410	470	3.1	0.52
	BDE-100	730	650			1000	1300			920	760		
	BDE-153	7700	7600	7.4	0.0034	1200	1400	2.28	0.379	1200	1600	1.00	0.167
	BDE-154	2200	2100	1.3	0.0012	660	660	0.231	0.0385	430	150	0.24	0.0404
	BDE-183	28000	25000	0.30	0.00048	5600	5700	0.065	0.0108	4500	4700	0.052	0.0087
	BDE-209	44000	46000	0.043	0.0015	64000	62000	0.060	0.0100	60000	62000	0.058	0.0096
	ΣPBDEs	83000	81000	0.072	0.012	73000	73000	0.064	0.0106	68000	70000	0.060	0.0100
24													
	BDE-47	81	31			350	340			120	120		
	BDE-85	9											
	BDE-99	150	160	1.1	0.04	430	500	3.3	0.14	640	300	3.3	0.138
	BDE-100	440	460			640	630			1200	790		
	BDE-153	370	400	0.2	0.01	410	410	0.34	0.014	1000	1200	1.17	0.049
	BDE-154	65	74	0.07	0.003	99	99	0.071	0.0030	92	580	0.19	0.0079
	BDE-183	2300	2200	0.026	0.001	2200	2000	0.024	0.0010	4800	6500	0.065	0.0027
	BDE-209	110000	63000	0.084	0.003	58000	63000	0.058	0.0024	74000	84000	0.075	0.0031
	ΣPBDEs	120000	66000	0.080	0.003	63000	67000	0.056	0.0024	81000	93000	0.076	0.0032
48													
	BDE-47	380	380			180	550			760	690		
	BDE-85	26	29				18			31			
	BDE-99	690	820	5.3	0.11	210	410	2.2	0.05	940	1000	6.8	0.14
	BDE-100	660	830			740	540			930	1100		
	BDE-153	890	920	0.6	0.01	1200	760	0.6	0.012	1100	1400	1.6	0.034
	BDE-154	190	180	0.16	0.003	200	140	0.17	0.0035	250	710	0.22	0.0046
	BDE-154	5000	5300	0.059	0.0012	6100	5100	0.064	0.0013	6500	7200	0.079	0.0016
	BDE-209	79000	76000	0.073	0.002	48000	63000	0.053	0.0011	80000	190000	0.13	0.0027
	ΣPBDEs	86000	84000	0.074	0.002	56000	71000	0.055	0.0012	91000	200000	0.13	0.0027

Table 5.13: Results of one-way analysis of variance with post hoc Tukey tests comparing PBDE congener concentrations determined in experiments examining the effects of DHM concentration on leaching; performed for each contact time.

	Contact time (h)	**6**		**24**		**48**	
Congener	**DHM conc. (mg L^{-1})**	**0**	**100**	**0**	**100**	**0**	**100**
BDE-47	**100**	.006		.002		.992	
	1000	.546	.004	.124	.003	.207	.186
BDE-85	**100**	.000		.518		.478	
	1000	1.000	.000	.518	1.000	.696	.897
BDE-99	**100**	.023		.222		.045	
	1000	.901	.029	.215	.999	.227	.015
BDE-100	**100**	.073		.566		.729	
	1000	.554	.175	.089	.217	.243	.124
BDE-153	**100**	.000		.917		.953	
	1000	.000	.952	.004	.005	.292	.382
BDE-154	**100**	.003		.988		.995	
	1000	.001	.121	.470	.536	.398	.366
BDE-183	**100**	.001		.969		.732	
	1000	.001	.715	.030	.026	.096	.180
BDE-209	**100**	.001		.487		.888	
	1000	.001	.267	.894	.710	.494	.322

p-values highlighted red = significant ($p<0.05$)

5.9. Statistical analysis of the whole data set.

A MLRA was performed for the entire data set for each PBDE congener. Leachate concentrations were used as the dependent variable, while DHM concentration, temperature, contact time, pH and whether the samples were agitated or not were used as independent variables. The independent variables for each PBDE congener are ranked by relative importance and significance and presented in Table 5.14. The coefficients for each significant independent variable are also presented and can be used to predict how much the dependent variable is expected to increase when that independent variable increases by one, holding all the other independent variables constant.

The effect of the length of contact time on BDE-209 concentrations gave a highly significant ($p<0.05$) positive correlation. The coefficients predict that BDE-209 concentrations increase by 720 ng for each additional hour of contact with the leaching fluid.

The effect of contact time also has highly significant positive effect on leachate concentrations for the lower brominated congeners BDE-47 and BDE-85. This perhaps suggests that they are being formed by debromination the longer the experiment continues. They are more soluble and relatively hydrophilic than the heavier congeners so you would perhaps expect them to elute early on if they were present in the plastics to start with. Or perhaps this can be explained by external diffusion of these congeners being a slow process that requires a greater contact time than 24 h.

Interestingly, the effect of agitation on PBDE leaching was found to yield a highly significant positive correlation for BDEs -153, -100, -99, -85, and -47. This supports the hypothesis of a PBDE “wash off” effect and perhaps suggests that mechanical abrasion during agitation contributes to debromination of PBDEs in leachate.

The pH of the leaching fluid has a highly significant positive effect on the leaching of BDEs -154, -100, -99, -85, and -47. The largest effect was observed for BDE-154. In all cases the alkaline 8.5 pH elicited the greatest concentrations.

The effect of the presence of DHM in the leachate elicits a significant positive effect on BDE-99 and BDE-100 leachate concentrations. However, this effect is ranked with the least importance when predicting the influence of the independent variables.

5.10. Summary.

Perhaps the most important finding of this study is that substantial concentrations of PBDEs can be generated in leachate from CRT waste despite unfavourable physicochemical properties for the heavier brominated PBDEs, such as relatively high hydrophobicity and relatively low aqueous solubility (Table 1.1, Chapter I). The concentrations for the sum of PBDEs (14,000 – 200,000 ng L^{-1}) are comparable to those reported in raw leachates from landfill and are 48 to 680 times higher than the highest reported PBDE concentration in a river system (295 ng L^{-1}) (Table 1.7 and 1.8, Chapter I). This study demonstrates that leaching of the higher brominated PBDEs from CRT plastics using distilled deionised water as a leaching fluid is a second order process. Following an initial period of source:leaching fluid contact during which leaching is relatively facile, subsequent leaching is slower. This is not the case for lower brominated congeners BDE-47, BDE-85 and BDE-99.

Table 5.14: Results for multiple linear regression analysis obtained for PBDE congeners for leachate from CRT plastics[a].

Congener	Independent variable	*Coefficient (ng L^{-1} unit-^{1})*	Std. error	*Sig.*	95 % Confidence interval		Importance
					Lower	Upper	
BDE-47	Agitation	190	42	.000	100	270	0.454
	Contact time (h)	6.6	1.5	.000	3.5	9.7	0.433
	pH	61	28	.032	5.5	120	0.113
BDE-85	Agitation	7.9	2.1	.001	3.6	12	0.338
	pH	4.7	1.4	.002	1.9	7.6	0.309
	Contact time (h)	0.26	0.078	.002	0.099	0.42	0.303
BDE-99	Agitation	360	63	.000	230	490	0.541
	pH	160	42	.001	72	241	0.234
	DHM concentration (mg $\mathbf{L}^{-1}$)	0.21	0.066	.002	0.079	0.34	0.173
BDE-100	Agitation	500	110	.000	280	720	0.407
	pH	220	52	.000	120	330	0.356
	DHM concentration (mg $\mathbf{L}^{-1}$)	0.24	0.083	.006	0.071	0.41	0.159
BDE-153	Agitation	990	450	.033	86	1,900	0.404
BDE-154	pH	1,000	300	.001	420	1,600	0.757
BDE-209	Contact time (h)	720	340	.039	39	1,400	1.000

[a]Data only shown for effects with greater than 95 % significance.

Although attempts were made to ensure each 5 g aliquot of CRT plastic chips were representative of the bulk chipped sample, the heterogeneous mixture of the CRT plastics perhaps has a confounding effect on trends. Conceivably not all plastic chips present in the bulk sample were flame retarded with PBDEs, while some were treated with Octa-BDE and others with Deca-BDE. Therefore, the starting concentrations of PBDE congeners in the different 5 g aliquot of the CRT plastic chips used in each leaching experiment may have been variable. Additionally, variability in the morphology of the CRT chips such as the thickness, surface area, porosity and/or strength of the of the plastic may have influenced the potential for PBDEs to partition into the leaching fluid resulting in different leaching rates from chip to chip (Brandsma et al., 2013a).

That being said, it does appear that by increasing the temperature of leaching fluids from 20 to 80 ºC, the leachability of BDE-209 and BDE-99 from plastics is enhanced. There is also some potential evidence for debromination of heavy congeners to the lower brominated and more bioavailable BDEs. Primarily this comes from the emergence of congeners BDE-47, -85 and -100 in the leachates, despite their absence from the CRT plastics themselves. This has implications for the potential for PBDEs to migrate into surface and ground waters due to the preferential physicochemical properties of lower brominated PBDEs.

The data presented here are preliminary and there are few comparable studies in the literature (Danon-Schaffer et al., 2013b; Choi et al., 2009). Further work is required to fill knowledge gaps and develop a greater understanding of PBDE leaching behaviour from WEEE polymers and other PBDE treated materials.

Chapter VI: Leaching behaviour of TCIPP from furniture PUF.

6.1. Synopsis.

In this chapter, the leaching behaviour of TCIPP from treated furniture PUF samples surveyed from the UK waste stream is investigated. Concentrations (mg L^{-1}), percentages leached (%), as well as percentage leached per unit time (*PLT*; % h^{-1}) values and leaching kinetics are presented for a range of landfill relevant conditions. Additional information detailing the experimental set-up of these leaching experiments can be found in chapter 2.2.1 and extraction and clean up techniques are detailed in chapter 2.3.1 and 2.4.1 respectively. A summary of the conditions explored are outlined in Table 6.1.

Table 6.1: Summary of conditions employed in TCIPP treated PUF leaching test protocols.

Experimental Scenario / Parameter	**Single batch, variable contact time**	**Serial batch**	**Single batch, variable temperature**	**Single batch, variable pH**
Extraction period (h)	6, 24, 48	6, 24, 48, 72, 96, 168	24	6
Agitation	200 rpm	200 rpm	None	200 rpm
Temperature (°C)	20	20	20, 50, 80	20
pH	6.5	6.5	6.5	5.8, 6.5, 8.5
DHM conc. (mg L^{-1})	0, 100, 1000	0	0, 100, 1000	0, 100, 1000

6.2. Initial TCIPP concentrations in the furniture PUF samples.

TCIPP is typically added to flexible PUF at 1-4 % by weight (pers. comm. Flexible Foam Research Ltd, 2014). Flexible PUF as used in furniture is made from a mixture of liquid starting materials individually pumped into a high speed mixing head. Flame retardants are added at this stage. Chlorinated phosphates such as TCIPP are liquids and can therefore be delivered direct to the mixing head from storage tanks. TCIPP is blended evenly into the foam, but remains unbound.

Figure 6.1 displays the initial concentrations of TCIPP determined in five 50 mg sub-samples of the treated furniture PUF sample used in this study. The mean initial concentration of TCIPP was 17,000 ± 13 mg kg^{-1} or 1.7 % by weight.

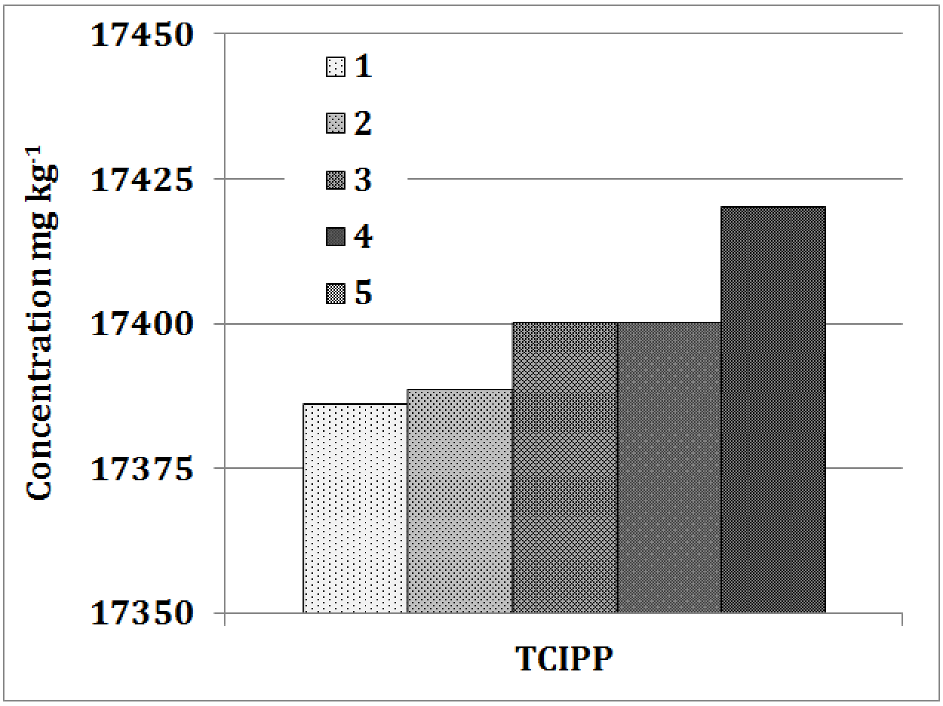

Figure 6.1 Concentrations (mg kg^{-1}) of TCIPP in furniture PUF used in this study (n=5).

6.3. Effects of contact time on TCIPP leaching from single batch experiments.

The influence of contact time on mean TCIPP concentrations in leachate in single batch experiments conducted at 20 ˚C is illustrated by Figure 6.2, with mean PLT values (% h^{-1}) in Figure 6.3. TCIPP concentrations (mg L^{-1}), mean PL (%) and mean PLT values (% h^{-1}) for the same experiments are provided in Table 6.2. Results of one-way ANOVAs with post hoc Tukey tests are provided in Table 6.3. There were no significant ($p>0.05$) differences in TCIPP concentrations between contact times. This suggests that contact time has comparatively little effect on TCIPP leaching from furniture PUF, therefore leaching from the PUF material appears to occur in the early stages of contact with the leaching fluid. The quantity of TCIPP being leached in experiments is much larger than was seen for the BFRs. The reduced concentrations of TCIPP found at 24 h and 48 h in deionised Milli-Q leaching fluid and at 48 h with DHM containing leaching fluids may have occurred as a result of degradation of TCIPP during periods of longer agitation.

Table 6.2: TCIPP leachate concentrations in duplicate (mg L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on furniture PUF with different contact times and DHM concentrations.

DHM conc. (mg L^{-1})	Contact time (h)	Conc. (mg L^{-1})	Conc. (mg L^{-1})	*PL* (%)	*PLT* (% h^{-1})
0	6	59	67	36	6.0
0	24	29	22	15	0.61
0	48	16	36	15	0.31
100	6	60	67	36	6.0
100	24	61	68	37	1.6
100	48	49	47	28	0.58
1000	6	70	69	40	6.7
1000	24	89	63	44	1.8
1000	48	45	68	33	0.68

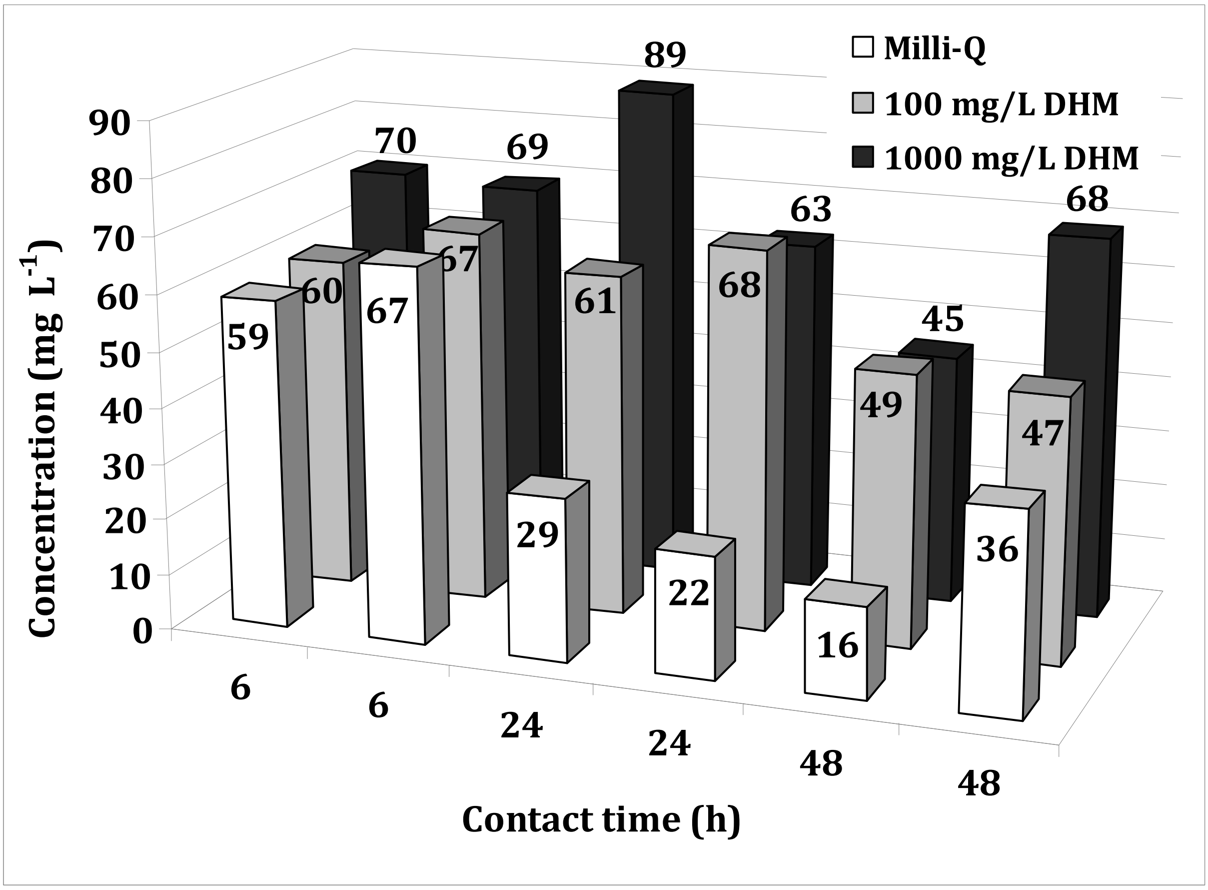

Figure 6.2: TCIPP concentrations in leachate (ng L^{-1}) produced from single batch experiments on furniture PUF for different contact times (each time examined in duplicate) with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids. Data labels on bars are rounded to two significant figures.

Table 6.3: Results of one-way analysis of variance tests with post hoc Tukey tests comparing TCIPP concentrations determined in experiments examining the effects of contact time on leaching; performed for each DHM concentration for furniture PUF.

DHM conc. (mg L^{-1})	0		100		1000	
Contact time (h)	**6 h**	**24 h**	**6 h**	**24 h**	**6 h**	**24 h**
24 h	.052		.931		.908	
48 h	.055	.997	.070	.055	.669	.468

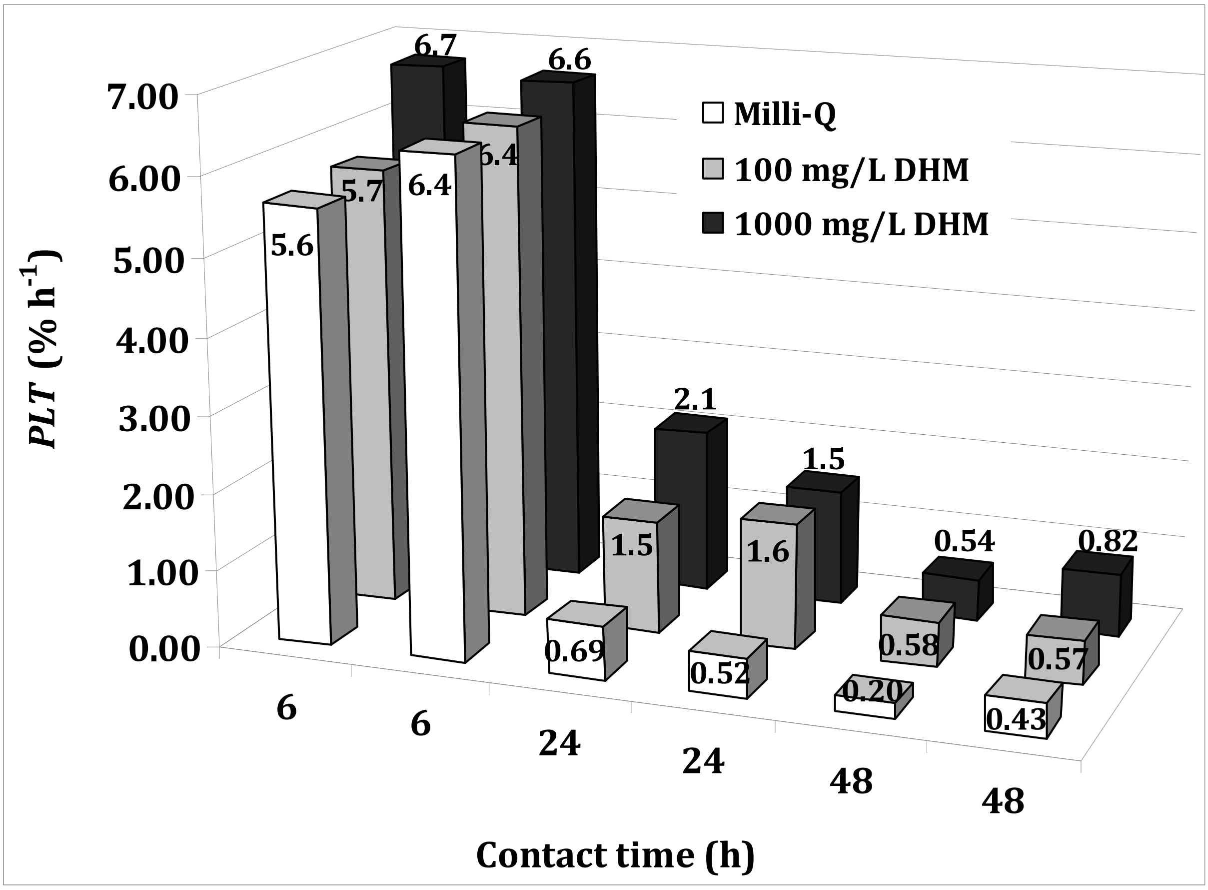

Figure 6.3: TCIPP *PLT* values (% h^{-1}) from single batch experiments with furniture PUF for different contact times (each time examined in duplicate) with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

6.4. Effect of cyclical wetting and draining on TCIPP leaching (serial batch experiments).

Mean concentrations of TCIPP (ng L^{-1}) detected in leachate and mean *PLT* values (% h^{-1}) obtained from these experiments on flexible furniture PUF are presented in Figures 6.4, with TCIPP concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) for the same experiments provided in Table 6.4. After 6 h contact time, concentrations of TCIPP leached from flexible PUF in these serial batch experiments diminish with increasing experimental duration. However, the extent of TCIPP leaching from the material is dramatic, and after a cumulative 168 h of leaching, the cumulative total of TCIPP removed from the furniture foam by the leaching fluids is close to 96 % of the initial mass present in the PUF sample used (Figure 6.5). Overall – although longer term experiments are required to confirm this - this serial batch experiment indicates that replenishment of leaching fluid as would be expected in a landfill could result in the total removal of TCIPP from PUF via leaching over long periods.

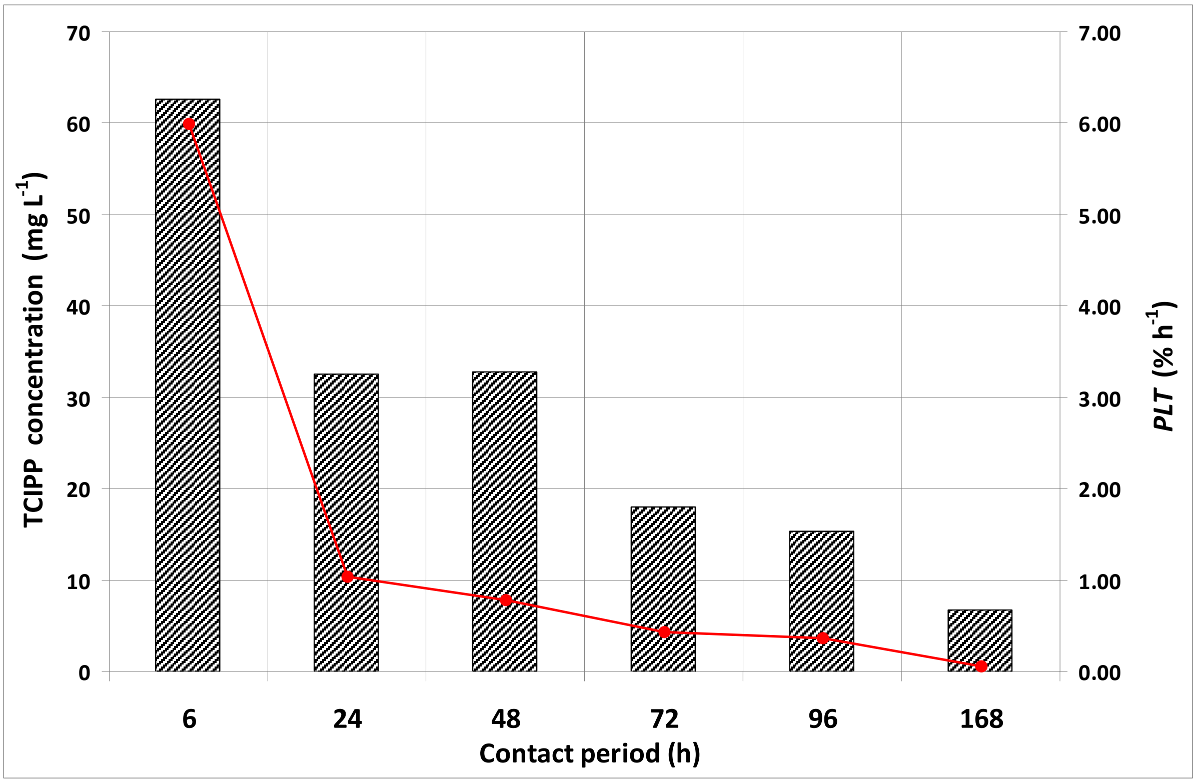

Figure 6.4: Mean (n=2) TCIPP concentrations (bars) and *PLT* (% h^{-1}) (red circles) in leachate produced during experiments on furniture PUF examining the effect of cyclical wetting and draining (serial batch).

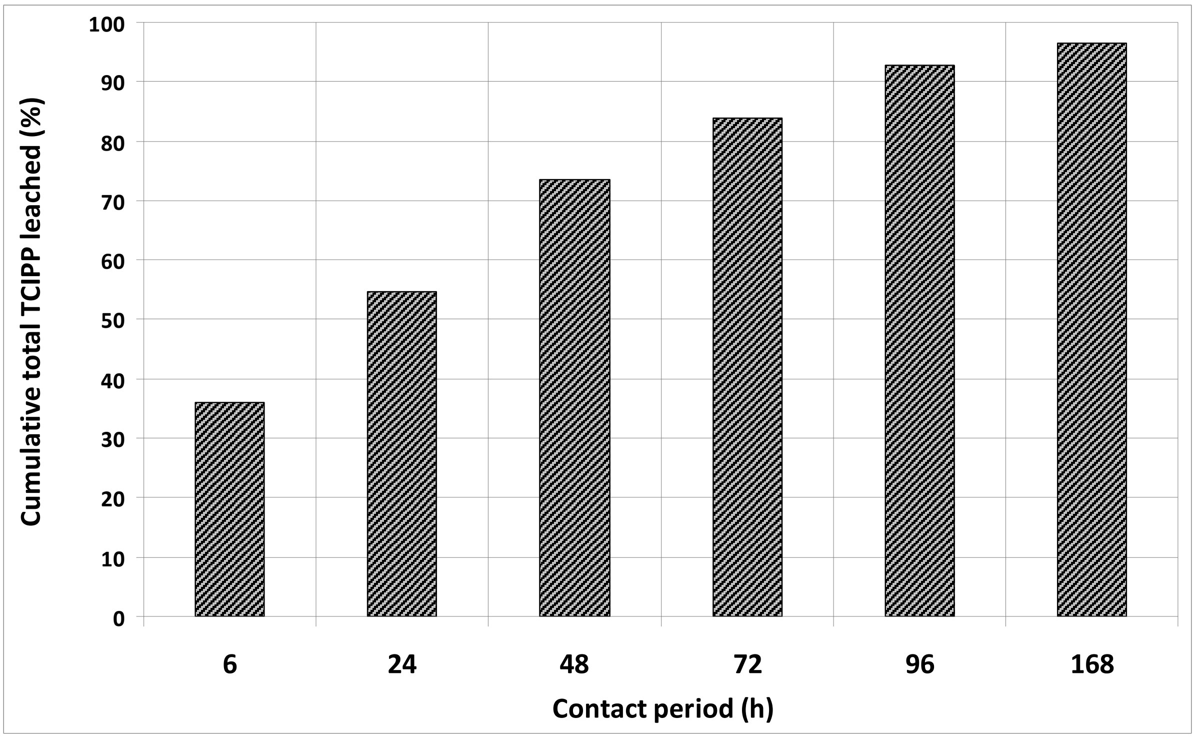

Figure 6.5: Cumulative total TCIPP leached (%) in experiments using furniture PUF to examine the effect of cyclical wetting and draining (serial batch).

Table 6.4: TCIPP leachate concentrations (mg L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on furniture PUF with different contact periods.

Contact period (h)	Conc. (mg L^{-1})	Conc. (mg L^{-1})	*PL* (%)	*PLT* (% h^{-1})
0 – 6	59	67	36	6.0
6 – 24	31	34	19	1.0
24 – 48	32	33	19	0.78
48 – 72	19	18	10	0.43
72 – 96	16	15	8.8	0.37
96 – 168	7.0	6.5	3.9	0.054

6.5. Leaching kinetics.

Plots were generated to test whether TCIPP leaching from PUF could be explained using second order leaching kinetics. In contrast to the analogous experiments with BFRs (chapters III, IV and V), the concentrations of TCIPP in leachates from serial batch experiments were not included in generating these plots because the larger emissions of TCIPP from the foam resulted in significantly lower initial concentrations in the PUF between batches. Therefore, only duplicate measured leachate concentrations in single batch experiments conducted at 20 ˚C for each contact time (6 h, 24 h and 48 h) and also for each DHM concentration were included in leaching kinetics calculations. Using the equations described in section 3.6, *t*/*Ct* was plotted against *t,* where *Ct* is the concentration of TCIPP (mg L^{-1}) in suspension at any given time and *t* (min). The resulting plots are shown in Figure 6.6 and show that the y-intercept and therefore *k* values are negative for each DHM concentration. This perhaps suggests that TCIPP leaching from PUF is not a second order kinetic process.

To test if the leaching is a first-order reaction we plotted the natural logarithm of TCIPP concentration versus time to see whether the graph was linear (Figure 6.7). We generated such plots for all single batch experiments conducted at 20 ˚C and for each DHM concentration. The graph is linear and has a negative slope in all instances; therefore the leaching of TCIPP from PUF appears to be a first-order process. . However, there is some degree of uncertainty with the kinetics because these conclusions are drawn only from the single batch experiments (6 data points). Moreover, only the first order kinetics plot for leaching fluids containing 100 mg L^{-1} DHM significantly correlates. The slope, Y-intercept, the leaching rate constant, *k (*min^{-1}*)*, two-tailed *p* values, and Pearson's correlation coefficients, *r*, are given in Table 6.5.

There are two possible explanations for why TCIPP does not fit with second order kinetics as has been previously observed for HBCDD and PBDEs in chapters III, IV and V. Firstly, the PUF material is more porous, permeable and has a larger surface area than other materials tested. This allows the leaching fluid to access far more surface area than in less porous materials. Secondly, there are significant differences in the physico-chemical properties between the chlorinated phosphates and the BFRs, with TCIPP possessing an aqueous solubility 20,000 – 800,000 times greater than PBDEs. It was also less susceptible to abrasion during agitation due to a softer more flexible rigidity.

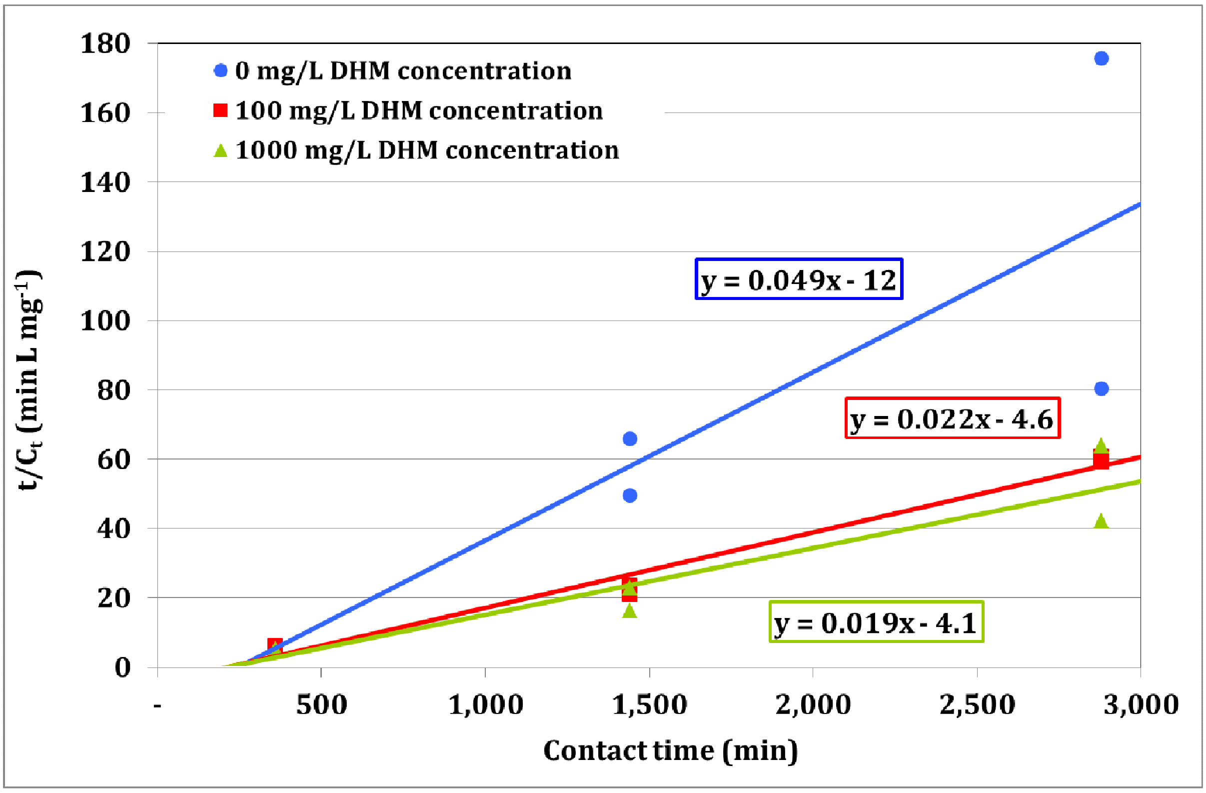

Figure 6.6: Plot of *t/C$_t$* versus *t* for TCIPP leaching from furniture flexible PUF in single batch experiments.

Table 6.5: First order leaching rate slopes, y-intercepts, constants (*k*), and *r* values obtained for TCIPP for flexible furniture PUF.

Constant / DHM Conc. (mg L^{-1})	Slope (log$_e$ mg L^{-1} /min)	y-intercept (log$_e$ mg L^{-1})	*k* (min^{-1})	*Two-tailed P value*	*Correlation coefficient: r*
0	-0.0004	4.1	0.000000031	.095	-0.737
100	-0.0001	4.2	0.0000000030	.044	-0.824
1000	-0.0001	4.3	0.0000000022	.316	-0.497

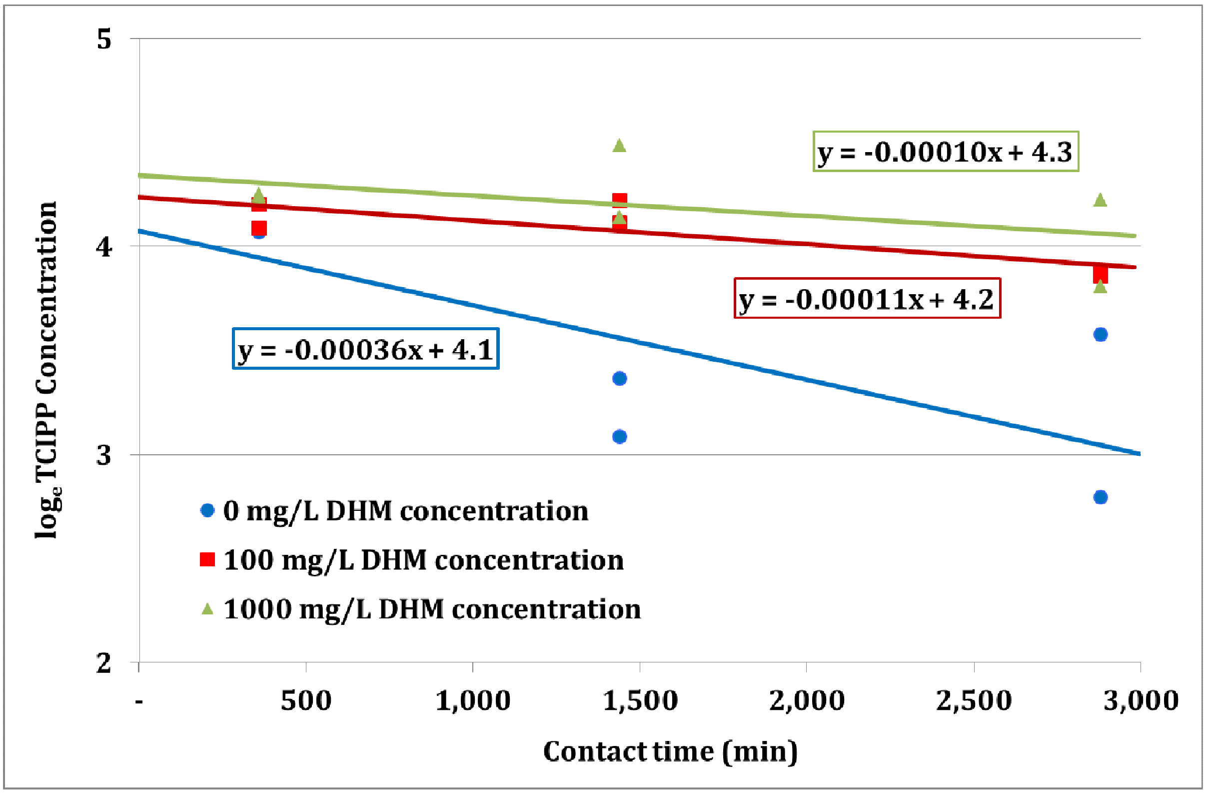

Figure 6.7: Plot of natural logarithm of concentration versus *t* for TCIPP leaching from furniture flexible PUF in single batch experiments.

6.6. Effects of temperature on TCIPP leaching from furniture PUF samples.

The influence of leachate temperatures of 20 °C, 50 °C and 80 °C, on TCIPP leaching behaviour was investigated. Leachate concentrations for TCIPP from flexible PUF at different temperatures and DHM concentrations are displayed in Figures 6.8. TCIPP concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) in these experiments (conducted in duplicate) are provided in Table 6.6, with the results of one-way ANOVAs with post hoc Tukey tests presented in Table 6.7.

There are significant differences in TCIPP concentrations in the leachate between 50 °C and 80 °C for both DHM containing leaching fluids, while the differences between these temperatures are only weakly significant (94.1 % probability) for deionised Milli-Q leaching fluid. There is also a weakly significant (94.3 % probability) difference between 20 °C and 50 °C for deionised Milli-Q leaching fluid. The reduced TCIPP concentrations present in leachates at 80 °C relative to those at 50 °C may be a result of enhanced TCIPP degradation at this higher temperature. TCIPP degradation products were not monitored for in LC-MS/MS analysis so this could not be confirmed.

Table 6.6: TCIPP leachate concentrations (mg L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on furniture PUF with different temperatures and DHM concentrations.

DHM conc. (mg L^{-1})	Temperature (°C)	Conc. (mg L^{-1})	Conc. (mg L^{-1})	*PL* (%)	*PLT* (% h^{-1})
0	20	13	16	8.3	0.35
0	50	76	130	59	2.5
0	80	15	16	8.9	0.35
100	20	64	47	32	1.3
100	50	80	130	59	2.5
100	80	12	14	7.4	0.31
1000	20	52	52	30	1.2
1000	50	100	68	49	2.0
1000	80	8.1	23	8.9	0.37

Table 6.7: Results of one-way analysis of variance tests with post hoc Tukey tests comparing TCIPP concentrations determined in experiments examining the effects of temperature on leaching; performed for each DHM concentration for furniture PUF.

DHM conc. (mg L^{-1})	**0**		**100**		**1000**	
Temperature (°C)	**20**	**50**	**20**	**50**	**20**	**50**
50	.057		.178		.211	
80	.999	.059	.220	.039	.184	.038

p-values highlighted red = significant ($p<0.05$)

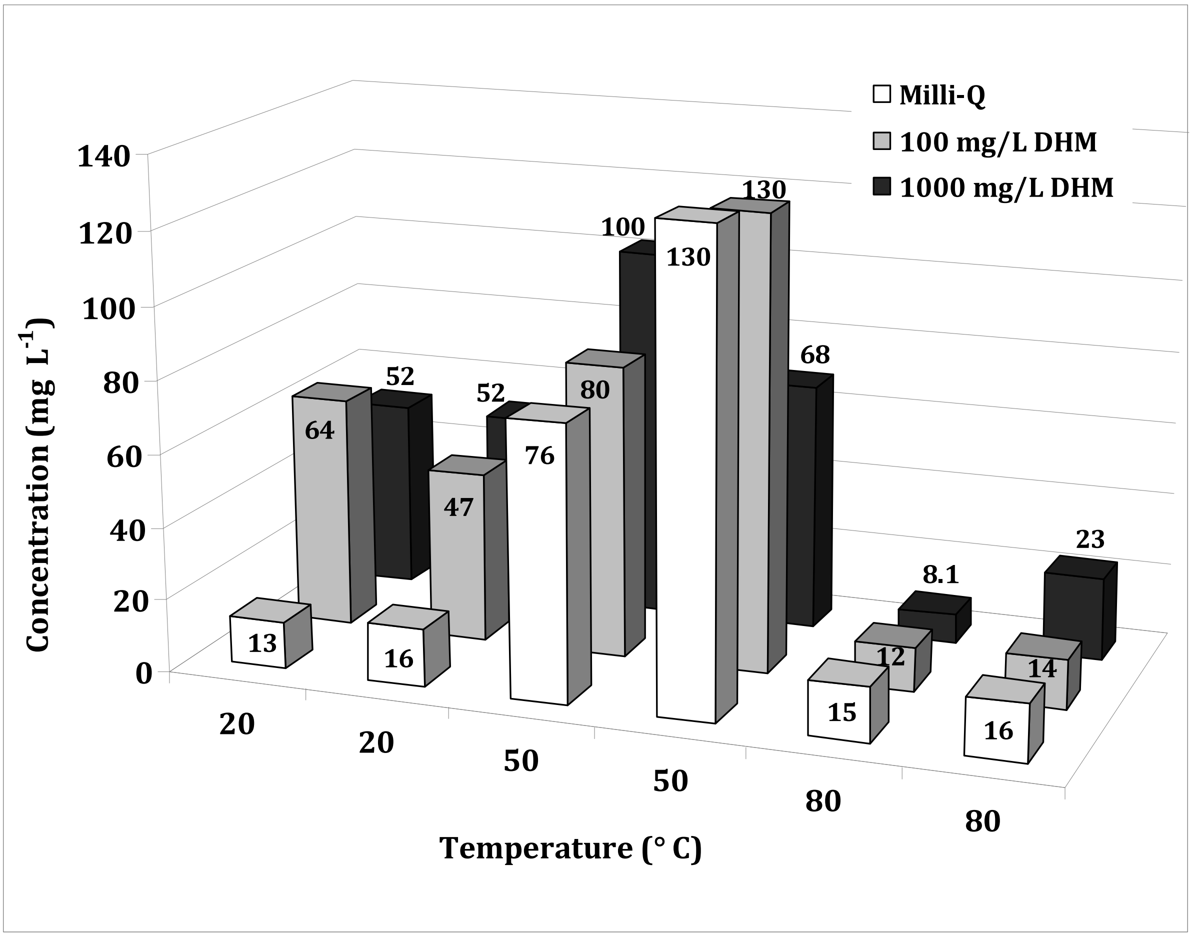

Figure 6.8: TCIPP concentrations (ng L^{-1}) in leachate produced during 24 h single batch experiments (run in duplicate) on furniture PUF at different temperatures with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids. Data labels on bars are rounded to two significant figures.

6.7. Effects of pH on TCIPP leaching from furniture PUF.

The influence of leachate pHs of 5.8, 6.5 and 8.5, on TCIPP leaching behaviour was investigated. Leachate concentrations values for TCIPP from flexible PUF at different pHs and DHM concentrations are displayed in Figures 6.9. Duplicate TCIPP concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) for the same experiments provided in Table 6.8, with the results of one-way ANOVAs with post hoc Tukey tests are presented in Table 6.9.

In leachates to which no DHM was added there were significant differences ($p<0.05$) in TCIPP concentrations between pH 5.8 and 8.5, and 6.5 and 8.5. In leachates in which 100 mg L^{-1} DHM was present, there was no significant differences in TCIPP concentrations between the pH levels explored. At 1000 mg L^{-1} there are significant differences between pH 5.8 and 8.5, and 6.5 and 8.5. The alkaline pH of 8.5 elicited the largest concentrations of TCIPP in the leachate for all three DHM concentrations explored.

Table 6.8: TCIPP leachate concentrations (mg L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on furniture PUF with different pH values and DHM concentrations.

DHM conc. (mg L^{-1})	pH	Conc. (mg L^{-1})	Conc. (mg L^{-1})	*PL* (%)	*PLT* (% h^{-1})
0	5.8	39	48	25	4.2
0	6.5	59	67	36	6.0
0	8.5	100	92	55	9.2
100	5.8	60	74	39	6.4
100	6.5	60	67	36	6.0
100	8.5	87	84	49	8.2
1000	5.8	72	65	39	6.6
1000	6.5	70	69	40	6.7
1000	8.5	130	120	71	12

Table 6.9: Results of one-way analysis of variance tests with post hoc Tukey tests comparing TCIPP concentrations determined in experiments examining the effects of pH on leaching; performed for each DHM concentration for furniture PUF.

DHM conc. (mg L^{-1})	**0**		**100**		**1000**	
pH	**5.8**	**6.5**	**5.8**	**6.5**	**5.8**	**6.5**
6.5	.093		.831		.914	
8.5	.006	.021	.123	.079	.001	.001

p-values highlighted red = significant (p<0.05)

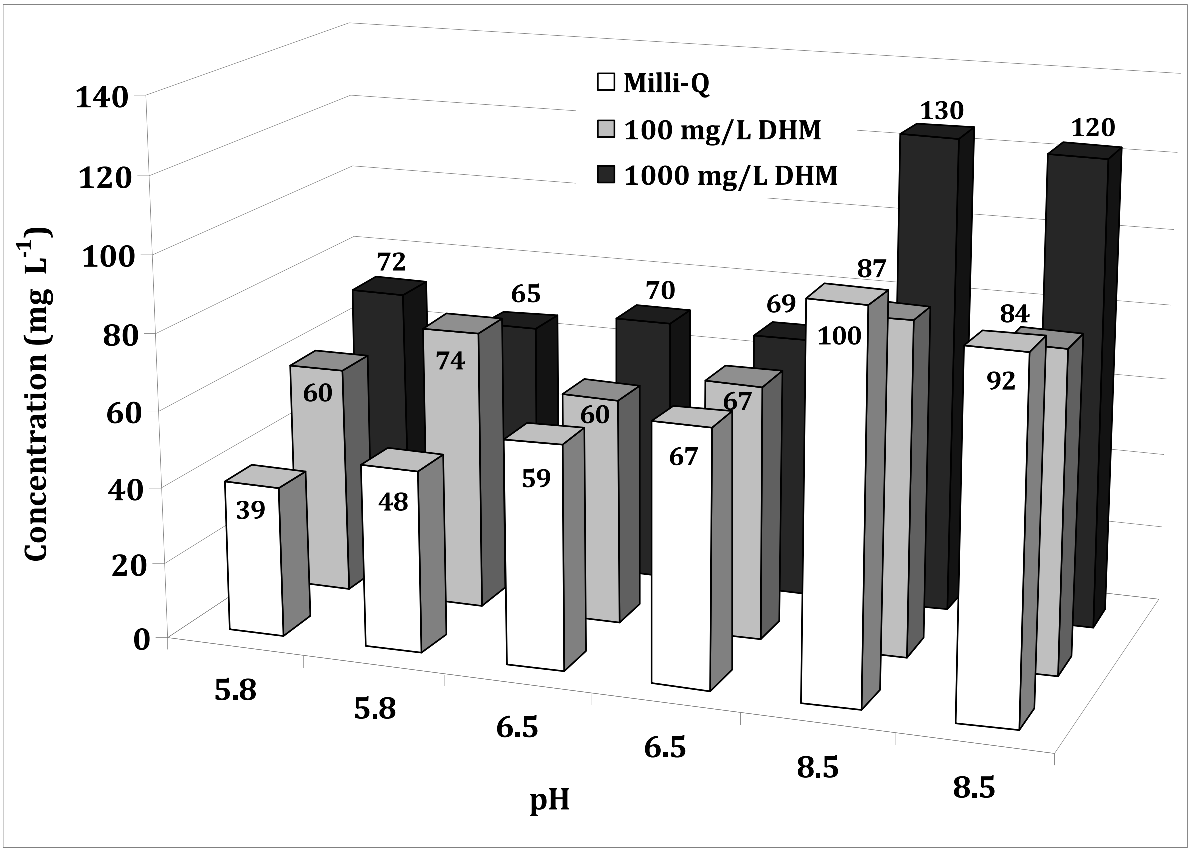

Figure 6.9: TCIPP concentrations (ng L^{-1}) in leachate produced during experiments on furniture PUF at different pH levels from 6 h single batch experiments (run in duplicate) with Milli-Q, 100 mg L^{-1} and 1000 mg L^{-1} leaching fluids. Data labels on bars are rounded to two significant figures.

6.8. Effects of agitation on TCIPP leaching from furniture PUF.

By comparing the results of experiments conducted at 20 °C using Milli-Q water with contact times of 24 h with and without agitation, the effect of agitation on TCIPP leaching from the PUF can be examined (Figure 6.10). The results of a paired sample t-test are presented in Table 6.10 and indicate that there are significant differences ($p<0.05$) in TCIPP concentrations between agitated and non-agitated samples. The effect of agitation on treated PUF is to slightly enhance TCIPP leaching across all three DHM concentrations examined; there was on average 43 % more TCIPP in the agitated samples between 0 mg L^{-1} DHM leachates, a 14 % increase between 100 mg L^{-1} DHM leachates and a 32 % increase between 1000 mg L^{-1} DHM leachates.

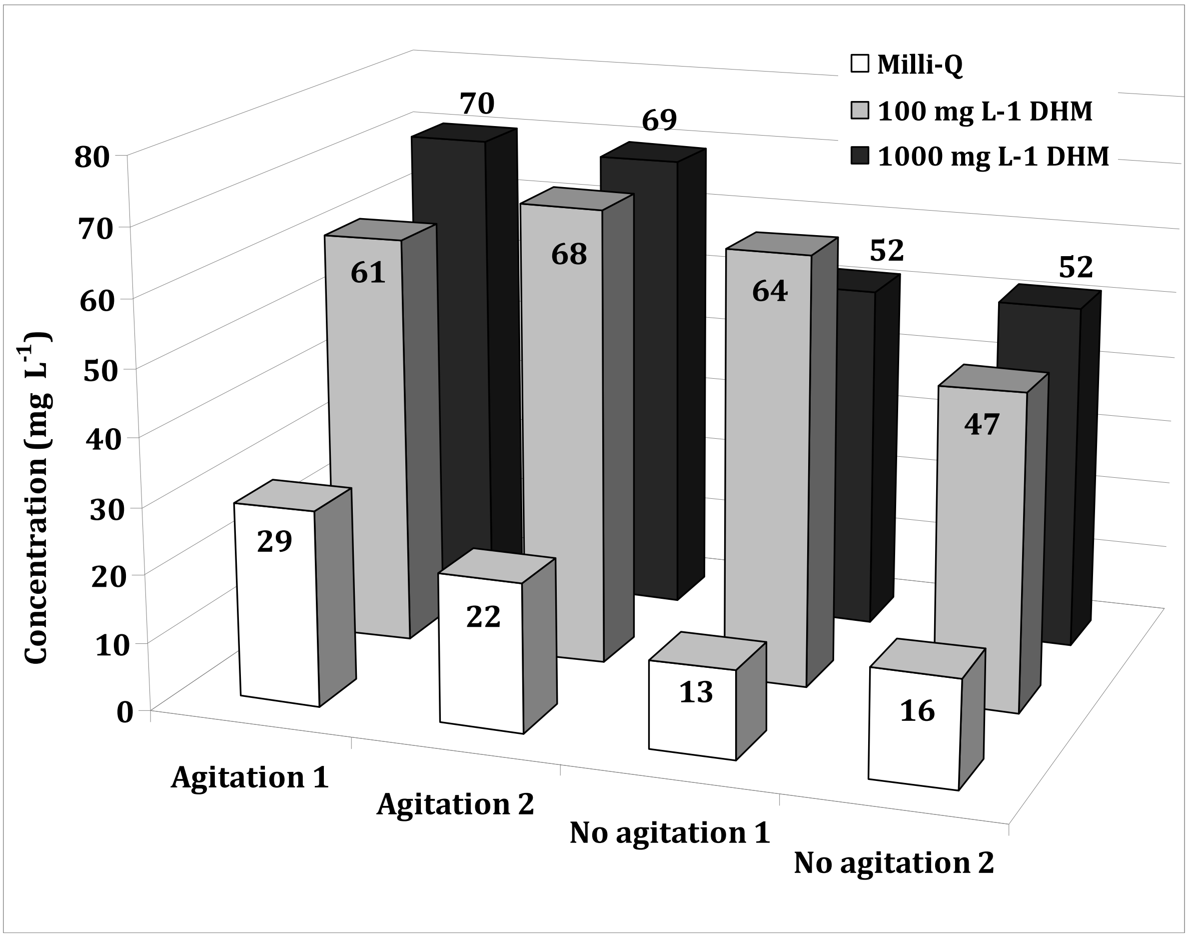

Figure 6.10: Duplicate TCIPP concentrations (ng L^{-1}) in leachate produced during experiments on furniture PUF from 24 h single batch experiments with and without agitation for Milli-Q, 100 mg L^{-1} and 1000 mg L^{-1} leaching fluids. Data labels on bars are rounded to two significant figures.

Table 6.10: Results of paired sample t-tests for comparing differences in TCIPP concentrations between agitated and non-agitated leaching; performed for each DHM concentration for furniture PUF.

Paired differences					*t*	df	*Sig.* (two-tailed)
Mean (mg L^{-1})	Std. Dev.	Std. error mean	95 % confidence interval of the difference				
			Lower	Upper			
15	6.5	2.7	8.0	22	5.6	5	.003

6.9. Effects of DHM on TCIPP leaching from furniture PUF.

The influence of leachate DHM concentrations of 0, 100 and 1000 mg L^{-1}, on TCIPP leaching behaviour was investigated. Duplicate TCIPP concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) for the same experiments provided in Table 6.11. The results of one-way ANOVAs with post hoc Tukey tests are presented in Table 6.12. The only significant difference observed in TCIPP concentrations in the leachate, was between leachates containing 0 and 1000 mg L^{-1} DHM after 24 h contact. In general, PLT values and concentrations appear to slightly increase with the presence of DHM in the leaching fluid but this is not shown to be significant by the ANOVA tests.

Table 6.11: TCIPP leachate concentrations (mg L^{-1}) in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1}) conducted on furniture PUF with different DHM concentrations and contact times.

DHM conc. (mg L^{-1})	Contact time (h)	Conc. (mg L^{-1})	Conc. (mg L^{-1})	*PL* (%)	*PLT* (% h^{-1})
0	6	60	67	36	6.0
100	6	60	67	36	6.0
1000	6	70	69	40	6.7
0	24	29	22	15	0.61
100	24	61	68	37	1.6
1000	24	89	63	44	1.8
0	48	16	36	15	0.31
100	48	49	47	28	0.58
1000	48	45	68	33	0.68

Table 6.12: Results of one-way analysis of variance tests with post hoc Tukey tests comparing TCIPP concentrations determined in experiments examining the effects of DHM on leaching; performed for each contact time for furniture PUF.

Contact time (h)	6		24		48	
DHM conc. (mg L^{-1})	0	100	0	100	0	100
100	.992		.079		.318	
1000	.373	.417	.042	.633	.173	.781

p-values highlighted red = significant (p<0.05)

6.10. Statistical analysis of the whole data set.

The results of MLRA for TCIPP treated flexible PUF are provided in Table 6.13. The importance value ranks the effects of the independent variables from greatest to smallest. Of the independent variables explored in these experiments, the pH of the leaching fluid had the greatest effect on TCIPP concentrations. The alkaline pH of 8.5 yielded the greatest TCIPP concentrations in leachate. The length of contact duration yielded a significant negative correlation with TCIPP concentrations in the leachate. This may be related to degradation of the TCIPP, however this will be heavily influenced by the inclusion of the serial batch experiments, in which the concentration of TCIPP in the PUF was heavily depleted with subsequent batches and therefore yielding lower concentrations with longer contact times. The effect of the presence of DHM in leaching fluids on TCIPP leaching from the foam was predicted to be least important, yet yielded a highly significant positive correlation. The effect of leaching fluid temperature is not significant in MRLA due to the degradation of TCIPP observed at 80 °C.

Table 6.13: Results for multiple linear regression analysis obtained for TCIPP for leachate from furniture PUF[a]

Independent variable	***Coefficient (mg L^{-1} $unit^{-1}$)***	**Std. error**	***Sig.***	**95 % Confidence interval**		**Importance**
				Lower	**Upper**	
pH	17	5.3	.002	6.7	28	0.399
Contact time (h)	-0.77	0.25	.004	-1.3	-0.26	0.343
DHM concentration (mg L^{-1})	0.021	0.0081	.011	0.0051	0.037	0.259

[a]Data only shown for effects with greater than 95 % significance.

6.11. Summary.

The water solubility of TCIPP has been measured at 1.6 g L^{-1} (van der Veen and de Boer, 2012). Chemicals with such relatively high water solubility are more likely to be transported into groundwater with runoff during storm events, be absorbed through the gastrointestinal tract or lungs, partition to aquatic compartments, undergo atmospheric removal by rain washout, and possess a greater potential for human exposure through the ingestion of contaminated drinking water. However, they are generally less persistent and have a lower potential to bioconcentrate. TCIPP has a measured bioconcentration factor in fish of 0.8-4.6 (EU RAR, 2008a). The estimated half-life of TCIPP in the atmosphere is 8.6 hours, where it is expected to degrade in by reaction with hydroxyl radicals (EU RAR, 2008a). TCIPP is considered to be inherently biodegradable, however it does not fulfil the criteria of the EU Risk Assessment Technical Guidance Document for degradation at a waste water treatment plant (WWTP) (EU RAR, 2008a). Additionally, Geurts and van Veenendaal, (2001), reported that TCIPP concentrations decreased by less than 1 % at pH 4, 7 and 9 in hydrolysis tests undertaken at 50 °C for five days. It is concluded by the author's that TCIPP is stable in water at pH 4, 7 and 9 at 25 °C and does not readily hydrolyse ($t_{1/2}$ >1 year in neutral conditions at ambient temperature). Despite this, TCIPP, while harmful is not regulated as a POP due to a perceived lack of persistence in the environment.

It is clear from these experiments that TCIPP in furniture foams disposed of at landfill will readily leach into percolating waters and total removal into leachate from such discarded foams is likely. This study demonstrates that leaching is extensive, occurs rapidly and appears a first order kinetic process. The EU risk assessment report predicts that a typical UK landfill with a leachate flow of 100 m^3 day^{-1} would emit a maximum TCIPP mass via leachate of 6.7 g day^{-1}.

This chapter suggests that it is very likely that landfill leachate arriving at WWTPs in the UK will contain TCIPP. The EU risk assessment report predicts that the fate of TCIPP at WWTPs is: 97.9 % to water; 2.1 % adsorbed to sewage sludge; 0 % to air; and 0 % is degraded (as estimated by the SIMPLETREAT program within EUSES). The UK's use of TCIPP as the primary FR in furniture PUF since 1988 gives cause for concern. More research is required to ascertain how much TCIPP and other PFRs are removed at WWTPs receiving landfill leachate in the UK by measuring effluent flows. It would also be of benefit to measure the quantity of PFRs in influent flows, to calculate removal efficiencies. It is likely that TCIPP has a great potential to contaminate groundwater and drinking water at concentrations much larger than reported for BFRs. TCIPP is not predicted to adsorb significantly to organic matter, based on an estimated soil organic carbon-water partitioning coefficient (log K_{OC}) of 2.24 L kg^{-1} used in the EU risk assessment of TCIPP (EU RAR, 2008a).

Chapter VII: Survey of flame retardants in the UK soft furnishings waste stream, 2011-12.

7.1. Synopsis.

In the UK, the use of FRs is driven by the Furniture and Furnishings (Fire Safety) Regulations 1988 (as amended in 1989, 1993 and 2010). To meet these regulations, a variety of FR chemicals have historically been used, but because it is not a labelling requirement to state which FR was used in each product, it is unclear which chemicals were applied, at what concentration and how frequently. These regulations do not apply to curtains and carpets, however, these products are covered under UK General Product Safety Regulations 2005.

Concentrations of PBDEs, HBCDD and a range of PFRs were measured in waste soft furnishings and furniture samples surveyed from a variety of UK domestic and office locations to help determine the total FR content entering the UK waste stream. In this chapter, concentrations of FR are reported in a range of materials including: carpets, curtains, mattress fabric, furniture PUF and furniture upholstery. These measurements are used to estimate the potential contribution of FR that this waste stream may be depositing to landfill annually in the UK. Additional information detailing the screening and extraction techniques is detailed in sections 2.3.6 and 2.3.7 respectively.

7.2. Sampling.

To address this data gap, we collected and analysed samples taken from a variety of domestic and office locations from across the UK during 2011-2012. The following samples were taken: domestic sofa/chair (n=5); domestic curtains (n=4); domestic carpet (n=4); domestic mattress (n=1); office chair (n=5); office carpet (n=3). Table 7.1 shows the complete list of products surveyed. The additional information column provides the location the item was collected from and the location where it was manufactured if known.

To qualify for this study, the participant had to be disposing of a product that met two criteria: 1) The product must have been purchased within the UK. 2) The product must be an item that is ready for disposal and would otherwise enter the UK waste stream. Owners were asked if they could provide the year of purchase for donated items but this was often not known and therefore was not used as acceptance criteria. Any product manufacturer's labels were also collected where possible, in an attempt to further characterise items by obtaining any additional information such as year and place of manufacture. However, often any labelling had been removed and lost by the product owner. Collected samples were wrapped in aluminium foil and sealed inside a plastic bag. When sampling from sofas and chairs, any accompanying textiles and composite layers were also taken along with the foam filling where possible.

Table 7.1: List of samples and materials analysed in the study.

Sample code	Furniture type	Materials sampled	Year of purchase	Year of manufacture	Additional information
Domestic 1	Dining chair	PUF	1995	u	Wembley
Domestic 2	Sofa	PUF & wool fabric	u	u	Harborne, Birmingham
Domestic 3	Sofa	PUF & cotton fabric	u	u	Ladywood furniture project
Domestic 4	Sofa	polyester fabric	2002	2001	Isleworth, Middx; made in Wales
Domestic 5	Armchair	PUF, cotton fabric & cotton batting	u	u	Harborne, Birmingham
Domestic 6	Curtain	cotton	u	u	Ladywood furniture project
Domestic 7	Curtain	cotton	u	1993	Ladywood furniture project
Domestic 8	Curtain	cotton	u	2001	Ladywood furniture project
Domestic 9	Curtain	cotton	u	2009	Haywards Heath, Sussex
Domestic 10	Carpet	blend[a]	2010	u	Wembley
Domestic 11	Carpet	blend[a]	1992	u	Wembley
Domestic 12	Carpet	polyester	1998	u	Wembley
Domestic 13	Carpet	wool	2002	u	Colchester, Essex
Domestic 14	Mattress	cotton or linen fabric & cotton and polyester batting	u	u	Harborne, Birmingham
Office 1	Desk chair	PUF & cotton fabric	u	u	University of Birmingham
Office 2	Desk chair	PUF & wool fabric	u	u	University of Birmingham
Office 3	Desk chair	PUF	1998	u	Wembley
Office 4	Sofa	PUF, fabric & polyester batting	u	u	University of Birmingham
Office 5	Stool	PUF & fabric	u	u	University of Birmingham
Office 6	Carpet	polyester	u	u	University of Birmingham, Room PH 210
Office 7	Carpet	polyester	u	u	University of Birmingham, Room PH 209
Office 8	Carpet	polyester	2008	u	Walton-on-Thames

[a] blend = 80/20 or 50/50 polypropylene wool; u = unknown

7.3. Results.

A total of 14 domestic and 8 office soft furnishing and furniture samples were collected for this study. The results of analysis for PBDEs and HBCDD are presented in Tables 7.2 and 7.3, respectively. PBDEs and HBCDD were not found at significant concentrations in any of the twenty-two analysed products. Therefore it is most likely that these compounds were not used to treat the samples.

The samples were screened for ten PFR compounds (TEP, TnPP, TiBP, TnBP, TCEP, TCIPP, TBEP, TPhP, TDCIPP and TCP). Eight of the PUF samples were found to be treated with PFRs and their concentrations were quantified, the results of which are presented in Table 7.4. TCIPP was found at percent levels in seven of the analysed waste furniture samples (domestic seat PUF (n=3); office seat PUF (n=4)), TDCIPP and TCEP were detected at a similar elevated level in one sample (domestic seat PUF).

Elevated HBCDD concentrations (~8,200 mg kg^{-1} ΣHBCDD) were observed in the cotton upholstery fabric of the “domestic 5” armchair sample. However, the underlying PUF of the armchair was treated with TCIPP. HBCDD is reported to be used as a textile coating agent in polymer dispersions applied to cotton or cotton/synthetic blends for residential upholstery fabrics (Weil and Levchik, 2008). While the percentage of HBCDD present in the fabric (0.82 % by weight) is relatively low, there is a possibility that the fabric was treated with HBCDD and the concentration has dwindled during the armchair’s lifecycle. Often sofa and armchair upholstery can be removed for cleaning and this may result in the additive, unbound HBCDD being depleted.

The “domestic 3” sofa sample was obtained from a waste pile of a charity that recycles furniture. The charity was not able to resell the sofa because it did not have the required fire safety labelling attached and therefore it did not meet UK resale criteria. Therefore, it is a possibility that the sofa’s manufacture predated the 1988 fire safety regulations and explains why no FR was measured in the sample. The polyester fibre filling material in the “domestic 4” sample was also not treated with PBDEs, HBCDD or any of the ten PFRs screened for. Due to the inherently flame retardant nature of the fibres it is likely that no FR was deemed necessary in the production of this material. Likewise, with the carpet samples no significant concentration of FR was detected in any of the samples and it is likely that the materials used were considered inherently flame resistant and therefore no FR was used in their manufacture. It is more common for the foam underlay of carpets to be treated with FRs.

TCIPP is the preferred FR used in the production of UK PUF due to lower production costs than other similar FRs such as TDCIPP (EU RAR, 2008c). Both TDCIPP and TCEP were measured at significant concentrations in the “office 3” desk chair purchased in 1998. However, TCEP has not been used in the production of UK PUF since the introduction of the 1988 flammability regulations (pers. comm., Flexible Foam Research Ltd.). TCEP is known to form as a reaction by-product in the manufacture of TDCIPP and can be present as an impurity (EU RAR, 2008b). TDCIPP is more commonly used as a flame retardant in US furniture where it was used as a drop-in replacement for Penta-BDE to meet the more stringent California Technical Bulletin of Home Furnishings 117 standard. TDCIPP was found in 50 % of samples in a 2012 survey of US residential furniture PUF (Stapleton et al. 2012). It is a strong possibility that this item was manufactured outside of the UK, most likely the US and subsequently found its way into the UK market.

Table 7.2: Concentrations of PBDEs in domestic and office samples.

Congener/ Sample code	Material	BDE-47 (mg kg^{-1})	BDE-85 (mg kg^{-1})	BDE-99 (mg kg^{-1})	BDE-100 (mg kg^{-1})	BDE-153 (mg kg^{-1})	BDE-154 (mg kg^{-1})	BDE-183 (mg kg^{-1})	BDE-209 (mg kg^{-1})
Domestic 1	PUF	0.044	0.00056	0.0051	0.025	0.00080	0.0012	<LOD	3.4
Domestic 2	PUF	3.8	<0.00024	<0.00011	<0.00014	<0.00017	0.00030	0.0076	25
Domestic 2	wool	<0.0080	<0.00024	<0.00011	<0.00014	0.015	<0.00020	0.012	<0.00084
Domestic 3	PUF	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	0.083
Domestic 3	cotton	<0.0080	<0.00024	<0.00011	<0.00014	0.020	<0.00020	0.016	0.18
Domestic 4	polyester	0.056	<0.00024	0.041	0.123	0.023	0.078	0.41	33
Domestic 5	PUF	0.075	0.0015	0.013	0.053	0.0036	0.0031	<0.00015	1.6
Domestic 5	cotton	<0.0080	<0.00024	<0.00011	<0.00014	0.024	<0.00020	0.018	4.6
Domestic 5	cotton batting	<0.0080	<0.00024	<0.00011	<0.00014	0.011	<0.00020	0.0097	0.12
Domestic 6	cotton	0.27	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	3.1
Domestic 7	cotton	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	42
Domestic 8	cotton	<0.0080	<0.00024	<0.00011	0.0049	<0.00017	<0.00020	<0.00015	0.026
Domestic 9	cotton	0.097	0.0036	0.0022	0.018	<0.00017	<0.00020	<0.00015	1.1
Domestic 10	blend[a]	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	0.097
Domestic 11	blend[a]	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	<0.00084
Domestic 12	polyester	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	<0.00084
Domestic 13	wool	0.0045	<0.00024	0.00072	0.0037	<0.00017	<0.00020	<0.00015	0.046
Domestic 14	cotton or linen	<0.0080	<0.00024	<0.00011	<0.00014	0.021	<0.00020	0.017	<0.00084
Domestic 14	cotton & polyester batting	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	<0.00084
Office 1	PUF	0.094	0.0018	0.019	0.085	0.0034	0.0051	<0.00015	<0.00084
Office 1	cotton	<0.0080	<0.00024	<0.00011	<0.00014	0.023	<0.00020	0.019	<0.00084
Office 2	PUF	<0.0080	<0.00024	0.0023	0.0089	0.0016	0.0032	0.0030	0.14
Office 2	wool	<0.0080	<0.0002	<0.00011	<0.00014	0.021	<0.00020	0.019	<0.00084
Office 3	PUF	0.073	0.031	0.02	0.096	0.0064	0.0087	0.0038	1.2
Office 4	PUF	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	0.015
Office 4	synthetic fibre topped with PVC	<0.0080	<0.00024	<0.00011	<0.00014	0.031	0.030	0.020	<0.00084
Office 4	polyester batting	<0.0080	<0.00024	<0.00011	<0.00014	0.0059	0.0020	0.0082	<0.00084
Office 5	PUF	0.21	0.057	0.11	0.37	0.010	0.029	0.0093	0.69
Office 5	wool	<0.0080	<0.00024	<0.00011	<0.00014	0.029	<0.00020	0.022	<0.00084
Office 6	polyester	0.055	0.0034	0.022	0.11	0.026	0.078	0.011	0.22
Office 7	polyester	<0.0080	<0.00024	0.0068	0.0088	<0.00017	<0.00020	<0.00015	0.041
Office 8	polyester	<0.0080	<0.00024	<0.00011	<0.00014	<0.00017	<0.00020	<0.00015	0.0055

Table 7.3: Concentrations of HBCDD diastereomers in domestic and office samples.

Diastereomer/ Sample code	Furniture type	Material	α-HBCDD (mg kg^{-1})	β-HBCDD (mg kg^{-1})	γ-HBCDD (mg kg^{-1})
Domestic 1	Dining chair	PUF	0.068	0.062	0.16
Domestic 2	Sofa	PUF	0.74	0.81	0.35
Domestic 2	Sofa	wool fabric	<0.0031	16	1.1
Domestic 3	Sofa	PUF	0.069	0.0073	0.71
Domestic 3	Sofa	cotton fabric	15	20	<0.0039
Domestic 4	Sofa	polyester	0.0035	0.0072	0.0075
Domestic 5	Armchair	PUF	0.11	0.040	0.14
Domestic 5	Armchair	cotton fabric	6100	1700	360
Domestic 5	Armchair	cotton batting	<0.0031	17	4.2
Domestic 6	Curtain	cotton	0.015	0.0093	0.018
Domestic 7	Curtain	cotton	0.93	0.33	0.17
Domestic 8	Curtain	cotton	0.20	0.10	0.072
Domestic 9	Curtain	cotton	0.068	0.0068	0.091
Domestic 10	Carpet	blend[a]	<0.0031	<0.0034	<0.0039
Domestic 11	Carpet	blend[a]	<0.0031	<0.0034	<0.0039
Domestic 12	Carpet	polyester	0.0050	<0.0034	0.0040
Domestic 13	Carpet	wool	<0.0031	<0.0034	0.0051
Domestic 14	Mattress	cotton or linen fabric	16	8.2	11
Domestic 14	Mattress	cotton and polyester batting	14	7.7	<0.00019
Office 1	Desk chair	PUF	0.053	0.014	0.0085
Office 1	Desk chair	cotton fabric	<0.0031	7.7	<0.0039
Office 2	Desk chair	PUF	0.010	0.0065	0.0094
Office 2	Desk chair	wool fabric	1.2	15	<0.0039
Office 3	Desk chair	PUF	0.42	0.14	0.48
Office 4	Sofa	PUF	<0.0031	<0.0034	<0.0039
Office 4	Sofa	synthetic fibre topped with PVC	26	4.3	<0.0039
Office 4	Sofa	polyester batting	4.1	8.3	7.1
Office 5	Stool	PUF	0.18	0.11	0.20
Office 5	Stool	wool fabric	19	3.8	<0.0039
Office 6	Carpet	polyester	0.46	0.24	0.23
Office 7	Carpet	polyester	0.040	0.18	0.26
Office 8	Carpet	polyester	0.24	0.20	0.18

Table 7.4: Concentrations of PFRs in domestic and office samples.

Target analyte/ Sample code	Furniture type	Material	TCIPP (mg kg^{-1})	TCEP (mg kg^{-1})	TDCIPP (mg kg^{-1})
Domestic 1	Dining chair	PUF	8,400	<0.00067	<0.0011
Domestic 2	Sofa	PUF	17,000	<0.00067	<0.0011
Domestic 3	Sofa	PUF	<0.00044	<0.00067	<0.0011
Domestic 4	Sofa	polyester	<0.00044	<0.00067	<0.0011
Domestic 5	Armchair	PUF	8,600	<0.00067	<0.0011
Domestic 6	Curtain	cotton	<0.00044	<0.00067	<0.0011
Domestic 7	Curtain	cotton	<0.00044	<0.00067	<0.0011
Domestic 8	Curtain	cotton	<0.00044	<0.00067	<0.0011
Domestic 9	Curtain	cotton	<0.00044	<0.00067	<0.0011
Domestic 10	Carpet	blend[a]	<0.00044	<0.00067	<0.0011
Domestic 11	Carpet	blend[a]	<0.00044	<0.00067	<0.0011
Domestic 12	Carpet	polyester	<0.00044	<0.00067	<0.0011
Domestic 13	Carpet	wool	<0.00044	<0.00067	<0.0011
Domestic 14	Mattress	cotton & polyester batting	<0.00044	<0.00067	<0.0011
Office 1	Desk chair	PUF	17,000	<0.00067	<0.0011
Office 2	Desk chair	PUF	38,000	<0.00067	<0.0011
Office 3	Desk chair	PUF	<0.00044	5,000	11,000
Office 4	Sofa	PUF	16,000	<0.00067	<0.0011
Office 5	Stool	PUF	29,000	<0.00067	<0.0011
Office 6	Carpet	polyester	<0.00044	<0.00067	<0.0011
Office 7	Carpet	polyester	<0.00044	<0.00067	<0.0011
Office 8	Carpet	polyester	<0.00044	<0.00067	<0.0011

7.4. Summary.

8 out of 10 surveyed furniture samples were treated with PFRs and of these 10 items, 9 were PUF and one polyester fibre filling material. Therefore, 77.8 % of sampled furniture PUF was treated with TCIPP with a mean concentration of 1.9 % (by weight). In 2000, 6800 tonnes (18%) of TCIPP was used in the production of flexible PUF within the EU (EU RAR, 2008a). TCIPP is the primary FR used in meeting UK flammability standards and regulations in furniture and the results of this small scale survey reflect this.

Despite approximately 95% of Penta-BDE in Europe being used in flexible PUF, no items surveyed were found to be treated in this manner (European Chemicals Bureau, 2000).

Despite the fact that one armchair’s fabric (domestic 5) was possibly treated with HBCDD, the evidence of this preliminary study is that at most a small proportion of soft furnishings and furniture waste now entering the UK waste stream were treated with PBDEs or HBCDD as primary flame retardants. It is possible that any soft furnishings and furniture products that were treated in this manner have already been processed through the waste stream and have most likely gone to landfill.

Chapter VIII: Closed chamber volatilisation experiments for TCIPP from furniture PUF.

8.1. Synopsis.

In this chapter, the volatilisation of TCIPP from treated furniture PUF samples surveyed from the UK waste stream is investigated. A 5 cm x 5 cm x 4 cm subsample cuboid of TCIPP treated furniture PUF weighing approximately 5 g was placed inside the chamber for 24 h. The system is a closed chamber environment simulating the environment of low to no airflow for furniture PUF buried within a landfill. Weight specific emission rates (SERw) and area specific emission rates (SERa**)** for TCIPP from furniture PUF are calculated and presented for a range of landfill relevant temperatures; 20 °C (293 K), 40 °C (313 K), 60 °C (333 K) and 80 °C (353 K). Additional information detailing the experimental set-up of these volatilisation experiments can be found in chapter 2.2.2 and extraction and clean up techniques are detailed in chapter 2.3.3 and 2.4.3 respectively. These measured emission rates are then used to assess the magnitude of this pathway in contributing towards TCIPP contamination in the vicinity of UK landfills.

8.2. Calculation of TCIPP emission rates.

The weight specific emission rates (SERw) of TCIPP were calculated using equation 8.1 (adapted from Kemmlein et al., 2003):

Equation 8.1: $$\text{SERw} = \frac{\left[\frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS} \right]}{t},$$

A_{NAT} = peak area of TCIPP in sample;

A_{IS} = area of internal standard in sample (d_{15}-TPhP);

RRF = relative response factor for the target pollutant;

M_{IS} = mass of internal standards (mg);

SS = sample size (kg);

t = time (h)

Area specific emission rates (SERa) of TCIPP were calculated using equation 8.2 (adapted from Kemmlein et al., 2003):

Equation 8.2: $$\mathrm{SERa} = \frac{\left[\dfrac{A_{NAT}}{A_{IS}} \times \dfrac{1}{RRF} \times \dfrac{M_{IS}}{\mathrm{SA}_{\mathrm{sample}}} \right]}{\mathrm{t}} ,$$

$\mathrm{SA}_{\mathrm{sample}}$ = Exposed surface area of PUF (m^2)

8.3. Initial TCIPP concentrations in the furniture PUF samples.

The PUF samples used in these volatilisation experiments were sub-samples of the same TCIPP treated furniture foam described in chapter 6.3. As such, the mean initial concentration of TCIPP was 17,000 ± 13 mg kg^{-1} or 1.7 % by weight. The foam was obtained from the UK waste stream at the point of disposal. Therefore it is not known how much TCIPP has been lost from the foam during the products’ lifecycle (i.e. between its manufacture and subsequent disposal).

8.4. Effects of temperature on TCIPP volatilisation from furniture PUF.

The influence of temperatures of 20 °C (293 K), 40 °C (313 K), 60 °C (333 K) and 80 °C (353 K), on TCIPP volatilisation in a closed system was investigated. These temperatures were selected to reflect the range likely to be encountered under active landfill conditions. SERw and SERa values for TCIPP from flexible PUF were plotted against temperature and are displayed in Figures 8.1 and 8.2, respectively, while the data for SERw and SERa and system blanks (performed for 24 h at 293 K) are presented in Table 8.1.

Both the weight specific and area specific emission rates significantly correlate with an exponential curve, meaning both expressions of the TCIPP emission rates increase exponentially when the temperature was raised. TCIPP is known by industry for being susceptible to volatilisation at elevated temperatures and as such is not used in the manufacture of foams for automobiles due to its poor performance in “fogging” tests (PFA, 2015). In fogging tests required by Ford General Motors, Mercedes, and Toyota, TCIPP gave the ‘worst’ results of the tested FRs for both gravimetric and photometric methods of fogging measurement.

In similar experiments on volatile emissions from upholstery PUF treated with TCIPP at 2 % by weight, Kemmlein et al., (2003) reported SERa values of 77 µg m^{-2} h^{-1} at 23 °C. The SERa values reported by Kemmlein are higher than the values reported in this study. This can be explained by the difference in sampling methods employed in the study of Kemmlein et al., in which active sampling with air flow rate through their emission test chamber of 1.1 m^3 h^{-1} was employed. In another study, Kemmlein et al., (2006) demonstrated that BDE-47 and BDE-99 emissions increased exponentially with increasing temperatures lending further support to our findings.

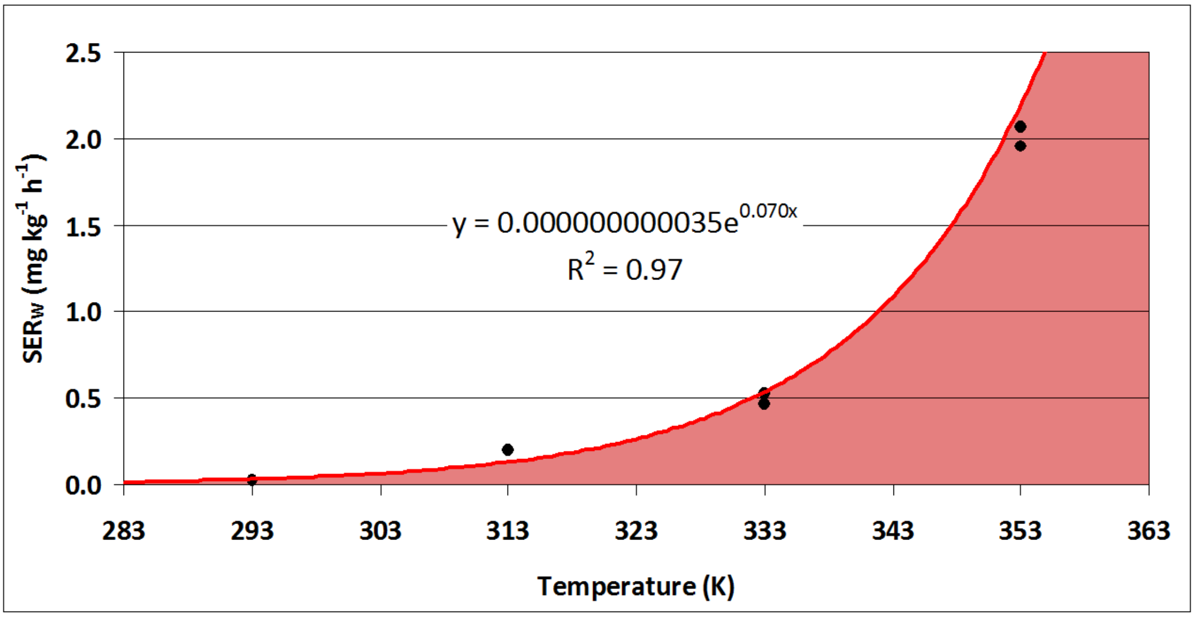

Figure 8.1: Weight specific emission rates (SERw) (mg kg^{-1} h^{-1}) of TCIPP from furniture PUF with increasing temperatures. n=8

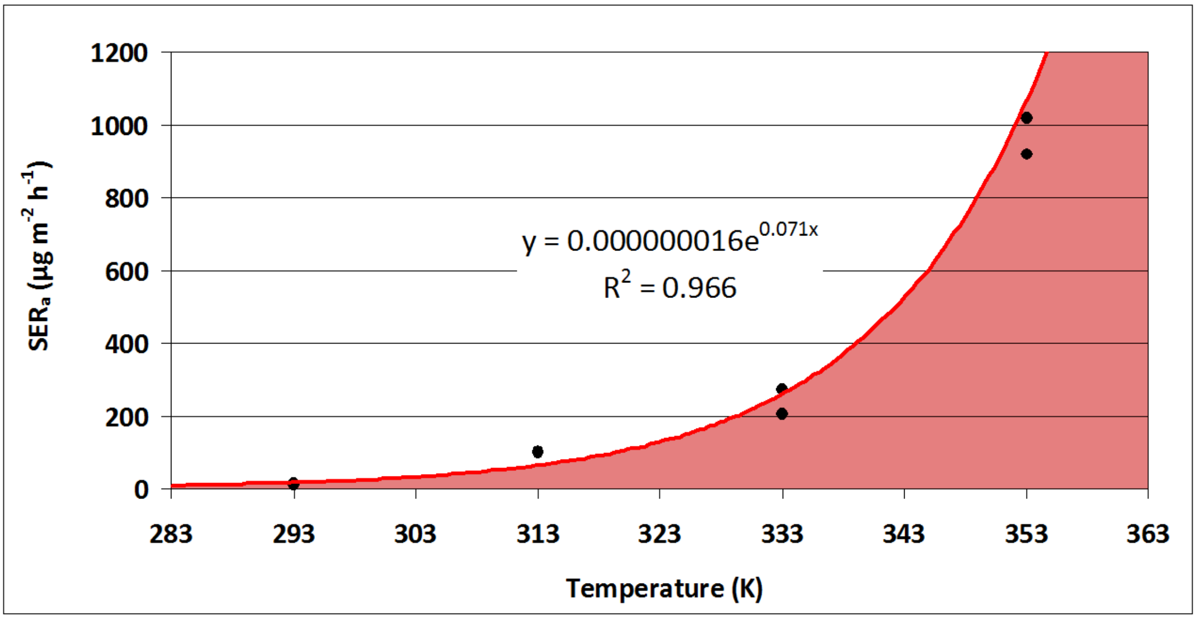

Figure 8.2: Area specific emission rates (SERa) (µg m^{-2} h^{-1}) of TCIPP from furniture PUF with increasing temperatures. n=8

Table 8.1: Weight specific emission rates (SERw) and area specific emission rates (SERa) for TCIPP from furniture PUF with different temperatures.

Temperature (K)	SERw (mg kg^{-1} h^{-1})	SERw (mg kg^{-1} h^{-1})	SERa (µg m^{-2} h^{-1})	SERa (µg m^{-2} h^{-1})
293	0.025	0.025	12	11
313	0.20	0.20	100	100
333	0.46	0.53	210	270
353	2.0	2.0	920	1,000
System blanks	0.000018	0.000022	0.0084	0.010

These emission rate values illustrate clearly the potential for emissions of TCIPP from landfilled PUF. What we have been unable to replicate in these proof-of-concept experiments however, is the extent to which such emissions will be attenuated by factors such as landfill capping and flaring of landfill gas. The values in Table 8.1 should therefore be viewed with caution and treated as upper end estimates of the emission rates prevailing under landfill conditions.

8.5. Estimating potential volatile TCIPP emission from UK landfill sites.

Modelling of landfill emissions is a difficult task not least because of the variety of design, age and use of UK landfills. Landfill is considered likely to be the most significant route of disposal of foam and other TCIPP containing products. Most furniture in the UK goes to landfill at the end of its useful life and as such the EU risk assessment report (2008a) assumes in its review that all furniture is landfilled at end of life. In 2012, WRAP reported that an estimated 670,000 (665,794) tonnes of furniture is disposed of by UK households annually (2010-11). Of this, sofas contribute ~140,000 (138,515) tonnes, armchairs ~54,000 (54,199) tonnes and chairs ~45,000 (44,802) tonnes totalling ~240,000 (237,516) tonnes. However, there will be wooden and metal components that will not be treated with FR present in these items and the exact weight of these components is not known. If we assume in a worst case scenario that 50 % by mass of this likely FR treated furniture waste was PUF, then ~120,000 (118,759) tonnes are disposed of annually. In the limited survey of furniture entering the UK waste stream presented in chapter 7, 77.8 % of sampled furniture PUF was treated with TCIPP with a mean concentration of 1.9 % (by weight). Applying these values to the mass and assuming that it is all sent to landfill, this yields a total mass of TCIPP sent to landfill in furniture of ~1,800 (1,755) tonnes yr^{-1}. In 2000, 6,800 tonnes of TCIPP were used in the production of flexible PUF (EU RAR 2008a).

However, this figure only accounts for the mass deposited in landfill for one year and TCIPP has been the primary FR used in UK furniture PUF since the introduction of the 1988 flammability regulations. So if we assume that emissions are from landfilled furniture accumulated over 10 years at the same disposal rate as in 2010-11 then the mass of TCIPP associated with waste furniture in UK landfill will be close to 18,000 (17,550) tonnes and the mass of TCIPP treated PUF would be ~920,000 (923,945) tonnes.

From here, emission rates for different temperatures can be applied to give a range of possible emission scenarios and they are explored from best case to worst case. The temperature within landfilled waste can differ site to site due to differences in site design, age of waste and waste type, temporally (depending on time of day or season) and also within the same site depending on the depth and spatial distribution of measurements (Yessiler and Hansen, 2003). Leachate recirculation may also have a positive effect on increasing waste temperatures within landfill (Yessiler and Hansen, 2003). The internal temperature of landfill is influenced by more than just the external atmospheric temperature, exothermic reactions from anaerobic activity may potentially occur depending on the phase of decomposition within the landfill (Kjeldsen, 2002). Temperatures within a landfill can sometimes rise as high as 80 – 90 °C (Environment Agency, 2002). Yessiler and Hansen (2003) conducted a detailed analysis of temperatures within a modern engineered municipal solid waste landfill located in the Midwestern U.S.A. The authors observed that seasonal variations in atmospheric temperature only had a varying effect on waste temperatures at shallow depths up to 8 m. At greater depths, measured temperatures in the waste were steadily elevated, with typical internal landfill temperatures ranging between 33 ºC and 60 ºC in wastes between 2 and 9 years old (Yessiler and Hansen, 2003).

The first scenario assumes average annual waste temperatures of 20 ºC (293 K) and therefore an SER_W of 0.025 mg kg^{-1} h^{-1}. All scenarios assume that all volatile TCIPP emissions are emitted to atmosphere. The SER_W is multiplied by the mass of TCIPP treated PUF estimated to be residing in landfills over a 10 year period (923,945,020 kg). Therefore, ~23,000,000 (23,098,626) mg h^{-1} would be emitted, multiplied by 8,765 hours in a year, emissions are equal to ~200 (202.46) tonnes yr^{-1}.

The second scenario assumes average annual waste temperatures of 40 °C (313 K) and a SER_W of 0.20 mg kg^{-1} h^{-1}. Therefore, ~190,000,000 (184,789,004) mg h^{-1} would be emitted, multiplied by 8,765 hours in a year, emissions are equal to ~1,600 (1,619.68) tonnes yr^{-1}.

Scenario three assumes average annual waste temperatures of 60 °C (333 K) and a SER_W of 0.46 mg kg^{-1} h^{-1}. Therefore, ~430,000,000 (425,014,709) mg h^{-1} would be emitted, multiplied by 8,765 hours in a year, emissions are equal to ~3,800 (3,725.25) tonnes yr^{-1}.

Finally scenario four assumes a worst case scenario average annual waste temperature of 80 °C (353 K) and a SER_W of 2.0 mg kg^{-1} h^{-1}. Therefore, ~1,800,000,000 (1,847,890,040) mg h^{-1} would be emitted, multiplied by 8,765 hours in a year, emissions are equal to ~16,000 (16,186.76) tonnes yr^{-1}. However, it is important to highlight that these figures have considerable associated uncertainty as e.g. they do not account for any attenuation of volatilisation in landfills, such as combustion of the landfill gas in engines or flares on site, and are based on emissions measured under zero air flow conditions. Emission rates are concentration dependent and will fall as emissions reduce the TCIPP concentration remaining in the landfilled PUF. Additionally other TCIPP emission pathways, such as leaching, will reduce the concentration of TCIPP in landfilled PUF. Chapter VI, demonstrated that depletion of TCIPP concentrations from PUF via leaching may be rapid and considerable. Such factors would likely mean our emission estimates are over-estimated.

8.6. Summary.

Volatilisation of TCIPP from flexible furniture PUF increases exponentially with increasing temperatures in a closed system. However, more tests are needed to confirm whether this volatilised TCIPP would be able to escape landfill as an emission to atmosphere. There are uncertainties over to what extent a buried piece of furniture PUF could emit to air, but these emissions could certainly free up the TCIPP from the PUF material enabling it to be readily available to any percolating waters/leachate. The volatility of TCIPP in these experiments does raise questions of its suitability as a FR used to meet flammability standards in UK furniture.

A campaign of monitoring of TCIPP in emitted landfill gas would be useful to assess the contribution of landfill gas to emissions of TCIPP to the atmosphere. Other halogenated organic compounds such as chloroethane, trichloroethene, and tetrachloromethane have been measured in trace landfill gas emissions (327 - 1239 mg m^{-3}) (Parker et al., 2002).

The EU risk assessment report (2008a) predicts that atmospheric TCIPP exposure is not expected to be significant. This prediction is made assuming low levels of releases, a relatively low volatility and moderate solubility and adsorption coefficient for TCIPP and a predicted atmospheric half-life of 8.6 hours for degradation by hydroxyl radicals. In this study, estimates of volatile TCIPP emissions from landfilled PUF furniture waste, range between ~200 and ~16,000 tonnes yr^{-1}. However, the actual quantity of any trace gases emitted will be perhaps considerably lower than the worst case scenario due to on site attenuation and other uncertainties listed at the end of the last section. Therefore, the third scenario assuming average annual waste temperatures of 60 °C (333 K) and annual TCIPP emissions equal to ~3,800 tonnes yr^{-1} is perhaps a better top end estimate.

Another concern for potential emissions could arise during transport of waste to landfills or incinerators. Often in the UK, waste furniture is placed outside to await removal and subsequent disposal by either local councils or private contractors. This potential exposure to elevated temperatures in direct sunlight and precipitation could result in fugitive emissions of TCIPP to the immediate environment.

Chapter IX: Summary and Conclusions.

The main aim of this project was to study both leaching and (to a lesser extent) volatilisation emissions of PBDEs, HBCDD, and halogenated PFRs from waste electronics, soft furnishings and building materials. It is apparent from the experiments conducted in this thesis, that despite the relatively hydrophobic physicochemical properties of PBDEs and HBCDD, they are able to leach from waste materials at substantial concentrations. Concentrations of ΣPBDEs in the leachate from the leaching experiments in this study ranged from 14,000 – 200,000 ng L^{-1}, while concentrations of ΣHBCDD ranged from 170 ng L^{-1} – 13,000 ng L^{-1} in textile leaching experiments and from 13,000 ng L^{-1} – 4,200,000 ng L^{-1} in building insulation foam experiments. While leaching of HBCDD from textiles was solubility limited, leaching from the EPS and XPS foams was not. This is most likely due to abrasion of the EPS and XPS materials allowing greater quantities of HBCDD to be present, associated with fine particles of EPS/XPS suspended in leachate. Leaching of HBCDD from EPS/XPS building insulation foams is therefore suggested as a possible significant pathway for large concentrations of HBCDD to landfill leachate.

The leaching of HBCDD from both textiles and building insulation foams; and PBDEs from CRT plastics appear to be second order processes. However, a degree of uncertainty is involved when interpreting kinetics in which serial batch experiments were used because the relationship and its constants will not have the same meaning as they would for a conventionally performed kinetic experiment. Although, leaching of TCIPP from PUF is possibly a first order process. Concentrations of TCIPP in the leachate from the leaching experiments in this study ranged from 13 mg L^{-1} – 130 mg L^{-1}. Such TCIPP concentrations exceed the maximum HBCDD values in leachate from textile experiments by a factor of 1,000 to 10,000 times and are 3.1 to 31 times greater than the maximum HBCDD values detected in leachate obtained from experiments examining leaching from XPS/EPS foams. In serial batch leaching experiments, TCIPP was almost completely depleted from the flexible PUF after the sixth batch (168 h total contact).

Since TCIPP is relatively soluble in water and leaching is shown to be facile, the likelihood of emissions from landfill sites via leaching should be considered and constitutes a potentially very significant pathway for emissions to the environment. This is especially relevant to the

UK, where TCIPP is the primary FR used in treatment of soft furnishings to meet flammability standards.

In experiments designed to examine the effect of elevated temperatures on the volatilisation of TCIPP from flexible PUF in a closed system, concentrations of TCIPP increased exponentially with increasing temperatures. Weight specific emission rates (SER_W) for TCIPP from flexible furniture PUF are reported as 0.025 mg kg^{-1} h^{-1} at 20 °C (293 K), 0.20 mg kg^{-1} h^{-1} at 40 °C (313 K), 0.46 – 0.53 mg kg^{-1} h^{-1} at 60 °C (333 K) and 2.0 mg kg^{-1} h^{-1}at 80 °C (353 K). Area specific emission rates (SER_a) are reported as 11 – 12 µg m^{-2} h^{-1} at 20 °C (293 K), 100 µg m^{-2} h^{-1} at 40 °C (313 K), 220 – 270 µg m^{-2} h^{-1} at 60 °C (333 K) and 920 – 1,000 µg m^{-2} h^{-1} at 80 °C (353 K).

Due to the variety of landfills, in respect of their design, age and use, theoretical modelling of landfill emissions is difficult. Assuming the mass of TCIPP treated PUF furniture waste sent to UK landfill annually is ~92,000 tonnes, extrapolation of our measured SER_W values leads to estimated emissions of TCIPP *via* volatilisation from landfilled PUF, that range between ~200 and ~3,800 tonnes yr^{-1}. However, these estimates do not account for any attenuation of emissions and do not account for attenuation of the TCIPP burden in landfill over time as it is emitted *via* both volatilisation and leaching pathways.

Another aim was to characterise the FR content of UK soft furnishings currently entering the waste stream. Concentrations of PBDEs, HBCDD and a range of chlorinated PFRs were measured in a small number of samples of domestic and office waste soft furnishings products entering the UK waste stream in 2011 and 2012. This preliminary study measured the FR content of: carpets (n=7), curtains (n=4), mattress fabrics (n=2), furniture foam (n=9), and furniture upholstery (n=10). This has enabled a preliminary evaluation of the mass of FRs associated with UK waste soft furnishings. Of the waste furniture PUF sampled in the survey, 77.8 % was treated with TCIPP with a mean concentration of 1.9 % (by weight). No samples appeared to have been treated with PBDEs and only one textile sample was possibly treated with HBCDD but had a somewhat depleted concentration of 0.82 % (by weight; 8,160 mg kg^{-1}).

While the chemical industry is pushing for the substitution of the brominated compounds with similar chemicals, the risk management evaluation for HBCDD, completed by the POPs

Review Committee (POPRC) of the UNEP Stockholm Convention, outlined a number of appropriate non-chemical alternatives in EPS and XPS foams. These included blankets containing rock wool, fibreglass or cellulose foam, cellular glass, foam glass, and reflective insulation systems. However as these methods are more expensive than the chemical alternatives being proposed by the chemical industry, they look unlikely to find widespread use until regulation or the market dictates otherwise. Likewise, non-chemical alternatives exist for the PUF market, but pressures to keep manufacturing costs low render these methods unattractive in comparison to costs of treating consumer products with TCIPP or alternative FRs.

9.1. Research gaps and future perspectives.

The work presented in this thesis makes a valuable contribution to our understanding of the mechanisms via which PBDEs, HBCDD and TCIPP may transfer from end-of-life products to leachate or air. However, there remain significant research gaps to be addressed.

During my PhD, I unfortunately encountered resistance from landfill site managers, to my proposals to directly sample leachate, air and soil from around UK landfill sites. As a result I was unable to conduct a field based element to my studies. There are still very few data published on concentrations of FRs in and around waste disposal sites, particularly for HBCDD and chlorinated PFRs. The complex and heterogeneous nature of waste in landfill sites means that estimating the contribution of this waste stream to any national emission inventory requires a detailed monitoring programme to be established. I would suggest a study of long term monitoring of PBDEs, HBCDD, PFRs and emerging novel FRs in landfill leachate and vented landfill gas at a number of active and closed landfill sites. Both raw and treated leachate should be obtained monthly over the course of a year should be taken from multiple wells and any on site leachate storage ponds/containers. Additionally collection of soil, air and groundwater samples from the immediate area around landfill sites would provide information on potential fugitive emissions that are still poorly understood.

The effects of flash flooding on potential emissions of FR from landfill sites to the immediate surrounding environment should also be considered.

An ongoing campaign of monitoring, sampling and analysis of levels of PBDEs, HBCDD and PFRs should be conducted for the influent and effluents of MSW leachate receiving WWTPs.

This would be extremely valuable in assessing the effectiveness of WWTPs in removing FRs and the risk of this potential emission pathway.

Continuation of lab based studies into leaching and volatilisation from end-of-life materials would further inform this risk. There are a number of follow up experiments that could be conducted to enhance understanding of the factors influencing emissions and of the potential for FR degradation under landfill conditions. In particular, further understanding of the potential for degradation of PFRs and HBCDD is vital.

There is a need for more detailed studies designed to elucidate fully the kinetics governing FR leaching from various waste categories.

Analysis of PBDEs, HBCDD and PFRs and other toxic compounds such as brominated and chlorinated dioxins and furans in flue gas vented from urban waste-to-energy facilities and incinerators is recommended, with measurements taken both during full operation and start up and shut down conditions.

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