UNIVERSITY OF BIRMINGHAM

HIGH MASS RESOLUTION AND MASS ACCURACY SPECTROMETRIC TECHNIQUES TO EXPLORE THE CONTAMINATION RELATIONSHIP BETWEEN BFRs AND BROMINATED/MIXED HALOGENATED DIOXINS AND FURANS

by

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For my mother Susan Peters,

Who without her (not just for the obvious reason), this project certainly would not have come to fruition.

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Abstract

Dioxins and furans are classes of toxic, persistent environmental contaminants. These compounds, despite never being deliberately synthesized in any great quantity are present in detectable concentrations in almost every environmental matrix. Brominated and Mixed halogenated dioxins and Furans, unlike their comparatively well studied chlorinated analogues have not received nearly as much scientific attention. Despite having comparable physico-chemical and toxicological properties are as yet are not officially listed as POPs. The lack of available scientific data pertaining to Br and mixed dioxins and furans is due principally to the almost prohibitive expense and analytical difficulty of their analysis. Isobaric interferences with PBDEs, PCBs and PBBs (among others) require extensive clean-up procedures, analysis exclusively by high resolution mass spectrometry, judicious selection of quantification ions and meticulous data interpretation. Also, until only recently have ^{13}C labelled surrogates standards become commercially available. Recent advances in high resolution high accurate mass instrumentation has the potential to overcome many of the analytical challenges presented with the analysis of these compound groups.

Despite limited data, current theory concerning the sources of these compounds in the environment has predominantly centred on their formation by high temperature thermolysis in the presence of PBDEs or other potential halogenated phenolic precursors. While substitutive evidence exists confirming their source commonality, extension of this relationship at points of contamination has yet to be explored rigorously.

Accordingly, to address this knowledge gap and overcome the analytical barriers hampering these research efforts, an appropriately sensitive and selective analytical methodology was developed. This method utilised the recently released and state-of-the-art Thermo Scientific GC Q Exactive mass spectrometer. Its suitability for the analysis of trace organic contaminants including the brominated and mixed halogenated dioxins and furans as well as polybrominated diphenyl ethers was

established through the analysis of certified reference standards. This technique further extended to provide for analytical quantification of these compounds in freshwater sediments, human breast milk as well as atmospheric particulate matter.

To address the presence and extent of contamination relationships in these matrices measurements were taken of all target compounds concurrently and concentrations examined for correlations. Contamination trends were generated through the use of radiometrically dated sediment cores and chronologies revealed statistically significant associations between a number of key individual compounds. Measurements of human breast milk confirmed for the first time the presence of brominated furans in UK mothers. Through the analysis of atmospheric particulate matter sampled during a fire event in the city of Santiago, Chile measurements made revealed the presence of elevated concentrations of brominated furans at sites affected by this event as well as congener compositional changes.

The adoption of this development analytical method and its application to relevant environmental and biological matrices the authors hope to reduce the analytical complexity of such measurement for future assessments and alleviate constraints to future assessments of these persistent and toxic environmental pollutants.

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Abbreviations

σ	Standard deviation
1°	Primary
2°	Secondary
3°	Tertiary
APGC	Atmospheric Pressure Ionisation Gas Chromatography
ATSDR	Agency for Toxic Substances and Disease Registry (US)
BFR	Brominated Flame Retardant
BW	Body Weight
^{13}C Labelled	Isotopically labelled compounds (^{13}C)
Congener	Individual compound representative of a particular chemical group
C-Trap	Ion trap component of the Orbital Trap Mass Spectrometer
DI	Daily Intake
dl-PCBs	Dioxin like Polychlorinated Biphenyls
DW	Dry Weight
EFR	Emerging Flame Retardant
FR	Flame Retardant
FS	Full-Ion Scanning Mode
FTICR	Fourier-Transform Ion Cyclotron Resonance
GC	Gas Chromatograph
Homologue	Individual congeners grouped on the basis of conjugation.
HR	High Resolution
HRMS	High Resolution Mass Spectrometry
Ion Current	The current generated by an accelerated ion beam
Lacustrine	Relating to or associated with lakes
Lb	Lower bound
LC	Liquid Chromatography
LW	Liquid Weight
Mass Specific	Corresponding to a defined mass to charge ratio (m/z)
Mb	Middle bound

MDL	Method Detection Limit
MRL	Minimal Risk Level
MS/MS	Triple quadrupole mass spectrometry
***no*-PCBs**	*non-Ortho* Polychlorinated Biphenyl
OC	Organic Carbon
Orbitrap	Orbitol Ion Trap
PBDD/F	Polybrominated dibenzo-p-dioxins and furans
PBDE	Polybrominated diphenyl ether
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzo-p-dioxins and furans
PHDD/F	Polyhalogenated dibenzo-p-dioxins and furans
PM_{10}	Particulate Matter with an aerodynamic diameter smaller than 10µm
Primipara	A woman who is giving birth for the first time
Profundal	The deep zone of an inland body of freestanding water
PXDD/Fs	Mixed halogenated dibenzo-p-dioxins and furans
TOF	Time of Flight
QM	Quantitation Ion
Resolving Power	Instrument's ability to distinguish two adjacent ions of equal intensity
RfD	Chronic Oral Reference Dose (USEPA)
RM	Ratio or Qualification Ion
SIM	Selected Ion Monitoring
STP	Standard Temperature and Pressure (273 K at 1atm)
TDI	Tolerable daily intake (WHO)
TEF	Toxic Equivalency Factor (WHO)
TEQ	Toxic Equivalency (WHO)
Ub	Upper bound
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation

Chapter 1 Introduction

1.1 General Background.

Brominated flame retardants (BFRs) consist of a multitude of brominated organic compounds that act to inhibit or restrict the combustibility of materials to which they are added. They have been observed to do so with remarkable efficiency, even when added at sub- percentage quantities to a variety of flammable materials [1]. Accordingly, they are commonly used as additives in a wide range of consumer and industrial products including textiles, furniture, electronic equipment and construction materials. For this purpose, vast quantities of these compounds have been produced since the early 1960s [2,3]. In addition to their ability to inhibit combustion, BFRs typically display a high degree of thermodynamic stability, semi-volatility and low chemical reactivity, properties particularly desirable for their intended use. Unfortunately, these same chemical and physical properties coupled with their wide spread use and manufacture has resulted in their ubiquitous presence in virtually all environmental compartments. More recently, conformation of their toxicity, tendency to bio- accumulate and circulate globally- a phenomena known as long range atmospheric transport (LRAT) [4], has led to the introduction of legislative restrictions targeting several BFRs, resulting in cessation of use and subsequent replacement [3,5].

Polyhalogenated Dioxins and Furans (PHDD/Fs), represent another group of persistent organic environmental contaminants. Unlike BFRs, these compounds have never been deliberately synthesised in any great quantity and have no known industrial or commercial purposes [6]. PHDD/Fs are categorised by the extent and exclusivity of their respective halogenations, those exclusively containing chlorine (PCDD/Fs), bromine (PBDD/Fs) and some combination of both (PXDD/Fs). PCDD/Fs have been extensively studied since the 1970s, when initial observations of environmental contamination was reported and their presence as unintentional by- products in widely used pesticide formulations confirmed [7,8]. Since such time, a detailed description of

PCDD/F toxicity and environmental behaviour has been established, which can be greatly, if not principally, attributed to the co- development of less exacting means of analytical quantification. The extent, dynamics and major influencing factors contributing to PBDD/F environmental contamination are comparatively less understood. PBDD/Fs have however, been identified and measured in a limited variety of environmental and human matrices lending some conclusions to be drawn with respect to their fate and the contamination status of some environmental compartments. Additionally, substantive evidence suggesting the existence of source commonality between PBDD/Fs and some BFRs, particularly the polybrominated diphenyl ethers (PBDEs), has led to the supposition that PBDD/F environmental contamination may be significantly related and potentially induced as a direct consequence of PBDE based BFR usage.

The extent of environmental or human contamination by PXDD/Fs remains even less defined than for the PBDD/Fs, with the breadth of current scientific knowledge restricted to a comparatively exiguous number of reported ambient measurements. The paucity of scientific insight related to PBDD/F and PXDD/F environmental contamination is almost certainly a result of the complexity and prohibitive financial cost involved to conduct a sufficient number of reliable analytical measurements with which to draw adequate conclusions.

1.2 Legislative Regulation on BFRs, POPs and Implications.

At state and national levels restrictions on the manufacture, importation and use specific guidelines pertaining to a large range of chemical products are in effect. At international levels, restrictions and legally binding instruments to minimise risks posed to human and environmental health of several identified toxic environmental contaminants was first envisioned in 1996 by the Intergovernmental Forum on Chemical Safety. Findings of this forum led to the establishment of the Stockholm Convention, adopted in 2001 and brought into force by 2004. Initially proposing restrictions pertaining to a list of 12, so called ‘dirty dozen’ compounds, this instrument set out guideline

chemical characteristics, definitions, and process for which additional compounds fulfilling these could be added upon later revisions. Characteristics for compound inclusion required a demonstration of established toxicity, environmental persistence, and tendency to bio- accumulate and potential to undergo transport over global scales [4]. Compounds fulfilling these requirements for inclusion were official designated as 'Persistent Organic Pollutants' (POPs). Included in the initial POPs list were the PCDDs and PCDFs. Subsequent revisions to the convention have included several BFRs including the three major technical congener mixes manufactured commercially. Pentabromo diphenyl ether (penta- BDE) and octabromo diphenyl ether (octa- BDE) formulations were listed as POPs in 2009, following EU regulations prohibiting their manufacture and new use in 2004. As of 2017 all three commercial PBDE mixtures have been listed with decabromo diphenyl ether (deca-BDE) added to Appendix A, due to the key consideration of this compounds potential to form lower order PBDE congeners through various debromination pathways [9]. PBDD/Fs and PXDD/Fs have as yet not been included to the framework. The effectiveness of the Stockholm Convention and its wide ratification has been demonstrated by positive responses in key environmental heath metrics, including confirmation of declines in the concentrations of many compounds listed [10]. Crucially however, the treaty does not provide clear guidelines as to the extent of scientific evidence required for a candidate compounds eventual inclusion. Also, neglected are adequate explanations or criteria by which non- POP compounds can be included on the basis of similarity with those listed. This legislative inadequacy has directly led to the large scale production of a variety of substitute compounds, many of which even upon rudimentary inspection are likely to mimic the contamination patterns of their predecessors. This situation, particularly relevant with respect to the BFRs, has resulted in the wide- spread environmental contamination of many substitute NBFRs or 'Novel Brominated Flame Retardants', several of which have either been subsequently listed or are candidates for inclusion to the Stockholm Convention [11]. This therefore, leaves the onus upon the scientific community to provide the undefined degree of evidential certainty required for a candidate compounds inclusion. A process which is often only deemed sufficient when substantial

environmental contamination has already occurred and when its extent has been widely described. The effectiveness of this legislative frame work therefore remains almost exclusively upon the rapid development of scientific knowledge, which in the case of trace level environmental contaminants is often hampered directly by the complexity and costs involved in obtaining accurate and meaningful ambient concentration measurements [12].

1.3 PBDEs

PBDEs represent of a class of brominated organic compounds sharing structural similarity to the PCBs (Figure 1.1). Individual congeners are classified on the bases of their halogenation profile and all conform to the generalised chemical formula: $C_{12}H_{10-i}Br_iO$. They exhibit the appropriate chemical and physical properties (Figure 1.2) which have led to their effectiveness and wide spread use as combustion inhibiting additives, as well as to their global distribution in environmental matrices.

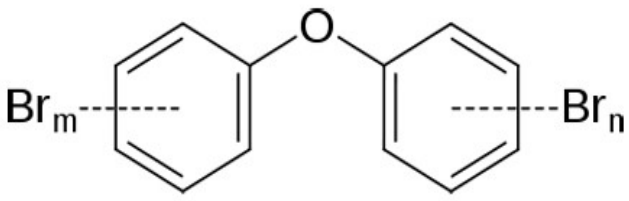


Figure 1.1: Generic molecular structure for PBDEs.

Table 1.1: Physical properties of selected PBDEs. Data from [13].

	Chemical Formula	Molecular Mass (g mol^{-1})	Melting Point (°C)	Water Solubility (g L^{-1} 25 °C)	Vapour Pressure (Pa 25 °C)	Log K_{OW}
BDE-28	$C_{12}H_7Br_3O$	406.9	64-64.5	0.7×10^{-4}	2.19×10^{-3}	5.94
BDE-47	$C_{12}H_6Br_4O$	485.8	83.5-84.5	1.5×10^{-5}	1.86×10^{-4}	6.81
BDE-66	$C_{12}H_6Br_4O$	485.8	104-108	1.8×10^{-5}	1.22×10^{-4}	6.73
BDE-100	$C_{12}H_5Br_5O$	564.7	100-101	0.4×10^{-4}	2.86×10^{-5}	7.24
BDE-99	$C_{12}H_5Br_5O$	564.7	90.5-94.5	9.4×10^{-6}	1.76×10^{-5}	7.32
BDE-85	$C_{12}H_5Br_5O$	564.7	119-121	0.6×10^{-5}	9.86×10^{-6}	7.37
BDE-154	$C_{12}H_4Br_6O$	643.6	131-132.5	8.7×10^{-7}	3.80×10^{-6}	7.82
BDE-153	$C_{12}H_4Br_6O$	643.6	160-163	8.7×10^{-7}	2.09×10^{-6}	7.9
BDE-183	$C_{12}H_2Br_8O$	722.5	171-173	1.5×10^{-6}	4.68×10^{-7}	8.27
BDE-209	$C_{12}Br_{10}O$	959.2	300-310	$< 1 \times 10^{-10}$	9.02 x 10-13	9.97

From the early 1970s their large scale production involved the commercialisation of three major products, consisting of distinctly different congener profiles, often referred to as technical formulations or commercial products [14]. Penta- BDE technical formulation consists primarily of the tetra (BDE- 49), penta (BDE-99 and -100) and hexa (BDE-153 and -154) BDE congeners; Octa-BDE contains primarily a hepta- (BDE-183) as well the hexa- (BDE-153 and -154) and several octa-BDE congeners; while Deca-BDE consists primarily of the fully brominated BDE-209 congener (La Guardia et al., 2006). According to Abbasi et al (2019), accumulative global production of all three major PBDE formulations has been estimated at > 1800 kilotons (kt), with Penta-BDEs, Octa-BDEs, and Deca-BDEs contributing ∼175, 135 and 1600 kt respectively. Annual production was reported to have peaked at ∼85 kt y^{-1} in 2003 with global consumption assumed to be reflective of production quantities [15]. The results of the Abbasi et al study appear broardly consistant with those values for Deca-BDE reported by the industry body- Bromine Science and Environment Forum (BSEF) whom report global production in 2003 at 56.4 kt yr^{-1} (BSEF, 2006 cited in [11]).

The United Kingdom consumed large quantities of all PBDE commercial products, was the largest consumer of the Penta- BDE formulation in Europe as well as the fourth largest global producer of PBDE commercial products [16]. Despite the large volumes of Penta- BDE produced and consumed by the UK, North American production (and consumption) was at all times substantially higher with consumption estimates of up to 95 % of global Penta-BDE production consumed [15]. Deca- BDE usage differences between Europe and the USA during the period in which it was mass-produced remained less dissimilar with Europe and the USA consuming 44 % and 33 % of global production respectively [17].

Subsequent human and environmental contamination of PBDEs was pronounced in both the UK as well as elsewhere with environmental levels found to be generally indicative of usage patterns. Observations in a variety of matrices including food items [18], human breast milk [19], blood [20],

serum [21], inhalable dust particulate matter [22], household surfaces as well as indoor and outdoor air have confirmed their ubiquitous presence [23].

The toxic effects associated with human and wildlife exposure to these compounds have also been reasonably well established [24] and are generally associated with negative endocrinological endpoints including: reduced sperm functionality, reproductive hormone imbalances, thyroid function disruption, neo- natal neurodevelopmental disorders and carcinogenesis [25]. Human routes of exposure to these compounds are diverse but are generally regarded to comprise in varying levels of importance: consumption of contaminated food items, dermal uptake upon contact with contaminated surfaces, ingestion of household dusts and ingestion of contaminated human breast milk [23,26,27]. Associations between many of these exposure routes and subsequent observed body-burdens have been established and include positive associations with dietary habits as well as dust exposures and indoor air concentrations [28] further resulting in an understanding of the interactions and relative importance of predominant exposure pathways and their contribution to observed contaminant body burdens [27]. Accordingly the US Environmental Protection Agency has provided guideline oral reference doses for several predominant PBDE congener groups. Oral reference doses (RfD) for PBDEs of: 7, 3, 0.1, 0.2, 2 μg kg^{-1} day^{-1} for deca-BDE, octa-BDE, tetra-BDE, hexa-BDE, and penta-BDE homologues, respectively have been established [29].

A relationship between toxicity and congener bromination extent as well as isomeric arrangement has been established showing increased expression of toxicological endpoints with lowering bromination extent. Indicating a higher toxicity for the lower, tetra conjugated congeners specifically with respect to their higher brominated counterparts (Birnbaum and Staskal 2004; Wikoff and Birnbaum 2011). While a precise explanation and mechanism for this observation remains unclear, it has been proposed that reduced bioavailability (as a consequence of physico-chemical properties; Table 1.1) of the higher brominated PBDEs, especially BDE- 209 is primarily responsible. These findings as well as a lack of sufficiently substantive evidence showing degradation to lower

brominated, more toxic PBDE congeners that resulted in the delayed inclusion of BDE-209 to legislative frameworks [11].

The degradation tendency of BDE -209 and indeed other PBDEs is now well documented with multiple studies confirming debromination reactions resulting not only in lower brominated PBDE but also PBDD/F congeners. Conditions suitable for PBDD/F formation from PBDE pre-cursors in most cases have been shown to be restricted to processes involving the addition of substantial energetic inputs, such as pyrolysis, combustion and photolytic reactions [31–34]. Studies performed from a variety of PBDE and other BFRs show a clear relationship between BFR bromination extent and PBDD/F formation tendency, with PBDEs in all cases observed as more efficient pre- cursors than other phenolic BFRs. Observations of PBDD/F formation upon PBDE exposures to temperatures between 250 - 270 °C have resulted in sum PBDD/F concentrations in excess of 1300 mg kg^{-1} starting material in polymer compounds treated with BDE- 209 [33]. These measurements as well as the large pool of PBDEs present in waste streams, provide a scale to which the extent of potential PBDD/F environmental contamination may occur.

Table 1.2: Concentration data for PBDEs in environmental matrices (Adapted from (Yang et al. 2014)).

	Description	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Air (pg m^{-3})				
	Rural-urban transect across a major UK conurbation	Average 2.8-23.3		Harrad and Hunter, 2006
	East-Central US	Up to 980		Hoh and Hites, 2005
	Various sites, US	ΣBDEs: 13-85; BDE-209: 0.2-65		Hoh et al., 2005
	E-waste storage facilities, Thailand	8-150		Muenhor et al., 2010
	E-waste site, China	2858-19815 (median 7149)		Yuan et al., 2008
	50 km away from e-waste site, China	80-209 (median 150)		
	Pearl River Delta, Southern China	42.0-188	196-9261	Shi et al., 2009
	Offices, UK	10-1416 (166)		
	Homes, UK	4-245 (52)		Harrad et al., 2006
	Public microenvironments, UK	29-162 (112)		
	Cars, UK	11-8184 (709)		
	E-waste recycling plant, Sweden		12-200	Sjödin et al., 2001
	Various working environments, Sweden		< 40 – 320	
	E-waste storage facilities, Thailand	46-350		Muenhor et al., 2010
	Dismantlers, electronic recycling facility, Sweden	ΣBDEs: 6.9-170 (60)	3.4-13 (6.6)	
	Other workers, electronic recycling facility, Sweden	ΣBDEs: 9.2-43 (20)		
	Unexposed, electronic recycling facility, Sweden	ΣBDEs:4.4-4.8 (4.6)	1.3-2.2 (1.6)	
	Homes, UK	7.1-250 (77)	n.d. -2200000 (260000)	Harrad et al., 2008
	Offices, UK	16-1100 (250)	620-280000 (30000)	
	Cars, UK	54-22000 (2300)	12000-2600000 (410000)	
	Home vacuum bags, greater Boston, US (2002-7)	980-44550 (4740)		Stapleton et al., 2009

Table 1.3: Concentration data for PBDEs in environmental matrices (Adapted from Yang 2014).

	Description	ΣBDEs (BDE-209 excluded)	BDE-209	Reference
Sediments (ng g^{-1} dw)				
	Pearl River Delta, Southern China	0.45-1.01	39.8-95.2	Shi et al., 2009
	E-waste dismantling site and 25 vicinal towns, southeast China (2008)	0.06-31.2		Fu et al., 2011
	Seine river basin, France	80-350	420-3000	Teil et al., 2014
	Scheldt Estuary and North Sea along the Dutch coast	around 1.6		Booij et al., 2002
	Lake Thun, Switzerland	17-78		Bogdal et al., 2010
	Lake Michigan	18 in dissolved phase;		Streets et al., 2006
	Coastal areas, Norwegian Arctic (2005)	0.043-0.19		Jiao et al., 2009
	13 estuarine sites, Auckland, New Zealand	0.55-573		Stewart et al., 2014
	San Francisco Bay	2.1-8.0		Klosterhaus et al., 2012
	Lake Superior	0.5-3.1 (1.4)		Song et al., 2004
	Lake Michigan	1.67-3.97 (2.99)		Song et al., 2005
	Nation-wide various sites, Australia	n.d.-60.9		Toms et al., 2008
	Five mangrove swamps, Hong Kong	0.57-14.4	1.53-75.9	Zhu et al., 2014
	12 Chinese Lakes	0.02-0.29 (0.18)	0.11-40.1 (8.2)	Wu et al., 2012
	Pearl River Delta, Southern China	2.60-60.4	32.7-2015	Shi et al., 2009
Human milk (ng g^{-1} lw)				
	General population, Birmingham, UK (n=35, 2010)	Σtri-hexa-BDEs 0.2-26.1	<0.06-0.92 (0.31)	Abdallah and Harrad,
	Swedish mothers (pmol g-1 lw, pool sample, 2004)	BDE47:1.9; BDE 99: 0.46		Fängström, et al., 2008
	Primipara and multipara mothers, Philippines (2008)	0.61-11 (3.3)		Malarvannan et al., 2013
	Production area, China		12.3-115 (31.3)	Jin et al., 2009
	Urban/suburban Beijing, China (n=103, 2011)	0.12-8.69 (1.04)	n.d.-131 (9.85)	Shi et al., 2013
	General population from 13 locations in the UK	0.63-420 (median 5.6)		Thomas et al., 2006
	Electronics Dismantlers, Sweden (n=19)	median 26; 15-75 (median 37) pmol g-1 lw		Sjödin et al., 1999
	Computer Clerks, Sweden (n=20)	median 4.1; 3.9-17 (median 7.1) pmol g^{-1} lw		
	Hospital Cleaners, Sweden (n=20)	median 3.3; 3.1-39 (median 5.4) pmol g^{-1} lw		
	Madrid population, Spain	Median 12		Gomara et al., 2007
	New Zealand	Mean 7.17 (4 congeners)		Harrad and Porter, 2007

1.4 PBDEs Environmental Fate and Temporal Trends.

Similar to the majority of other semi-volatile POPs, the organic carbon rich environmental compartments such as soils and sediments serve as the major environmental sinks for these compounds (Table 1.2, [36]. Their accumulation in both marine and freshwater sediments has been well documented and provides unique opportunities to investigate contamination retrospectively. Contaminant mobility, once deposited to sediments has been shown to be reduced sufficiently such that concentration measurements in conjunction with sedimentation dating techniques can provide a repository for the construction of long term contaminant trends [37]. These data are significant, in that they not only provide indications as to present day levels, or to past trends and onset years, but can also provide insights into the presence and extent of relationship occurring between multiple contaminant compound classes. By providing data relating the year of deposition to concentrations observed that also provide a metric by which to evaluate the effectiveness of legislative processes. Accordingly sediment core measurements been used quite extensively however, the construction of temporal trends is particularly labour intensive, requires specialist sampling techniques as well as access to radiometric dating tools. For these reasons the extent of their application remains relatively limited. The interpretation of sediment core contaminant trends should be conducted with caution, especially in attempts to conclude environmental responses. This is particularly evident in a report by Vane et al in 2010, which used dated sediment concentration profiles obtained at 8 different sites to deduce PBDE contamination trends. In this study, all cores were sampled within close proximity (~10 km) to each other in a UK estuary, with the magnitude of trends present in the uppermost sediment section (most contemporaty) presented as indicators as to potential contamination scenarios. Results reported, despite the relatively large sample size (8 cores), the small spatial coverage of sampling locations, as well as all cores sampled concurrently yielded vastly different indications as to future contamination status, with several trends ending in strongly positive (increacing) slopes and others indicating the contrary [38]. In studies of this nature the effects present at local scales, such as mixing profiles and locations of sporadic point source

contamination discharge are often difficult to estimate or adequately control for, and highlight the need for additional confirmations to ensure the observation of levelled trends are not simply products of local area effects. Several recent investigations have been successful in reporting as well as providing confirmation by reanalysis levelling off trends for a range of PBDE congeners and homologue groups at sampling sites in North America [1,39] and Europe [40].

In a recent investigation of PBDE contamination trends in UK freshwater sediment cores (n=7) Yang et. al (2014) established for the first time contamination trends for composite BDE groups with bromination substitutions from tri-hexa ($BDE_{tri\text{-}hx}$, generally reflective of the Penta- BDE commercial product), a predominately observed hepta- BDE (BDE- 183, considered a marker compound for Octa- BDE commercial mix) and BDE- 209 (the primary congener present in the Deca- BDE technical product). The results of the Yang et al investigation are revisited for comparison with data generated in this study and are thoroughly described in Chapter 3. Briefly however, results obtained in this study suggest that concentrations of $BDE_{tri\text{-}hx}$ are beginning to decline across the majority of sites sampled. BDE- 183 reductions in the later years of the chronology were observed only at some sites, with at all sites sampled showing a continued steady increase in BDE- 209. These results appear to be reflective of environmental responses to control measures introduced, with trends broadly reflecting the sequence with which legislative activities were enacted for the PBDE- commercial products. At the time of sampling, BDE- 209 usage was still ongoing and accordingly this also appears reflected in the contamination trends constructed [41].

1.5 PBDD/Fs and PXDD/Fs.

The polybrominated and mixed halogenated dioxins and furans refer to a two discrete classes within the group of polyhalogenated-p-dibenzo dioxins and furans. These classes share significant structural and physical commonality with their polychlorinated counterparts however, some important differences remain. For the most part, commonality is more pronounced for the lower

brominated PBDD/F and PXDD/F congeners and is attributed primarily to differences in the relative dissociation energies presence between aromatically bonded carbon and chlorine (C- Cl= 405.9 kJ mol^{-1}) and that with bromine (C- Br= 343.1 kJ mol^{-1}, Buser 1986). The extent of which appears additive in nature and tends to impart reduced thermodynamic stability and environmental mobility with increasing bromine substitutions [43].

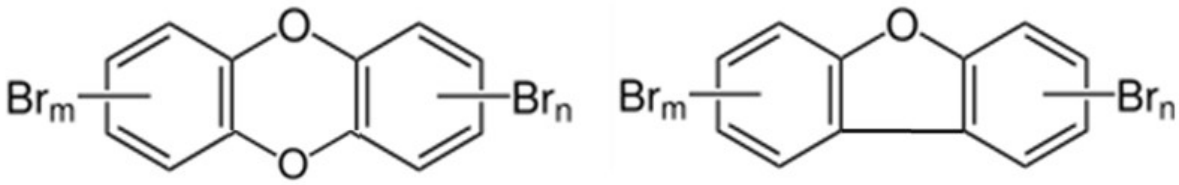


Figure 1.2: Generic molecular structures of PBDDs (left) and PBDFs (right).

Table 1.4: Physical properties of selected PBDD/Fs. Data from: [44].

	Chemical Formula	Molecular Mass (g mol^{-1})	Melting Point (°C)	Water Solubility (log mol L^{-1})	Vapour Pressure (Pa at 25 °C)	Log K_{OW}
Tetra-BDD	$C_{12}H_4Br_4O_2$	499.6	334-336	-8.72	6.4 x 10^{-7}	6.69
Penta-BDD	$C_{12}H_3Br_5O_2$	578.5	N/A	<0.254	N/A	7.19
Hexa-BDD	$C_{12}H_2Br_6O_2$	657.4	N/A	N/A	N/A	7.69
Hepta-BDD	$C_{12}HBr_7O_2$	736.3	N/A	-10.89	N/A	8.13
Octa-BDD	$C_{12}Br_8O_2$	815.2	376	-11.69	4.1 x 10^{-11}	8.6
Tetra-BDF	$C_{12}H_4Br_4O$	483.6	240-302	-7.99	3.9-4.5 x 10^{-7}	6.38
Penta-BDF	$C_{12}H_3Br_5O$	562.5	N/A	-8.71	3.6-5.6 x 10^{-8}	6.88
Hexa-BDF	$C_{12}H_2Br_6O$	641.4	N/A	-9.43	4.6 x 10^{-8}	7.36
Hepta-BDF	$C_{12}HBr_7O$	720.3	N/A	N/A	9 x 10^{-11}	7.79
Octa-BDF	$C_{12}Br_8O$	799.2	N/A	N/A	N/A	8.26

The chemical structure and associated physical properties of PBDD/Fs and PXDD/Fs are also characteristic of other well known POPs specifically the PCDD/Fs, and accordingly these compounds are expected to behave similarly to those with respect to environmental behaviour as well as toxicity [32,45–47]. Toxicity of the PCDD/Fs has been well established. With a multitude of epidemiological and toxicological studies carried out over the past 50 years. Established negative health effects including: lethality, wasting, thymic atrophy, teratogenesis, negative reproductive effects, chlor-acne, immunotoxicity, enzyme induction, decreases in T4 and vitamin A, and increased hepatic

porphyrins are just some which have been described for PCDD/F exposure. For the most part studies investigating the health effects of PBDD/Fs agree that observed human and environmental toxicological profiles are at least similar to those of PCDD/Fs as confirmed by a limited number of relevant reported studies [6,44,47,48]. PCDD/Fs toxic mode of action in the first instance is through activation of the AhR (dioxin) receptor (Birnbaum 1994). The severity of health effects associated with exposure to PCDD/F is scaled against their specific binding affinities for this receptor. These affinities vary according to the extent as well as the geometric pattern of halogenations present and are scaled by the response of the most potent receptor agonist, 2,3,7,8- TetraCDD and has led to the establishment of congener specific Toxic Equivalency Factors (TEFs). Through application of these values a systematic approach to estimate the toxicity of a variety of different 2,3,7,8- PCDD/Fs present as a mixture can be derived and is designated a Toxic Equivalency value (TEQ; [50]). On the basis of toxicological similarity, recommendations for PBDD/F inclusion to the WHO TEQ system and assigned identical congener TEFs have been made [51]. AhR receptor binding affinities for PXDD/F have also been established and with respect to the PXDFs showed higher potency than counterpart PCDD/F congeners. This finding shows their increased relative toxicity and therefore highlights the potential to underestimate TEQ values if assigned corresponding PCDD/F TEFs [45,52]. Accordingly, as case for PBDD/Fs, PXDD/Fs have not as yet been included to WHO TEQ system [53].

1.5.1 Sources and Formation Pathways.

A comprehensive description of PBDD/F and PXDD/F contamination sources remains loosely defined, certainly more so with respect to the PXDD/Fs. PBDD/Fs have been identified as unintentional by-products and have been observed in a variety of PBDE commercial mixtures [54]. A survey of technical PBDE mixes corresponding to each of the three major technical products showed the consistent presence PBDF congeners at concentrations ratios (PBDE: PBDF) on the order of 10^{-5}, with virtually all PBDD congeners analysed for observed below detection limits. PBDF congener

contributions analysed revealed a strong association between the bromination extent of each of the PBDE technical products and PBDFs present, with Hepta- BDF observed at concentrations of 1-10 ng g^{-1} in the Deca- BDE products analysed. Levels as high as these as well as the vast quantities of Deca-BDE product manufactured suggests that formation of at least tons of PBDFs have occurred by this mechanism alone [54]. Studies investigating the presence of PBDD/Fs in dusts generated from household electronic products known to have been treated with PBDEs noted the occurrence of PBDF enrichment in dusts with respect to the values reported in technical mixtures. Enrichment of over an order of magnitude was found for dusts generated from Japanese televisions resulting in PBDF: PBDE ratios of between 10^{-4}- 10^{-3} across the sample set [55]. The implications of these findings are significant, as they suggest an enhanced presence of a more toxic compound class to be present at concentrations elevated from those in the original starting material and present in matrices known to represent a major human route of exposure. Further, the provision of the concentration ratio metric also provides a rational means to approximate the sources of PBDF contamination as measured in environmental compartments, as deviations from this ratio may indicate formation of PBDFs by alternative processes.

PBDD/F and PXDD/F formation has also been observed to occur as a result of reactions involving the thermolysis [56,57] and photolytic degradation of both PBDEs and other phenolic BFRs [34]. In these studies PBDD/F formation by thermolysis was preferred, with increased conversion efficiencies of approximately 5 fold observed for thermolysis with respect to photolytic formation. Unsurprisingly, given the structural and physical similarities to PCDD/Fs the preferential formation route by thermally intensive processes have also been observed for the formation of PCDD/Fs from pentachloro phenyl (PCP) pesticide formulations [8].

In a review of thermolytic and pyrolytic formation of PBDD/Fs from BDE- technical mixes, a relationship between temperature and resultant ∑PBDD/F concentration was reported. Experiments reviewed were conducted over a temperature range of 600- 900 °C and showed increasing

concentrations of resultant ∑PBDD/Fs from 600- 700 °C with a maximal conversion occurring at 700 °C at observed concentrations of in excess of 330400 ppm. Conversion at temperatures above 800 °C showed ∑PBDD/F concentrations substantively below those observed by formation at 700 °C , a schematic detailing the potential PBDD/F and PXDD/F formation pathways from Deca- BDE is illustrated in Figure 1.3 [58]. Weber and Kuch, 2003 also observed significantly enhanced formation of PBDD/Fs with the addition of various transitional metal catalysts including Cu and Fe, both likely present in a variety of municipal waste streams and highlights the potential for catalysed formation in municipal waste incineration processes in the absence of appropriate control measures. Additionally, this study also observed a relationship between thermolysis temperature and relative homologue group contributions to ∑PBDD/Fs concentrations. Higher temperatures were shown to favour the formation of higher brominated PBDD/Fs such as Hepta- and Octa- BDD/Fs. Unfortunately, beyond reporting bromination order the relative contributions of PBDFs to ∑PBDD/Fs was not established [58].

A review of formation processes for PBDD/Fs which was extended in some cases to provide information on selected PXDD/F homologue groups was conducted under normal operating conditions at a municipal waste incinerator (MWI). Feed stocks, flue gas as well as ash materials were measured and PBDF: PBDE ratios established for all three. PBDF: PBDE concentration ratios between feed stocks and flue gas, while significantly elevated were found to be two orders of magnitude lower than those observed in ash materials, indicating that under these conditions a reduced quantity of PBDFs with respect to PBDEs was observed to be emitted to the atmosphere than was previously observed in laboratory based thermolysis experiments (Du et al. 2010 [59] as reviewed in [60])

Combustion processes at large scale operational MWIs were also found to result in detectable quantities of PXDD/F congeners in both flue gas as well as ash, however approximations of conversion efficiencies and combustion factors were not ascertained due to their presence in

combustion feed- stocks at concentrations below limits of detection [61]. Of note, are several observations of enhanced emissions of both PBDD/F and PXDD/F in flue gases where the presence of transition metals in feed stocks were confirmed [59]. Figure 1.4 illustrates the major pathways for PBDD/F and PXDD/F formation in thermal processes.

Studies concerning the combustion of electronic waste and other household items likely treated with BFRs under both controlled and non-controlled burning scenarios report significantly elevated PBDD/F and PXDD/F formation during insufficient combustion, for example under smouldering or oxygen limited conditions. Extreme concentrations of both PBDD/F and PXDD/F have reported in pyrogenic particulate matter sampled from both the clothing of fire fighting professionals as well as surfaces immediately surrounding the fire affected locations during combustion under 'insufficient conditions' [62,63], likely attributable to the efforts of fire fighting professions who's presence there is primarily for its extinguishment. Smouldering conditions were also observed to significantly enhance the formation of PBDFs in the uncontrolled combustion of municipal waste. Here, a large contribution of lower brominated PBDFs were observed in measurements taken directly above the fire and are in line with the laboratory measurements reported by Weber and Kuch, 2003 suggesting formation of lower brominated PBDD/Fs at lowered combustion temperatures.

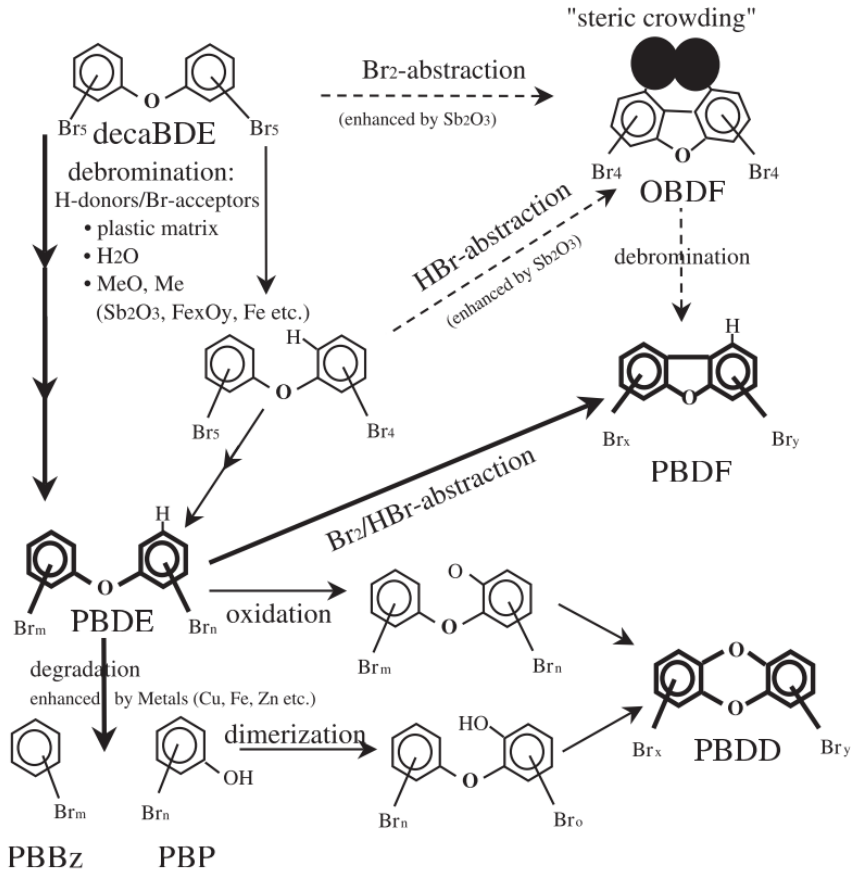


Figure 1.3: Formation mechanism of PBDD/F from the thermal degradation of BDE- 209. Adapted from Weber and Kuch, 2003 [58].

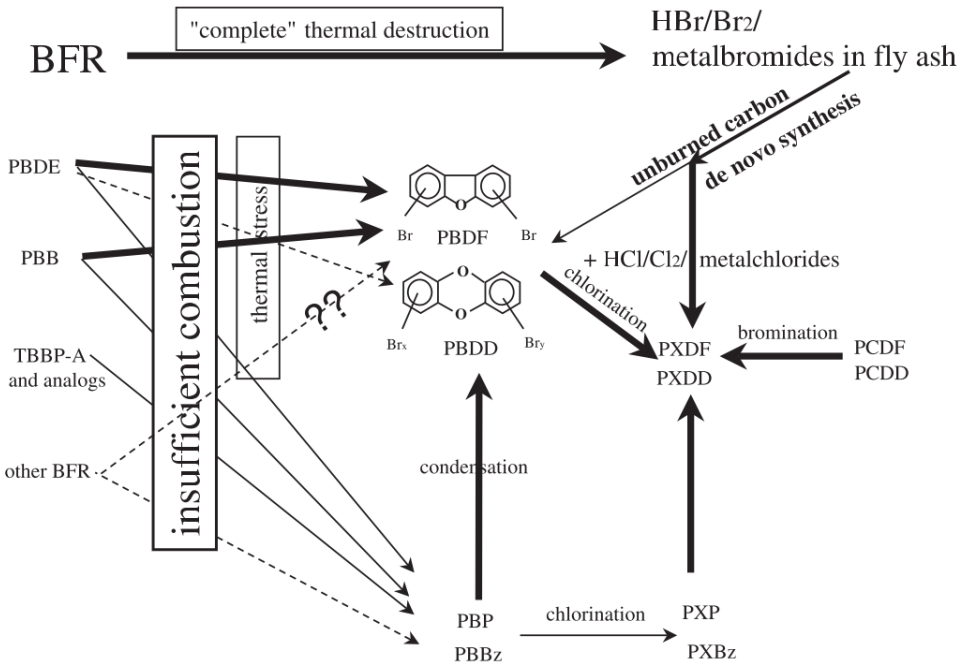


Figure 1.4: Formation pathways of PBDD/Fs and PXDD/Fs in thermal processes showing with broken lines the potential formation of PBDD/Fs from likely present alternative BFRs. Adapted from: Weber and Kuch, 2003 [58].

Given the almost exclusive role of combustion in the formation of PBDD/Fs and PXDD/Fs, formation by natural mechanisms was virtually ruled out. This was however, until measurements of PBDD from within species of Baltic sponges (*Ephydatia fluviatili*) showed lower brominated PBDD congeners as well as some PXDD/F congeners at concentrations elevated by a factor of 10^5 with respect to those of surrounding waters. These measurements, alone do not confirm natural formation, nor do they entirely rule out the potential for PBDD selective sequestration, however strongly suggest the possibility of biologically mediated conversion processes, from the presence of appropriately halogenated pre- cursor compounds [64].

1.5.2 Environmental Fate.

Similarities in the physico- chemical properties of PBDD/Fs and PXDD/Fs with respect to their chlorinated analogues as well as the PBDEs suggests reflective accumulation in common environmental compartments, with sediments, soils and higher trophic organisms acting as the predominant PBDD/F and PXDD/F environmental sinks. As has been observed for the PBDEs, congener specific degradation potential as well as environmental mobility is likely to be a function of bromination extent [65].

Overall, the number of studies which have successfully quantified PBDD/F or PXDD/F environmental and human matrices are considerably low with comparison to those conducted for PBDEs [57], especially so with respect to PXDD/Fs [66]. An even fewer number of reports are available which concurrently investigate levels of potential pre- cursor BFRs. Although they are not without precedent with measurements for both PBDD/Fs and PBDEs in sediments (Table 1.5), human breast milk (Table 1.6) as well as air (Table 1.7). Drawing meaningful conclusions as to contamination relationships between PBDD/Fs and PBDE here is difficult, mostly due to the number of comparative studies reported. This number however, becomes substantially lower upon investigation of the number of and type of PBDD/F congeners analysed. Many of the available studies tend to focus on

the more toxicologically relevant 2,3,7,8- substituted PBDD/Fs alone. Further, due to analytical challenges, quantification of the higher brominated congeners such as the potentially highly contributing hepta- and octa- BDD/F homologues is often not conducted which in the event of their presence in high concentrations would substantially underestimated sum PBDD/F concentrations. Some conclusions however, can be drawn from sediment and air sample concentrations which show the expected general trend of elevated concentrations in urban rather than rural sites. For the most part these data provide a qualitative indication of contaminant levels observed across various matrices and confirm the ubiquitous nature of PBDD/F contamination. A more detailed interpretation of these data is provided in Chapters 3- 5.

Quantification of higher brominated congeners has been found to be of particular relevance for PBDF source apportionment. Studies focusing on concomitant quantification of PBDEs and PBDD/Fs have on several occasions observed high congener relative contributions of 1,2,3,4,6,7,8-HpBDFs in samples also observed to contain large concentrations of BDE- 209. In a study by Hayakawa et al. in 2004 statistically significant correlation was observed between concentrations of these congeners exclusively in atmospheric deposition samples [67]. A relationship which was subsequently confirmed by additional measurements from sediment cores and elsewhere [68] and is supported, in theory by this compounds high degree of bromination. The establishment of a contamination relationship between BDE- 209 and 1,2,3,4,6,7,8-HpBDF is important for a number of reasons. Firstly, the 1,2,3,4,6,7,8-HpBDF being substituted in the 2,3,7,8- positions imparts particular toxicological relevance to this congener and secondly, its positive association with BDE- 209, a consistently dominant contributor ∑PBDE concentrations measured, suggests the environmental presence of large quantities of the toxic 1,2,3,4,6,7,8-HpBDF in associated matrices.

Table 1.5. Total concentrations of PBDD/Fs, and PBDEs in soil and sediments in various environments.

	ΣPBDD/F	ΣPBDE	Reference
	(ng/g dw)	(ng/g dw)	
Freshwater lakes			
Rural/urban lakes, Sweden	0.44-0.54		Hagberg et al. (2005a)
Urban river, Sweden	0.41-1.7	29-62	Lundstedt (2012)
Rural lake Sweden	0.082-0.085	4.4-16	Lundstedt (2012)
Urban lake, China	0.00048-0.0057		Zhou et al. (2012)
Pond and stream, Sweden (fire affected)	0.061-8.7	0.73-150	Lundstedt (2012)
Stream at dump site, Peru	0.012-0.074	3.7-6.1	Naturvårdsverket (2011)
Lake, industr. Area, Thailand	0.037-1.5	3.4-58	Naturvårdsverket (2011)
Marine sediments			
Coastal, Hong Kong/Korea	nd.-0.46		Terauchi et al. (2009)
Cores, Tokyo Bay, Japan	0.0052-0.070	10-78050	Choi et al. (2003a)
Coastal, Osaka, Japan	0.0041-0.077	8.0-352	Ohta et al. (2002)
Coastal, Osaka, Japan – also cores	0.0024-0.59	53-910	Takigami et al. (2005)
Coastal and offshore, Sweden	0.050-10		Dang (2009)
Rural soil			
Lanna, Sweden	0.028-0.054	0.065-1.3	Lundstedt (2012)
Urban soil			
Umeå and Norrköp., Sweden	0.0011-0.22	0.18-66	Lundstedt (2012)
Bangalore and Chennai, India	0.0060-0.31		Ramu et al. (2008)
Kyoto, Japan	0.28		Hayakawa et al. (2004)
Industr. area, China	nd.-0.43	2.03-269	Ma et al. (2008, 2009)
Industr., Thailand	0.019-0.16	1.8-13	Naturvårdsverket (2011)
Dump site, Peru	0.0086-0.32	3.6-92	Naturvårdsverket (2011)

Table 1.6: Human breast milk PBDD/F, PCDD/F and PBDE concentrations in previously reported studies. Table adapted and expanded from Lundstedt 2016 [65].

	ΣPBDD/F	**ΣPCDD/F**	**ΣPBDE**	**Reference**
	(pg /g lipid)	**(pg TEQ/g lipid),**	**(pg/g lipid)**	
Breast Milk				
Mother's milk, 17 countries		0.04-0.63	0.70-370	Kotz et al. (2005)
Mother's milk, Japan	25-500	0.13-1.2	2-13	Ohta et al. (2004)
Mother's milk, Ireland	1.4-6	0.58-1.2	2.7-9.4	Pratt et al. (2013)
Mother's milk, Belgium		0.67	2	Colles et al. (2008)
Mother's milk, Flanders, Belgium		0.34		Croes et al. (2013)
Mother's milk, Vietnam	nd.-1.5	nd.-0.2		Tue et al. (2013)
(e-waste affected)	0.012-0.074	0.021-0.17	3.7-6.1	Naturvårdsverket (2011)
Mother's milk, Sweden		0.0036*		Haglund et al. (2014)
Biological Fluids				
Blood serum, fire fighters, USA	nd.-2778	nd.-732	48-442	Shaw et al. (2013)
Adipose Tissue				
Adipose tissue, Sweden	0.41-3.67	0.11-1.81	1.16-7.46	Ericson Jogsten et al. (2010)
Adipose tissue, Sweden	0.33-3.9			Hagberg et al. (2011)
Adipose tissue, Sweden	0.12-2.24			Ericson et al. (2008)
Adipose tissue, Tokyo, Japan	1.9-8.3		0.0068-2.75	Choi et al. (2002); Choi et al. (2003)

** wet weight basis*

Table 1.7: Concentrations of PBDD/Fs and PBDEs in air from various rural, urban and industrial environments. Both total levels and toxic equivalents (TEQ_{05}) are given for PBDD/Fs. Table adapted and expanded from Lundstedt 2016 [65].

	ΣPBDD/F	**ΣPBDD/F**	**ΣPBDE**	**Reference**
	(fg/Nm^3)	**(fg TEQ Nm^3)**	**(pg Nm^3)**	
Rural/Remote				
Various, China	3.4-20			Wang et al. (2008)
Råö, Sweden	7.2-690		0.49-9.8	Remberger et al. (2014)
Pallas, Finland	14-30		0.94-1.4	Remberger et al. (2014)
Guangzhou, China	57-390		110	Chen et al. (2006); Li et al. (2011)
Urban/Industrial				
Gothenburg, Sweden	2.5-86		2.9-9.2	Remberger et al. (2014)
Varoius, China	15-30			Wang et al. (2008)
Sci.park, China	58-130			Wang et al. (2008)
Shanghai, China	700-1400			Li et al. (2008)
Guangzhou, China	140-1700		88	Chen et al. (2006); Li et al. (2011)
Kyoto, Japan	1800-12000		4400-80000	Hayakawa et al. (2004)
Taizhou, China	3500-81000	13-310	41-160	Zhang et al. (2012)
Guiyu, China (e-waste site)	8100-61000			Li et al. (2007)
Taizhou, China (e-waste site)	37000-155000	96-690	160-540	Zhang et al. (2012)
Guangzhou, China (industrial site)	420-4200		230-3700	Chen et al. (2006); Li et al. (2011)
Close to MSWI, Taiwan	420		52	M-S Wang et al. (2010)
Close to BFR- fac. Japan	10000-1000000			Tadami et al. (2008)
Air, e-waste dismantling hall	2400000		510 000	Takigami et al. (2006)

The relationship between these congeners has also been observed (at statistical confidence of >95 %) across a series of core and surficial sediment samples taken at Tokyo Bay in 2002 [69]. Here, Goto et al. established the first set of temporal profiles of PBDD/F contamination and was able to contrast those measurements against a previously established PBDE concentration chronology derived from identical core sample material [70]. Results obtained across all cores showed expected consistency with respect to location, with higher overall PBDD/F concentrations observed at sampling locations in close proximity to receiving water interfaces. Significantly, this study provided the first measurements of PBDD/F contamination onset year, established the presence of a significant lag period with respect to PBDD/F contamination onset and that of PBDE, re- confirmed and temporally extended observations of the contamination relationship between the 1,2,3,4,6,7,8- HpBDF/ BDE-209 concluding its presence as far back as the mid 1970s. Figure 1.5 shows the temporal profile of 1,2,3,4,6,7,8- HpBDF present in one of the core samples analysed. Additionally observed were temporally constant PBDD profiles, particularly with respect to the lower tri- and di- substituted congeners. This was consistent with those observed to be associated with the Baltic sponge as reported by Unger et al. [64] which led the authors' to suggest a natural formation source of these congeners is likely present in waters of the coast of Japan also. The utility of these measurements to provide further understanding and descriptions of environmental contamination relationships is significant, and highlights the benefits of conducting multi- residue contaminant assessments in appropriately selected time- integrated environmental matrices.

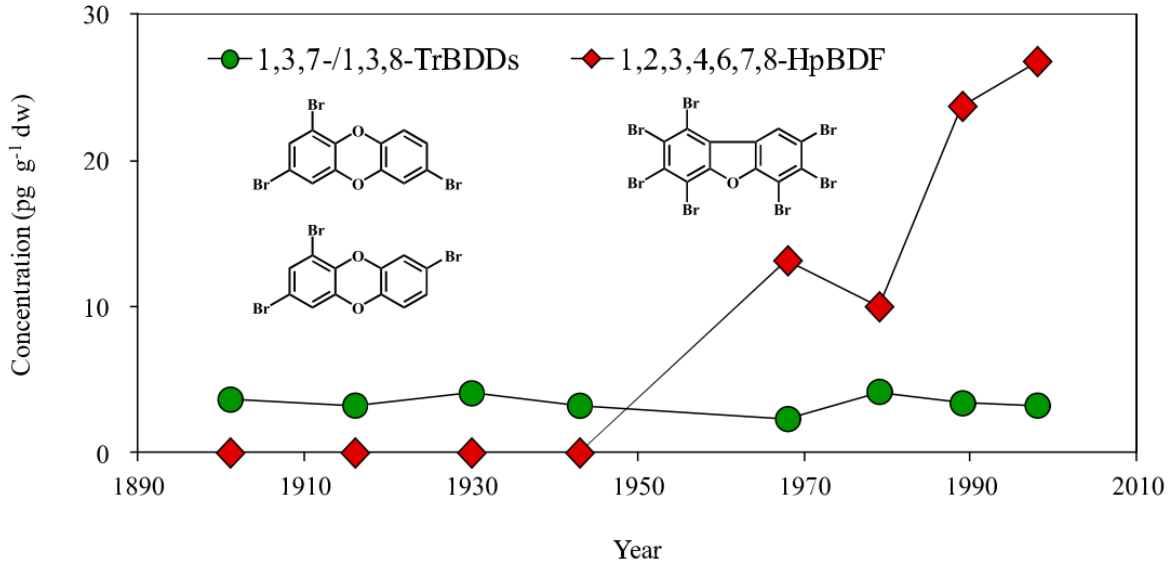


Figure 1.5: Temporal concentration profiles of tri-BDDs and 1,2,3,4,6,7,8- HpBDF as observed in marine sediments sampled in 2002 at Tokyo Bay Japan. Data from TP-1 sediment core, sampled at close proximity to major receiving waters interface. Figure taken from Goto et al. 2017 [69].

Studies showing the extent of environmental contamination by PXDD/Fs are extremely limited and when present are generally restricted to single measurements reporting qualitative identification alone [43]. There exists however, several comprehensive quantitative data sets on PXDD/F contamination of food items, also carried out in conjunction with quantifications of PBDD/Fs and PBDEs (Fernandes et al. 2014a). Measurement concentrations for sea foods vary, but are generally within the range of <5 fg g^{-1} to 3.7 pg g^{-1} PXDD/F individual congeners and are reported here to provide reference as to concentration ranges of PXDD/Fs observed. Incidentally, across a range of PXDD/F measurements of various food items no statistically significant correlations with PBDE concentrations were observed (Rose and Fernandes 2017).

1.6 Analytical Measurement of Trace- Level Environmental Organic Contaminants.

The paucity with respect to the number of studies and quality of data reported for both the PBDD/Fs as well as the PXDD/Fs is predominately due to the "daunting" complexity of their measurement (Rose and Fernandes 2017). Measurement complexity and the need for precise instrumental and

methodological parameterisation are critical for the analysis of both the PBDD/Fs and PXDD/Fs. This therefore requires not only access to suitable analytical instrumentation but also to experienced operators capable of refining instrumental and methodological settings adequately, such to maintain the strict requirements of both the sensitivity and selectivity of measurement [12].

PBDD/F and PXDD/F analysis share common challenges, compounded by their considerably low concentration in ambient environmental matrices. PBDD/F analysis further requires the almost intricate tuning of sample introduction and chromatography procedures as their high thermal lability often results in gross loss of analyte as well as the production of interfering 'ghost' peaks. Additionally, the analysis of PBDD/Fs, particularly those with higher bromination order contribute rapidly to significant source fouling. While the selection of higher ion source temperatures holds the potential to negate this effect somewhat, it has also been shown to decrease sensitivity, again through the degradation of target analytes [73].

Further hampering analysis efforts, and placing constraints on their separation are the multitude of potential isomeric and congener specific combinations possible for these compounds. For example, a total number of possible halogen combinations restricted to Br and Cl substitution results in 4600 possible individual congeners for PXDD/Fs with 1550 and 3050 for PXDD and PXDF respectively- all of which have virtually equal potential to be present in contaminated matrices. A large number of these combinations exist as structural isomers and therefore produce identical mass spectra making separation by MS resolution impossible, and relying on chromatographic separation alone. Indeed with current gas chromatographic technology, separation of all isomers remains impossible, and is probably unnecessary for data interpretation in any case. This challenge is not as relevant with respect to PBDD/F analysis as halogen substitution combinations are far less in number, and the potential for isomeric interference can be appropriately managed with sufficient chromatographic method optimisation. However, PBDF analysis suffers with additional exact accurate mass interferences produced by the presence of PBDE ions [60]. The treatment of this is generally

conducted by rigorous purification and physical separation during sample clean up. Although the large concentration differences observed between these compound groups in ambient environmental samples is such that even sub- percentage contamination of the PBDE sample fractions (in the absence of additional separation protocols) has the potential to render PBDF measurements essentially useless [74].

Both PBDD/F and PXDD/F molecular structures are composed entirely of Br, Cl, C, O, and H, elemental compositions which are shared by a large number of other environmental contaminant compounds. Many of these, including the ubiquitous PCBs and PBDEs have commonality of mass fragments upon ionisation. Accordingly the need for adequate selectivity is paramount to avoid the presence of isobaric interference and subsequent false positive identifications and quantifications (Rose and Fernandes 2017).

Availability of appropriate mass labelled and other reference standards is another element retarding the development of PBDD/F and PXDD/F analysis. While some commercial standards do exist for these compounds, their congener compositions are based mostly on the small number of environmental detections reported to date, as well as those of toxicological relevance (such as 2,3,7,8- substituted congeners). In addition to their scarcity, purchasing costs for these standards is very high, with calibration series primary standard sets for PBDD/Fs retailing for ~5000 USD (at the time of purchase- 2015), further restricting the number of measurements performed.

The instrumental requirements imposed for the analysis of these compound groups, namely sensitivity and selectivity have for the most part restricted their measurement to high resolution mass spectrometric (HRMS) techniques, generally by analysis on magnetic- sector instrumentation [75]. Some approaches however, trade-off detection sensitivity for gains in ionisation efficiency as is the case with APGC base approaches, here selectivity of measurement is achieved using triple quadrupole fragmentation and the detection of transition ions restricted by formation to those of the analytes targeted [76].

Essentially each analysis approach entails its own inherent benefit, as well as associated disadvantages. Accordingly, selection should, availability permitting, reflect the specific data requirements of the individual analysis performed.

1.6.1 Organic Contaminant Analysis by GC Q Exactive HRAM MS.

The very recently released Thermo Scientific GC Q Exactive HRMS platform is a high resolution, high accurate mass (HRAM) mass spectrometer based on ion detection and mass separation by Orbitrap mass analysis first described by Alexander Makarov in 2000 [77]. Released officially to the market in 2016 following the success of a liquid chromatograph (LC) hyphenated version released in 2005. The LC based platform has been highly successful in its application to the quantification of LC amenable 'small molecule' environmental contaminants as reflected by the large number (> 200) of yearly publications utilising this platform in the field of environmental contaminants research [78]. It also represents the most recent significant development to MS technology relevant for the analysis of environmental contaminants. Its suitability for application to environmental contaminant quantification however, remains untested and will require the 'ground-up' development of instrumental as well as wet chemical clean up methodology.

The Q Exactive range of MS platforms operate on the basis of extensive ion filtration, accumulation and quantized injection of ion packets to the Orbital Trap (Orbitrap) detector (Figure 1.6). Ionisation is conducted below atmospheric pressure and yields an efficiency approximating 1/1000, not significantly different from traditional HRMS magnetic- sector field based instruments. Ion beams are focused by a series of RF lenses and flatapoles and quadrupole filtered prior to collection and accumulation in a gas filled curved linear ion trap (C-Trap). Ion packets isolated in the C-Trap are sequentially passed to the Orbitrap detector where ion currents are measured for specific masses based on mass discrete oscillation frequencies induced through their rotation around an axial central electrode, and by which frequency is the sole determinant of ion m/z ratio (Equation 1.1). The

degree of discretisation in mass specific oscillation frequency is basis for which analysis by this method can produce highly accurate mass detection and resolution well beyond the capacity of traditional instrumentation employed for quantitation of analytes.

Equation 1.1: $$\omega = \sqrt{\frac{m}{z}} \times k$$

Where: ω represents the frequency of ion harmonic oscillations, *m* is the ion mass, *z* is the ion charge and *k* is a platform specific constant.

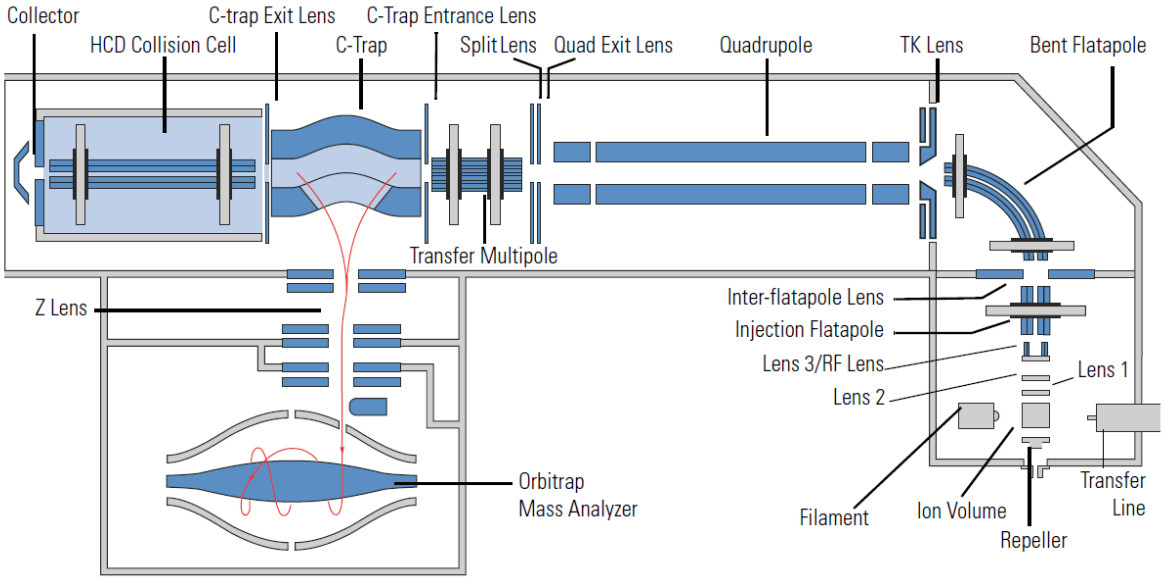


Figure: 1.7: Operational design schematic of the GC Q Exactive Mass Spectrometer platform. Figure used with permission of Thermo Scientific GmbH, Dreieich, Germany. Available: https://planetorbitrap.com/q-exactive-gc#tab:schematic, Accessed: 04/01/2019.

The advantage of ion quantification by this technique, provides for a remarkable enhancement with respect to the selectivity required for PBDD/F and PXDD/F measurements, specifically through the high resolving powers achieved. Selection of resolution for measurement on this instrument ranges

from 15k- 120k resolution at full width half maximum (FWHM). However, resolution selection is a direct function of scan rate, with this suffering significantly at high resolution settings. While several other MS platforms provide ion mass resolving powers equal to or in excess of the Orbitrap system, for example other Fourier-transform ion cyclotron resonance mass spectrometry systems (FTICR), or those based on Time-of-Flight (TOF), the advantage of the Q Exactive platform is evident in its capacity to measure specific mass ion currents (associated with the presence and quantify of specific ions generated from analytes at the ion source) with an appropriately high degree of accuracy and reproducibly over a dynamic range sufficiently large to be useful for producing quantitative and not merely qualitative analyses of analytes. A high degree of sensitivity, an additional necessary MS requirement for trace organic contaminant analysis is also provided by the GC Q Exactive, with instrument detection limits (IDLs) for PCDD/Fs reported at levels ranging from 9- 47 fg (on column) [79], slightly elevated to those achieved by analogous APGC-MS/MS measurements [80] and approximately equivalent to those conducted by traditional magnetic sector based instrumentation [81].

Unlike, APGC-MS/MS or Magnetic Sector based instrumentation, data acquisition modes on the Q Exactive GC allow for Full Ion Scan (FS) as well as Selection Ion Monitoring (SIM) without a significant reduction in analyte sensitivity. The use of this mode provides for the quantification of a far larger range of analytes in single injections, particularly advantageous in cases where sampling material is scarce, or a high degree of extract concentration prevents multiple MS injections. The limitations as to the extent of analytes acquired is therefore based almost solely upon the presence of mass interferences, negated for the most part by the high resolving power available, as well as compound separation through appropriate chromatographic parameterisation. Further, unlike traditional sector field analysis approaches scan rates are not limited by the ion mass range of the analysis and therefore provides unique techniques for the discrimination of mass interferences occurring between analytes over a large mass range. Also, in FS mode all ions present within the range of measurement are recorded, which can provide a basis for archiving samples and retrospectively

quantifying additional target compounds through additional injection and quantification by external calibration.

Despite the clear indications for the suitability of this instrumental platform to perform trace organic contaminant quantification, several limitations exist. Many of these can be overcome however, by appropriate sample preparation approaches. A principle limitation of analysis on this platform presents itself through the overloading of the C-Trap. In these cases, ionic competition for injection to the Orbitrap analyser results in intense ion suppression of target ion peaks, especially in cases where target quantification ions (QMs) are derived from the presence of low concentration analytes, as is often the case with trace analysis. Adequately refined clean up and sample purification procedures placing emphasis upon sufficient removal of background ion contamination are therefore of great necessity.

In all, given the success of the LC Q Exactive platform to provide repeatable and accurate analysis of LC amenable environmental contaminants, it is with a reasonable degree of certainty that this platform will eventually prove itself as a reliable and robust alternative to traditional MS approaches for trace level organic quantification in environmental research.

1.7 Aims and Objectives.

The primary objectives of this thesis are:

1. To establish a suitable analytical and methodology, based on the very recently developed and released Thermo Scientific GC Q Exactive orbital trap MS for the reliable quantification of PBDEs, PBDD/Fs and PXDD/Fs.
2. To evaluate the performance of this method to establish the presence of a contamination relationship between PBDEs and PBDD/Fs across three appropriately selected matrices.

3. To describe this relationship, where present, by means of relative congener profile contributions and statistical correlations for each of these compound classes.

The secondary objectives of this study are:

1. To refine the developed analytical methods sufficiently, such that they may be easily adopted by environmental analysts and facilitate the rapidity at which reliable measurements of trace level organic contaminants can be produced.
2. Extend this analytical methodology to a broader range of environmental contaminants, including the PCDD/Fs, dl- PCBs and selected NBFRs.
3. Apply the measurements made in a meaningful and relevant manner to extend concentration data generated to provide additional insight to relevant associated metrics.

To achieve these objectives, we propose to apply the quantification and analytical methods developed and reported in **Chapter 2**: **Materials and Methods**, to assess the contaminant concentration trends in a series of radiometrically dated sediment cores from UK fresh water lakes **(Chapter 3)**, UK human breast milk **(Chapter 4)**. We also propose to develop and evaluate the performance of measurements performed by external calibration alone, performed on relevant archived samples of atmospheric particulate matter **(Chapter 5)**. By doing so we aim to demonstrate the performance of the developed analysis to semi- quantify samples previously analysed for alternative contaminant classes and provide indications as to the suitability for retrospective contaminant analysis.

We also aim to apply this method to extend established concentration time series PBDE data obtained at identical sampling sites to re-assess concentration responses to legislative restrictions, and establish time trends of PBDD/Fs specifically to address the question of:

"Has increased use of BFRs had led to an increase in environmental contamination of PBDD/Fs".

Additionally we aim to attempt the establishment of PXDD/F temporal concentration trends in UK fresh water sediment cores and provide the first such measurements of their kind performed to date. Data and analysis of such is reported in **Chapter 3.**

We also plan to perform an assessment of BFR and PBDD/F contamination in UK human breast milk **(Chapter: 4)** to:

1. Investigate the presence of contamination relationships between these compound groups present.
2. Provide the first assessments of PBDD/F contamination of UK human breast milk.
3. Through extension of the analytical method provide the quantification of PCDD/Fs and dl-PCBs present in these samples also.
4. Apply these data to evaluate infant dietary up-take values for these contaminants.

Chapter 5 reports on the application of a semi- quantitative method performed in the absence of internal standardisation to:

1. Assess the presence and dynamics of a potential contamination relationship between PBDD/Fs and PBDEs in sampled ambient atmospheric aerosols.
2. Establish the extent to which fire effected aerosols alter the relationship and contributions of PBDD/Fs and PBDEs in these samples by contrast between measurements taken concurrently at sites affected and not affected by a fire event at municipal waste repository.
3. Construct and evaluate PBDD/F congener and homologue profiles obtained with respect to available literature.

Chapter 2 Development and Validation of Analytical Procedures for the Quantification of Halogenated Contaminants by HRGC/HRMS on the Thermo Scientific Q Exactive GC.

2.1 Introduction. This chapter describes the procedures employed for the sampling, extraction, wet-chemical purification and mass spectrometric analysis for the quantification of halogenated environmental contaminants. Environmental and human samples were obtained and processed by a variety of methods, each involving the application of the purification process and developed HRMS quantification technique. In all, 3 different matrices were investigated: English lacustrine sediment (3 cores from different locations), human breast milk from English mothers, as well as atmospheric particulate matter (PM_{10}) sampled in Santiago City, Chile. All three were analysed for a variety of environmental contaminants including BFRs, PBDD/Fs, PXDD/Fs, PCDD/Fs as well as dl-PCBs. The extent to which each matrix was analysed for these compound groups varied, for the most part due to the availability of internal standard solutions, the quantity of sample available for analysis as well as time constraints arising from the availability of analytical instrumentation. Two of the three sediment cores sampled were analysed for PBDEs, PBDD/Fs and PXDD/Fs with the third core analysed for PBDEs and PBDD/Fs alone. Human breast milk samples were analysed for PBDEs and selected NBFRs, PBDD/Fs, PXDD/Fs, PCDD/Fs and dl-PCBs; while the PM_{10} samples were analysed for a smaller number of indicator PBDEs (quantification conducted externally), and PBDD/Fs.

2.2 Sample Origins and Collection Procedures.

2.2.1 UK Freshwater Sediments.

2.2.1.1 Sampling Locations and Site Characteristics.

A total of 3 fresh water sediment cores were sampled from different locations across England at sites previously characterised for a range of contaminants including PBDEs, PCBs and HBCDs (Yang et al. 2016, 2014). Sampling locations and designations are presented in Figure 2.1. S1 indicates the location of Sampling Site 1 at Edgbaston Pool, within the grounds of the Birmingham Botanical Gardens, Birmingham. S2 refers to Sampling Site 2 at Wake Valley Pond, located approximately 15 km NNE of Central London on the northern edge of the Greater London Urban Area, District of Essex. S3 indicates the location of Sampling Site 3, Holt Hall Lake, Holt, North Norfolk County.

Figure 2.1: Map of Sediment Sampling Sites. S1 -Edgbaston Pool, S2 -Wake Valley Pond and S3 -Holt Hall Lake.

Figure 2.2: Photograph of S1 Edgbaston Pool taken on sampling date: 21 July 2015.

Figure 2.3: Photograph of S2 Wake Valley Pond taken on sampling date: 20 July 2015.

Figure 2.4: Photograph of S3 Holt Hall Lake taken on sampling date: 22 July 2015.

Table 2.1: Limnological and social attributes of the study sites.

Site Name	Coordinates (DMS, Decimal)	Altitude(m asl)	Lake Area(ha)	Mean Depth (m)	Profundal Depth (m)	Local Governmental Authority and Population density (people km^{-2})
Edgbaston Pond (S1)	52°27'17.4"N 1°55'15.3"W 52.454824, -1.920903	127	7.2	0.9	2.1	Birmingham (4079)
Wake Valley Pond (S2)	51°40'10.5"N 0°03'11.8"E 51.669591, 0.053277	96	1	1.7	3.7	Harlow (2730)
Holt Hall Lake (S3)	52°54'58.0"N 1°05'10.7"E 52.916219, 1.086565	47	0.7	0.6	1	North Norfolk (106)

Table updated and adapted from Yang 2014.

Altitudes and areas from: http://www.uklakes.net

Population Density of England by local or unitary authority, 2015 Data from: http://www.statistics.gov.uk/

2.2.1.2 Sediment: Sample Collection Procedure.

Single fresh water sediment cores were collected by the authors from each of the sites indicated in Figure 2.1. All samples were collected during a single sampling campaign conducted from the 23rd – 26th June 2015. Cores were sampled from as close to the maximum depth at each site as feasible and were collected from a purpose built pontoon to a depth of between 0.75-0.95 m below the benthic surface using the large diameter sediment core apparatus ('Big-Ben') developed by Patmore et al. 2014 [83]. The sediment corer, piston and core covers were all thoroughly decontaminated with hexane before and after use. The 'Big-Ben' corer, being larger than conventional piston corers (~50 - 80 mm dia) provided sediment cores with a cross- sectional area of ~220 mm^2 (140 mm dia.) and thus resulted in far greater sample for analysis, which was integral for the analysis of PBDD/Fs and PXDD/Fs. Sediment cores post sampling were settled for approximately 1 h, after which time individual slices consisting of 10 mm core depth each were extruded from the upper most section of the core and stored at -20° C in individually sealed Whirl-Pack^{TM} environmental sampling bags until extraction analysis. Sample contamination derived from use of Whirl-Pack^{TM} sampling bags manufactured from low density polyethylene (LDPE) was controlled for with the use of sampling blanks, which consisted of 30 g pre- cleaned Na_2SO_4 spiked with 10 µL $^{13}C_{12}$BDE-138. Sampling control blanks were opened to the atmosphere for approximately 30 min to allow the sampling spike solvent to evaporate, before being homogenised and sealed until analysis. Three sampling blanks were employed per site and treated analogously to sediment samples, including extraction and analysis. Recoveries of $^{13}C_{12}$BDE-138 ranged between 50 - 110 % with a mean of 85.4 ± 35.2 % (Mean ± 1SD) and all cases (n= 9) yielded BFR concentrations below limits of quantification confirming that the sample collection procedure did not contribute to sediment contamination of PBDEs.

2.2.2 Human Breast Milk: Sample Donor Information and Collection Procedure.

Milk samples ranging in wet volume from 70- 200 mL were collected by researchers from The Health and Environment Dept., Imperial College London from healthy primipara mothers nursing children at a gestational age of between 38 and 42 weeks. Data obtained at the time of sampling (2017) indicate that all participants were between the ages of 29 – 40, who lived and worked in professional roles within the greater metropolitan area of the City of London. No participants were employed in occupations which was likely to dramatically increase their risk of exposure to the selected target set of compounds analysed, for example recycling of electronic components or furniture manufacture. No further information on the origin of samples including the subjects' smoking habits was provided to the analysis group. Informed consent was obtained from all participants and samples were collected entirely anonymously with all participant information kept confidential. Samples obtained were immediately stored at -85 °C and kept as such until thawed prior to chemical and physical analysis. Human milk samples, while not considered as a vector for inflection were at all times treated according to the Centres for Disease Controls (CDC) protocol for Proper Handling and Storage of Human Milk [84]. All ethical approvals were confirmed prior to the authors receiving sample materials.

2.2.3 PM_{10} Atmospheric Particulate Matter: Sample Collection Procedure.

2.2.3.1 Sample Custody.

Atmospheric particulate samples were provided by Dr. Karla Pozo, Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Czech Republic. All sampling, extraction and clean-up procedures were conducted under the auspices of Dr. Pozo and the RECETOX Trace Analytical Laboratories group in accordance with established methodologies and appropriate QA/QC procedures under ISO/IEC 17025 laboratory accreditation.

2.2.3.2 Sampling Locations and Site Characteristics.

Samples provided to the authors were originally obtained from air monitoring stations located in and around the city of Santiago, Chile. Santiago with its population of over 7 million inhabitants lies at between 500- 650 MASL and is located within the *Santiago Basin,* a large bowl shaped valley almost entirely surrounded by the *Sierra de Ramón* mountain range extending to 6570 MASL in locations visible from the central Santiago business district. The topography of these mountains, coupled with predominate easterly winds contributes heavily to the occurrence of a low mixed atmospheric boundary layer. This consequently acts to contain and concentrate atmospheric pollutants and has led to considerable photochemical smog production, specifically in winter months [85]. Sampling was conducted over the period of the 12th to the 31st January 2016, during which time a fire event took place at the municipal landfill site of Santa Marta (33°41'50.13''S 70°48'3.87''W| -33.69726, -70.80107; Figures 2.5 and 2.6), located approximately 12 Km Southwest of Santiago at Talagante. Landfill operations began in 2002 and this site was designed to receive 6x10^{7} kg of municipal refuse per month serving a population of over 1 200 000 inhabitants. The site covers an area of 296 hectares and is expected to reach capacity by 2022. The fire event began on the morning of the 18th of January and was not completely extinguished until the 22nd January 2016.

Monitoring stations from which samples were obtained are managed as part of the SINCA Network (SINCA, www.sinca.cl) by the Chilean Ministry of the Environment. Sampling was conducted at the 4 locations indicated in Figure 2.6 and consisted of: S1 *Cerrillos* (33°29'34.22''S, 70°43'9.77''W| -33.49284, -70.71938); S2 *Ñuñoa* (33°26'57.92''S, 70°34'18.22''W| -33.44942, -70.57173); S3 *San Bernardo* (33°37'36.26''S, 70°42'5.83''W| -33.62674, -70.70162); and S4 *La Pintana* (33°36'56.95''S, 70°37'57.11''W| -33.61582, -70.657173).

Figure 2.5: Photograph of the Santa Marta Landfill fire event. Photograph taken on the evening of the 18th January (http://www.t13.cl/noticia/nacional/incendio-vertedero-santa-marta-provoca-insoportable-hedor-afecta-miles-capitalinos, accessed 30 November 2018).

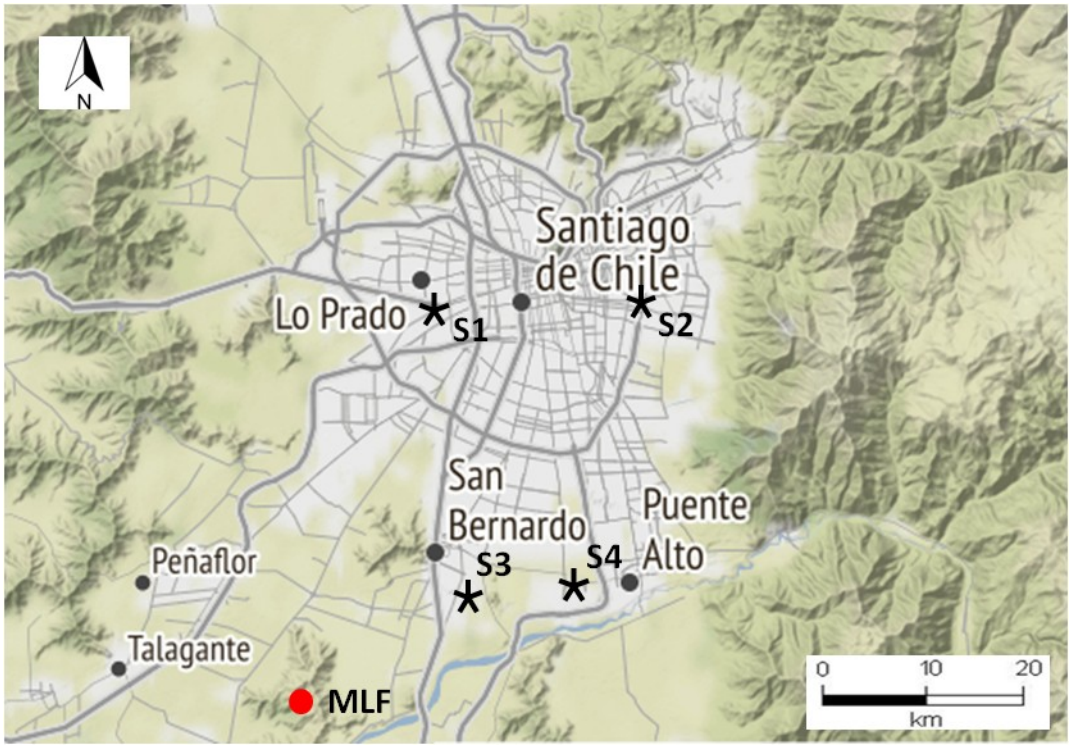


Figure 2.6: Map of Santiago, Chile and surrounding topography showing the locations of sampling sites S1- 4 with respect to the Municipal landfill (MLF), Santa Marta. Sampling locations S1- 4 refer to sites: (S1) Cerrillos, (S2) Ñuñoa, (S3) San Bernardo and (S4) La Pintana respectively.

2.2.3.3 PM_{10} Air Sampling Procedure.

A total of 10 individual PM_{10} samples were collected on pre-cleaned quartz fibre filters over 24 hour periods from individual samplers located at each of the sampling sites. Sampling was conducted intermittently from the 12th January 2016 to the 31st January 2016. In all, 2 samples each were collected on the 12th and 18th January from site (S1) Cerrillos and (S2) Ñuñoa on the 15th and 31st January 2016, with 3 samples each collected from sites (S3) La Pintana on the 12th, 18th and 30th January and (S4) San Bernardo on the 15th 21st and 27th of the same month. The fire event at the Santa Marta Landfill took place entirely within the period of sampling at sufficient proximity as to potentially affect air quality at the sampling locations. Visual observations of air quality at the San Bernardo sampling site indicated heavy atmospheric particulate loadings as evident from photographs of the vicinity taken during the fire (Figure 2.5).

2.3 Sample Physical Analysis and Pre- Extraction Procedures.

2.3.1 Sediment: Physical Analysis.

Sediment physical characteristics including dry weight (dw) and, Total Organic Carbon (TOC) were determined by the author in the laboratories of The Environmental Change Research Centre, University College London. Sediment dw and TOC were determined gravimetrically by mass loss from a 2 g (whole weight) sample, oven dried at 105° C for 3 h (dw) and a further 2 h at 550° C to determine TOC by loss on ignition [86]. Sediment water contents (%) and TOC values (%) for each sediment core with respect to depth are presented in Figure 2.7.

2.3.1.1 ^{210}Pb Radiometric Dating and Sedimentation Rates

Radiometric analysis of sediments was conducted following the procedures outlined in Appleby 2001 and Appleby et al. 1986 by Dr. Handong Yang at the Environmental Change Research Centre, University College London. Full details and results of the analysis are provided in Appendix A. Briefly,

sediment core slices (5 g, whole weight) were sub-sampled from those taken at the benthic surface in ~50 mm increments across the full extent of the core to establish the year of and rates of sediment deposition. Sediment chronologies were calculated using the known and predictable first order decay rate of the naturally occurring ^{210}Pb isotope (half- life =22.3 y) present in the benthic layer post atmospheric deposition. Wavelength specific gamma emissions derived from the presence of this isotope were quantified in individual sub-samples of sediment on two occasions pre- and post- an incubation period of 3 weeks. The extent of isotopic decay observed in each sample over this period, with respect to loss of ^{210}Pb in the surface layer (establishing initial conditions at t= 0) is then used to approximate the relative sedimentation year. Errors in these measurement, principally derived from the short period of incubation, are constrained using time specific isotopic references point 'anchors', including ^{241}Am and ^{137}Cs known to be present in the sediment chronology exclusively due to fallout from the atmospheric testing of nuclear weapons in 1963 (widely used marker). Results of these analyses for S1 Edgbaston Pool, are displayed in Figure 2.8 and Table 2.2 with the results for S2 and S3 in Appendix A.

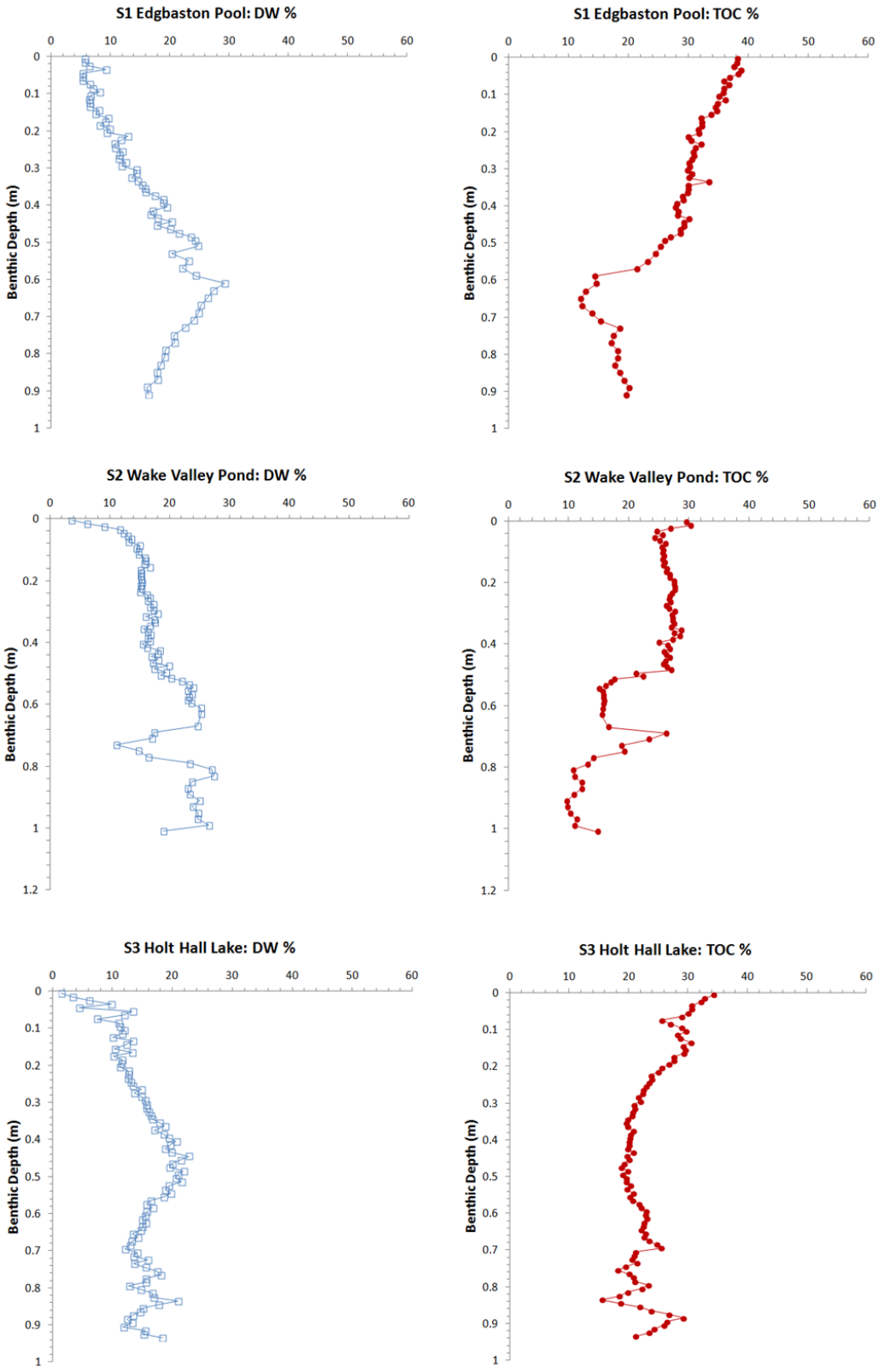


Figure 2.7: Dry weight % and TOC % at sampling sites 1-3 with respect to sampled benthic depth.

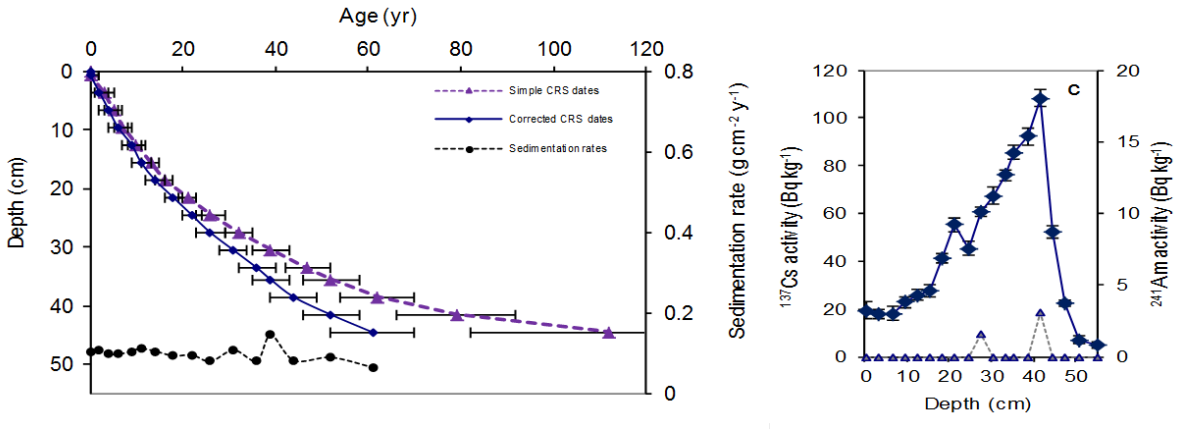


Figure 2.8: (Left) Sediment chronology and sedimentation rates at S1 Edgbaston Pool, as established by the relationship of ^{210}Pb decay with respect to core benthic depth, (Right) ^{241}Am (upper graph) and ^{137}Cs activity (lower graph) with respect to core depth used to constrain ^{210}Pb estimates. Maximum activity spike of ^{241}Am observed at 41.5 cm depth corresponds to the presence of this nuclide as deposited from the testing of atmospherically detonated nuclear weapons in 1963 as confirmed by the additional maximum activity of ^{241}Am occurring concurrently.

Table 2.2: S1 Edgbaston Pool radiometrically calculated sedimentation year and deposition rate with respect to benthic depth.

Depth	Dry mass	Chronology			Sedimentation Rate		
(cm)	(g cm^{-2})	Date (CE)	Age (y)	±	(g cm^{-2} yr^{-})	(cm yr^{-1})	± (%)
0	0	2015	0				
0.5	0.0311	2015	0	2	0.1057	1.527	12.8
3.5	0.2424	2013	2	2	0.1089	1.615	9.9
6.5	0.4359	2011	4	2	0.0997	1.447	12.9
9.5	0.6556	2009	6	2	0.0976	1.31	11.4
12.5	0.8833	2006	9	2	0.1061	1.32	12
15.5	1.1381	2004	11	2	0.1123	1.174	14.3
18.5	1.4575	2001	14	2	0.106	0.923	10.8
21.5	1.8271	1997	18	2	0.0941	0.739	13.7
24.5	2.2215	1993	22	2	0.0963	0.739	16.6
27.5	2.6087	1989	26	3	0.0805	0.58	13.6
30.5	3.0543	1984	31	3	0.1084	0.703	23.6
33.5	3.5346	1979	36	4	0.0813	0.494	17.5
35.5	3.8765	1976	39	4	0.1454	0.794	31.4
38.5	4.4501	1971	44	5	0.0825	0.405	27.2
41.5	5.0984	1963	52	6	0.0903	0.411	35
44.5	5.7673	1954	61	9	0.0655	0.274	38.3

2.3.1.2 Sediment: Freeze Drying Procedure.

Samples selected for chemical analysis were freeze dried using the programmable Christ Beta 2-8 LCS Plus freeze dryer. This apparatus provided for the complete lyophilisation of large volumes of sediments (80- 120 g) containing high percentage water contents (up to 90 %) rapidly through the use of independently heated shelves and the monitoring of sample internal temperatures by which lyophilisation extent could be monitored. Samples were pre-frozen to -85° C sealed in their original sampling bags before being opened to the atmosphere and introduced to the system. Vacuum was applied immediately after sample introduction to avoid boiling and subsequent sample cross contamination. Shelf temperatures, chamber vacuum and procedure duration were optimised to reduce volatile compound losses and ensure maximum target compound recoveries through labelled spike recovery tests of mono- deca BDEs. Despite attempts to control for losses of mono- BDEs, in all cases these compounds were lost from samples at this stage and were not able to be quantified with this method. Recoveries of all other BDEs were not significantly impacted by this procedure. Given the similarity of vapour pressures between BDEs and PBDD/Fs of similar bromination extent, it was assumed that losses of these compounds would also not be significantly impacted by this process. Optimised freeze drying parameters were as follows: shelf temperature= 30 °C and, chamber vacuum= 2 $x10^{-2}$ torr. Internal sample temperature monitoring provided indication that adequate lyophilisation had occurred when sample temperature matched that of the heated shelf, and varied depending on the amount of sample to be dried, however in all cases was complete within 36 h.

2.3.2 Human Breast Milk: Physical Analysis and Pre- Extraction Procedure.

2.3.2.1 Breast Milk: Physical Analysis.

Whole human breast milk (n= 15) samples were provided to the authors for chemical analysis by researchers from the Health and Environment Dept., Imperial College London, in individually sealed

50 mL HDPE centrifuge tubes, maintained at -85 °C. Volumes ranging from 20- 200 mL derived from individual mothers were thawed to 4 °C and measured for wet density by recording the mass of a 5 mL aliquot. Milk samples were subsequently re-frozen to -85 °C and stored for freeze drying.

2.3.2.2 Breast Milk: Freeze Drying Procedure.

Samples were lyophilised in accordance with the procedure outlined in Section 2.3.1.2 for sediment samples and were also introduced to the Christ Beta 2-8 LCS Plus system, frozen to -85 °C, in original sampling containers open to the atmosphere. In this case perforated Al foil covers were placed over the sample containers to further prevent cross contamination.

2.3.2.3 Breast Milk: Lipid Content Determination.

Lipid content was determined on freeze dried samples, following a procedure modified after the EN 1528- 2: 1996 European Standard for the extraction of fat, pesticides and PCBs, and determination of fat content in fatty foods. This method required the extraction of an equivalent mass of freeze dried sample corresponding to 10 mL (whole volume) and was subsequently modified here to provide fat content of an equivalent freeze dried milk mass corresponding to 2 mL whole volume. This was a necessary requirement, due to the small volumes obtained from the study participants, and the likely very low concentrations of target compounds present. The modified protocol was conducted as follows: 2 mL mass equivalent freeze dried milk was weighed and transferred to a 50 mL separation funnel containing 0.5 mL saturated potassium oxalate, 5 mL technical grade ethanol and 10 mL 1: 1 analytical grade hexane: diethyl ether (v/v). This mixture was agitated for a period of 15 min before transfer of the subnatant layer to an additional 20 mL separating funnel containing a further 5 mL 1:1 hexane: diethyl ether (v/v) and 10 mL ethanol. The resulting subnatant was discarded, and the supernatant added to that retained in the previous extraction. 10 mL milli-Q grade H_2O was then added and the non-organic subnatant was then separated and discarded.

Organic phase supernatant, retaining the milk lipid content was subsequently filtered through a column of anhydrous Na_2SO_4 to remove residual H_2O and rinsed with 5 mL hexane to release lipids from the column and into 20 mL pre-weighed glass Erlenmeyer flasks. Filtrates were evaporated at 50 °C to evaporate the liquid phase and lipid mass recorded as the difference between flask mass pre- and post- filtrate addition. Care was taken at all stages of this procedure to endure lipids were thoroughly washed from the glass surfaces of the separating funnels as well as the upper section of the Na_2SO_4 column. Resulting lipid masses of between 10- 45 mg were recorded for these analyses, as measured on a Sartorius Cubis® analytical balance, with a reported resolution of ± 0.01 mg, well within the range of that of the lipid extracted. To ensure the validation of this procedure, 5 replicate extractions were performed on a single breast milk sample of 200 mL provided to the authors. Replicate lipid masses of (mean ±1SD, n= 5) of 29.3 ± 5.2 mg were observed and corresponded to a lipid percentage content of 2.5 ± 0.6 %, deemed to be within an appropriate margin of error for this assessment.

2.3.3 PM_{10}: Air Sample Volume Assessment.

Accurate determination of air volumes pertaining to the quantity of particulate matter collected per sampling period was a necessary requirement for the calculation of contaminant concentrations on a per m^3 ambient air basis. These values were accurately recorded at the time of collection as a function of the sampling equipment (EcoTech Hi- Vol 3000) utilised. These values ranged from 1220-1258 m^3 across all sampling periods and locations.

2.4 Sediments and Breast Milk: Wet Chemical Extraction and Purification.

2.4.1 Selection, Pre- Cleaning and Preparation of Labware and Reagents.

The analysis of organic contaminants at 'ultra' trace concentrations presents additional considerations with respect to the potential for samples contamination from external sources.

Contamination sources in this respect were not likely to contain target compounds themselves, rather the addition of analytically interfering compounds to the overall sample extracts needed to be controlled and monitored throughout the extraction, purification and MS analysis procedures. The following sections describe the selection and preparation of reagents, laboratory instrumentation and solvent selection.

2.4.2 Reagents Selection and Preparation.

All reagents used for these procedures were of at least analytical grade purity and were subjected to additional purification where necessary. All solid reagents, including anhydrous Na_2SO_4, Cu (s), H_2SO_4-impregnated Silica gel were sourced at the highest grade available, and additionally purified following the guidelines provided by the USGS Standard Operating Procedures for the Preparation of Clean Reagents and Labware [89]. All solid reagents used were additionally extracted by pressurised liquid extraction (PLE) on a Thermo Scientific ASE- 350. In all, 3 rinse cycles were performed, each utilising a different solvent combination reflecting that to be used for the extraction of samples. Firstly cells containing filters and reagents for preparation were extracted with hexane: dichloromethane (3:2, v/v), followed by 2 cycles in toluene. ASE parameters for this procedure were as follows: T= 100 °C, Pressure = 1500 psi, Hold time= 1 min, Cycles= 1/ solvent. Extracted reagents were then dried at 140 °C for 24 h and stored at this temperature until use.

2.4.3 Laboratory-ware Selection and Preparation.

All glassware used throughout this study was, soaked in an aqueous solution of Mucasol (2% v/v) for a period of 24 h, before being through scrubbed and rinsed in Milli-Q H_2O. Glassware was then dried at 140 °C for 3 h before being rinsed in a series of solvents decreasing in polarity: acetone, followed by hexane and toluene. Glassware was then dried at S.T.P and stored covered until use.

ASE- 350 cells prior to use for the extraction of samples, were separated and soaked in a 2 % (v/v) aqueous solution of Mucasol for 24 h before being thoroughly scrubbed clean and dried at 140 °C for at least 8 h. All parts of these extraction tubes were rinsed in accordance with the procedure used for glassware with acetone, hexane and toluene. At this point cells were re- dried, assembled for use with the inclusion of new non-used metallic frits (150 μm pore size) and 2x glass fibre filters (terminal end), filled to capacity with pre- rinsed hydromatrix ready for sample extractions.

2.4.4 Analytical Standards

Commercially available analytical standard sets including primary 5 point calibration lines were used for the analysis of BFRs (Wellington Laboratories, BFR- CVS, n= 41 native compounds), PBDD/Fs (Cambridge Isotope Laboratories, CIL- EDF -4507, -4508, -4509 and -4510, n= 14 native compounds) and PCDD/F and dl- PCBs (CIL- EDF -4144, -4145, n= 16 PCDD/F, 4 dl-PCB native compounds). PXDD/F labelled internal standards were not available at the time of analysis. Native standards of PXDD/Fs (n= 10, 6 PXDDs and 4 PXDFs) were provided by Dr. Alwyn Fernandes, FERA, UK. Internally standardised 5 point calibration curves were prepared from CIL- EDF -5410 ($^{13}C_{12}$ 2,4,6,8- TBDF) maintaining a constant (5 pg μL^{-1}) concentration of labelled TBDF with native PXDD/Fs ranging from 50- 1000 fg μL^{-1}. Compounds, concentrations and designations of all standards used in this study are listed in Appendix B. Standards once opened were transferred to 1.5 mL capillary vials and stored at 4 °C.

2.4.5 Sample Extraction and Concentration.

Extraction of selected sediments and breast milk samples was conducted by pressurised liquid extraction (PLE) on the Thermo Scientific Accelerated Solvent Extractor (ASE). Dry weight sample quantities ranging from 3- 6 g were mixed with a 20 % mass percentage of pre-cleaned anhydrous Na_2SO_4, loaded to pre- cleaned ASE tubes and spiked with appropriate internal standards. Samples in

ASE tubes were stood for a period of 15 min to allow for the evaporation of solvent added with the internal standard spikes. Sediment and breast milk samples were both extracted using an optimised method based on adequate sample recovery of all internal standard compounds. ASE parameters of: T= 90°C, Pressure= 1500 psi, Hold Time= 5 min, Cycles = 2/ solvent. A mixture of hexane: dichloromethane (3:2 , v/v) served as the first extractant followed by toluene resulting in a total of 4 extraction cycles per sample. Importantly $Cu_{(s)}$ was not added to ASE extraction tubes for the removal of sulphated contaminants, as is common practice, as this has previously been shown to catalyse the formation of PBDD/Fs from PBDEs at the temperature and pressures employed in extraction [73,90]. Attempts to conduct 'in- cell' clean- up of samples, as has been previously conducted for PBDEs [91] was not successful here, as PBDD/Fs showed very low recoveries, typically < 30 %. Sample extracts were at all times shielded from light by covering glass collection vials and concentration tubes in Al foil to avoid the photolytic degradation of higher brominated PBDEs and PBDD/Fs. Sample extracts were concentrated on a TurboVap evaporator (Biotage, Sweden) in 250 mL pre- cleaned tubes to volumes < 1 mL for transfer to clean- up columns. Ambient particulate samples were provided pre- extracted and were not extracted by the authors. Extraction and clean-up procedures for atmospheric particulate matter are outlined in Section 2.4.8.

2.4.6 Sediment: Wet Chemical Purification.

To meet the specifications required for the MS analysis of PBDD/Fs, the adequate separation of PBDEs as well as low background was required. Accordingly, samples were purified following an adaption and expansion to the method of Yang et al. 2010, for the analysis of PBDE and PCDD/Fs in fish lipids. For this, sample extracts were purified and matrix separated from target compounds using pre- cleaned and conditioned acid impregnated silica columns. Separation of PBDEs and PBDD/Fs (as well as other planar targets) was performed by non/planar fractionation on activated carbon columns from Cape- Technologies (Maine, USA). These were utilised with the addition of

several reagents to ensure as complete purification of target compounds as was possible. The experimental set- up and methodology are explained in the following sections.

2.4.6.1 Sediment: Column Chromatography using Cape- Tech Tandem Acid- Si/ Carbon Columns.

The experimental apparatus used are displayed in Figures 2.8 and 2.9 and required the use of 2 Cape- Tech (ASC15-12) acid silica columns arranged in tandem and 3 Cape-Tech (CCXC2-12) 2 g ultra-clean carbon columns per sample extraction. An additional 10 g $Cu_{(s)}$ and 5 g ANH- Na_2SO_4 were added to the top of each A series column with an additional 3g H_2SO_4- Si (44 % w/w) added to the top of each B series column (Figure 2.8). Columns series A and B post addition of supplementary reagents were each rinsed with 30 mL dichloromethane followed by an additional 30 mL hexane, allowed to drain due to gravity through the columns. Solvent was then discarded. All C series carbon columns (3 per sample: $C_{1,2,3}$) were rinsed with solvents (15 mL each) in the following order: toluene, dichloromethane and hexane. For this carbon columns were untied with solvent reservoir columns and pressurised with N_2 to provide a flow of approximately 1 mL min^{-1} $column^{-1}$ (Figure 2.9). Post rinse, column series A and B were in-line coupled and evaporated sample extracts (< 1 mL volume) were quantitatively transferred to A columns and spiked with 10 µL BFR- SCS (Figure 2.10- 1) as a non-planar internal clean- up standard. 15 mL hexane was added to A series columns to begin the elution process, from the upper A column series to their respective B series column counterparts. Exactly 5 mL eluate was allowed to pass through the B series column, before C_1 series carbon columns were attached to the terminal end of each B series column. This was found to be a critical process, as this fraction was found to contain the vast majority of interfering matrix, and where not performed required additional post- column clean- up purification. Importantly, no target compounds were observed in this fraction. Post initial elution of A series columns, into their respective coupled B and C_1 columns, the A series were elevated clear, and B- C_1 series columns

were connected with individually sealed caps and connected to the N_2 manifold. N_2 was introduced to the columns at a pressure of approximately 1.2 atm providing a flow of ~1 mL min^{-1} $column^{-1}$. Once complete, columns were depressurised, the N_2 manifold was removed and A and B- C_1 series columns reconnected. An additional 10 mL hexane was then added to further elute the A series columns into the B series columns by gravity once more. Upon conclusion of this, A series columns were again elevated, N_2 attached once more to the B and C_1 coupled series columns, re-pressurised and eluted completely. All solvent eluted to this point was then discarded, as all target compounds eluted thus far were found to be retained on the C_1 carbon columns (Figure 2.10- 1). This procedure was repeated a further 2 times, each with 15 mL hexane, and eluate retained in pre- cleaned 50 mL TurboVap collection vials. A and B series columns were discarded and C_1 series columns removed from B series and connected with pre- cleaned solvent reservoirs (Figure 2.9) maintaining their original flow orientation. These were then eluted with 30 mL hexane, followed by 10 mL dichloromethane: hexane (85: 15, v/v) and 5 mL dichloromethane in the forward direction. These fractionates were combined with those previously retained and designated the $F1_a$ non-planar sample extract fraction. C_1 series carbon columns were reversed and eluted with 30 mL toluene, under pressure, fractionates from this were retained and designated the $F2_a$ planar sample extract fraction (Figure 2.10- 2). To ensure complete non/ planar fractionation, $F1_a$ and $F2_a$ fractions were each evaporated to < 1 mL, quantitatively and separately re- fractionated with additional pre-cleaned series C_2 and C_3 carbon columns, following the above procedure. Fractionates from both the $F1_a$ and $F2_a$ combined post C_2 and C_3 elution with hexane, dichloromethane: hexane, and dichloromethane were combined to form the $F1_b$, final non-planar fraction (Figure 2.10- 3, 4). As was consistent with the first secondary fractionation, the $F2_b$ final planar fraction consisted of the reverse toluene fractionate from the C_2 and C_3 columns containing the planar fractions previously present in the $F1_a$ and $F2_a$ fractions (Figure 2.10- 3, 4). Both $F1_b$ and $F2_b$ fractions were subsequently evaporated to near dryness at 30 °C under a gentle flow of $N_{2(g)}$ and quantitatively transferred to 2 mL MS vials with integrated 30 µL micro-inserts. These were then also evaporated to dryness and

sealed and stored at 4 °C for transport to the analysis facility. Upon arrival, sample fractions were reconstituted in appropriate volumes (F1= 10 µL, F2= 5 µL) of corresponding recovery standards, stood for at least 1 h and thoroughly vortexed prior to injection to the analysis instrument.

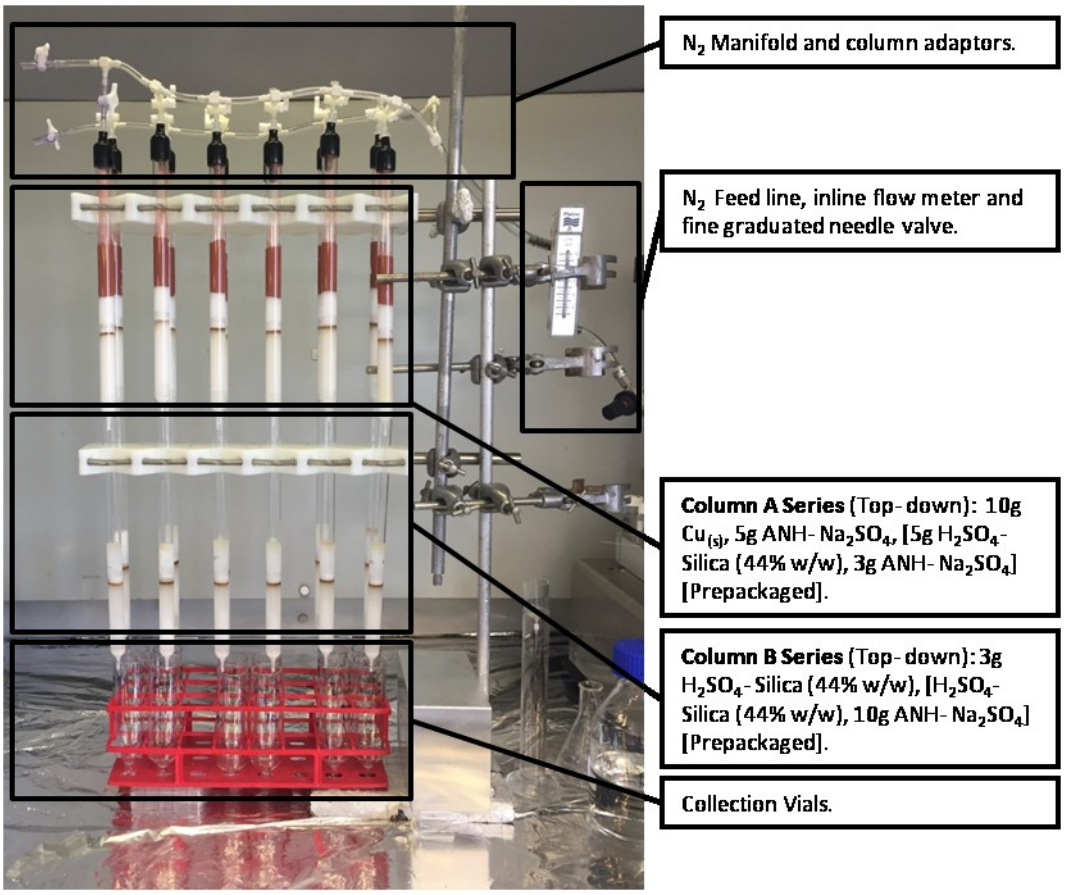


Figure 2.8: Sample chromatographic purification column apparatus, showing the N_2 manifold and column adapters, N_2 flow meter and needle valve, Series A and B columns and reagent additions, and eluate collection vials.

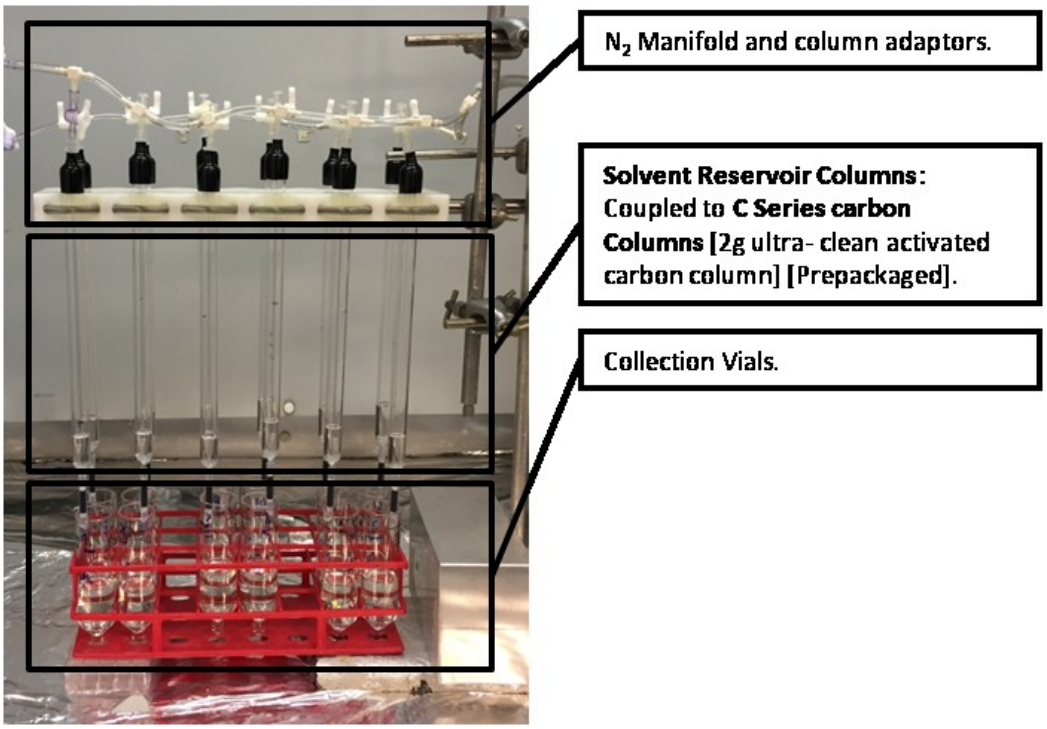


Figure 2.9: Solvent reservoir columns coupled to C Series carbon columns for elution of F1 non-planar and F2 planar sample fractions to their respective collection vials.

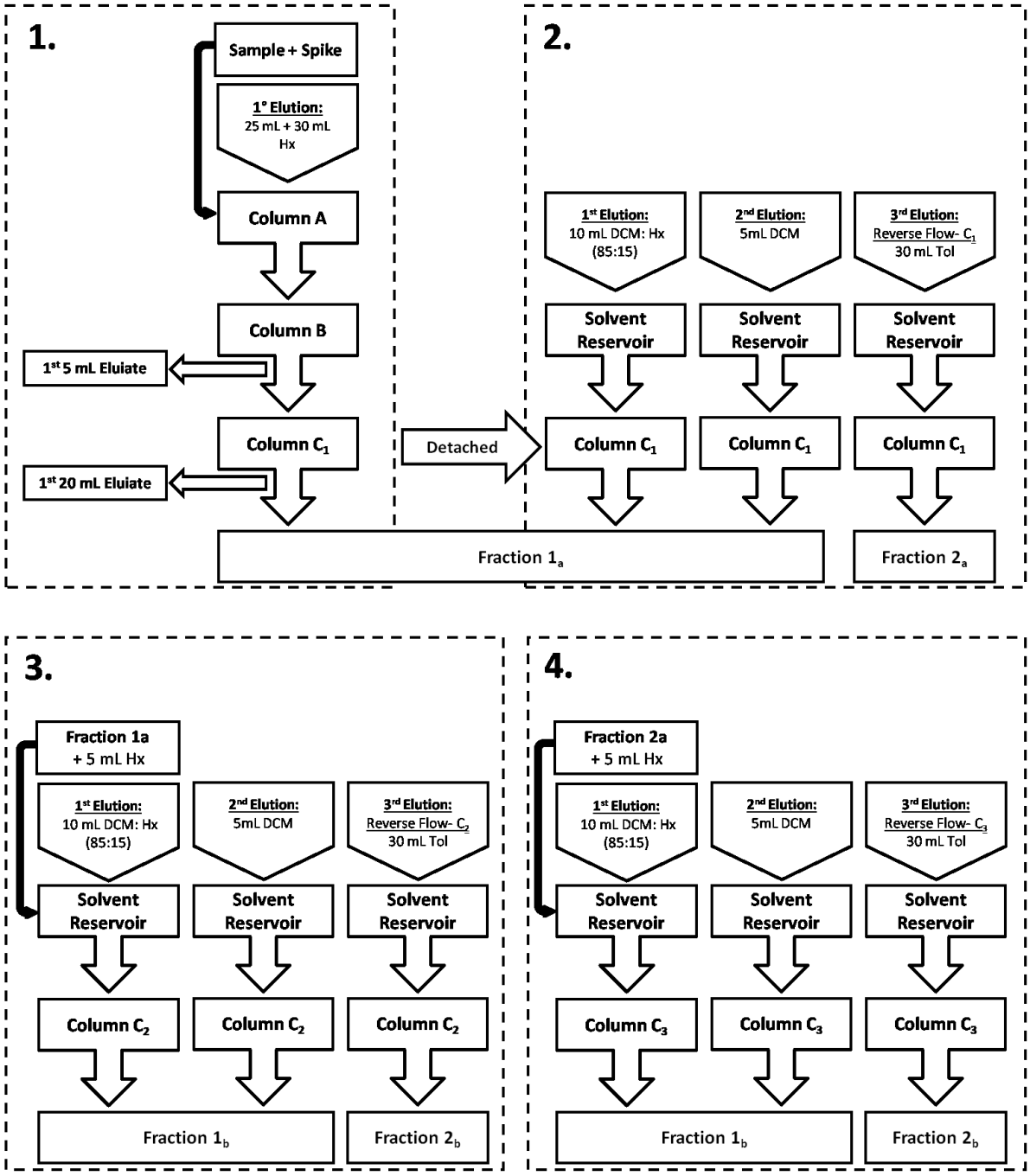


Figure 2.10: Sample Purification Protocol: Extraction procedure follows the indicated numbering sequence: 1. Primary elution, 2.Primary Fractionation, 3. Secondary Fractionation of $F1_a$ non- planar fraction and 4. Secondary fractionation of the $F2_a$ planar fraction to produce 2 final fractions: $F1_b$ (planar) and $F2_b$ (non-planar). Solid arrows indicate additions of sample, clean- up spike and $F1_a$- 2_a fractions. Arrows leaving column B and column C_1 indicate eluate to be discarded.

2.4.7 Breast Milk: Wet Chemical Purification.

Human breast milk samples were extracted in an identical manner as the sediments, however $Cu_{(s)}$ was not added to the A series columns. Breast milk samples were also subjected to an additional lipid removal procedure prior to column purification. For this, milk extracts were evaporated to ~5 mL in 50 mL TurboVap tubes. 10 mL hexane was introduced to samples along with 2.0 mL H_2SO_4 (99.99 %). This solution was stood for a period of 15 min with periodical agitation to facilitate the oxidation of lipids. At this point, clear subnatants comprising the organic fraction containing target compounds were quantitatively removed and re-evaporated (< 1 mL) for transfer to purification columns.

2.4.8 PM_{10}: Wet Chemical Purification.

Particulate samples were provided to the authors by Dr. Karla Pozo, Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Czech Republic. Extraction and clean-up procedures were conducted under the auspices of Dr. Pozo and the RECETOX Trace Analytical Laboratories group in accordance with established methodologies and appropriate QA/QC procedures under ISO/IEC 17025 laboratory accreditation. Samples obtained were analysed for a large suite of compounds including PAHs, PCBs, PCDD/Fs as well as PBDEs. The following procedure was obtained from Dr. Pozo: Known amounts of ^{13}C-labelled internal surrogates of all seventeen 2,3,7,8-substituted PCDD/Fs and twelve dioxin-like PCBs dissolved in n-nonane were added onto quartz fiber filters from ambient air sampling and packed in extraction cartridges of a B-811 extractor (Büchi, Switzerland). Sample matrices were extracted with toluene for 1.5 h at 100°C. Extracts after partial concentration by Syncore Analyst vacuum concentrator (Buchi, Switzerland) were split up at a ratio 9:1 w/w. 10 % of each crude extract was set aside for PAH analysis, with the remainder used for the analysis of PCDD/Fs, PBDD/Fs, dioxin-like PCBs and PBDEs. Toluene was evaporated under a stream of nitrogen and residues dissolved in n-hexane. A multilayer silica

column containing (from bottom) silanized glass wool, silica, potassium silicate, silica, 44% H_2SO_4 on silica, silica and anhydrous Na_2SO_4 was used for the cleanup of the air extracts. The n-hexane eluates were concentrated by a TurboVap evaporator (Biotage, Sweden) and residues dissolved in cyclohexane. A column containing AX-21 active carbon mixed with Celite 545 (1:19 w/w) was used for further extract purification and fractionated to obtain three fractions: cyclohexane-dichloromethane-methanol (2:2:1 v/v) containing non-dioxin-like PCBs and PBDEs (Fraction 1), toluene containing dioxin-like PCBs (Fraction 2) and a reverse flow toluene containing PCDD/Fs and PBDD/Fs (Fraction 3). The carbon column eluates were concentrated to ~0.5 mL and quantitatively transferred to 1.2 mL conical vials with n-hexane. Post final concentration, ^{13}C-labelled recovery standards in n-nonane were added (PCB 162 to fraction 1, PCB 162 along with BDE -29 and -180 to fraction 2 and 1,2,3,4-TCDD to fraction 3). Fraction 1 (PBDEs) Analysis was conducted by the Trace Analysis Group of the University of Masaryk, Brno, Czech Republic. Quantified PBDE congener concentrations were provided to the authors by Dr. Karla Pozo, RECETOX. Fraction 3 of each air sample was subjected to PBDD/F analysis by the authors. On receipt, samples were reconstituted in 8 µL n-nonane, retaining the original dilution present prior to dl- PCB and PCDD/F analysis (1 µL taken/ compound class), sealed and left to stand for 1 hour before thorough sonication and vortexing.

2.5 Analytical Quantification.

Quantification of target compounds and congener groups was conducted on the novel Thermo Scientific GC Q Exactive HRGC/HRAM MS platform. To the best of the authors' knowledge, this work represents the first reported measurements of these analytes produced by this instrumentation. Accordingly extensive instrumental optimisation was required as well as the development of suitable QA/QC protocols for analyte confirmation and quantitation. We describe here the necessary calibration, maintenance and performance specifications of the instrument required, as well as a

detailed description of the optimised GC and MS detection methods employed. In total 3 separate analytical methods were developed, each based on a single 2 µL injection of sample:

1. A screening procedure based on and external calibration, for the semi- quantitative analysis of PBDD/Fs in atmospheric PM_{10} samples.
2. A fully quantitative Selective Ion Monitoring (SIM) isotope dilution method for the analysis of BFRs in the F1 non- planar fractions obtained from both sediment and breast milk samples.
3. A comprehensive Full- Scan (FS) method for the simultaneous analysis of PBDD/Fs and PXDD/Fs in sediment samples. This method was extended to include also the simultaneous detection of PBDD/Fs, PCDD/Fs and dl- PCBs in breast milk samples.

2.5.1 Instrumental Calibration, Maintenance and Analysis Ready-State Specifications.

Prior to the introduction of samples or calibration standards, an assessment of the instrumental performance specifications was required. This procedure ensured that measurements of samples performed were conducted under instrumental conditions sufficient to produce analyte peaks in accordance with the confirmation protocol established (Section: 2.5.1). Instrument readiness was assessed by measurement sensitivity and mass accuracy and was monitored by the injection of a sensitivity standard, HBB (Hexabromobenzene) at a concentration of 1 pg μL^{-1}. Prior to instrument calibration and final tuning, the ion source was removed and subjected to maintenance. Effective ion source maintenance was assessed (post initial tuning) at the temperature of analysis (280 °C) by the monitoring of calibration gas (FC- 43) ion intensities. An observed ion current of the FC- 43 M+2 peak (m/z 209) at intensities > 1 $x10^8$ absolute counts was considered indicative of a sufficiently maintained ion source. Frequent monitoring of this instrument specification was required throughout the analysis of samples and standards, particularly with respect to PBDD/F injections, which required ion maintenance after every 5 injections of samples or CS-5 level calibration standards. Upon successful re- introduction of ion sources, automated mass calibration procedures were conducted to ensure the multiple measurements of FC-43 ions within a mass tolerance of ± 5

ppm across 20 measurements. Ion lenses and acceleration voltages were optimised for maximum transmittance of FC- 43 through the auto-tune procedure. Tuning was considered acceptable when through multiple optimisations peak intensity differences did not exceed 4 % (inter- tune) and the FC- 43 M+2 peak (m/z 209) intensities were > 1 $x10^8$ absolute counts. In addition to these requirements, the use of HBB standard solution was employed to ensure successful instrumental calibration and to record long term instrumental changes. Observed HBB QM and RM peak intensities > 1 $x10^8$ counts at a mass accuracy of <±5 ppm vs. theoretical at 60K resolving power (FWHM) was deemed satisfactory to confirm the instrument was within specifications suitable for sample analysis.

2.5.2 Sample Introduction and Separation- Gas Chromatography.

Appropriate selection of injector port module, liner and chromatographic column as well as appropriate associated parameterisation are critical for the successful analysis of PBDD/Fs and PBDEs especially for the higher brominated more thermally labile analytes (Hagberg 2009). Inadequate selection of parameters or peripherals invariably results in gross analyte loss, regardless of MS detector sensitivity and therefore must be thoroughly investigated and optimised. Accordingly, sample introduction by programmable temperature vaporisation (PTV) was selected as the preferred injection mode in this study. A survey of injection port liners and chromatographic columns based on results of target compound intensities and peak stability over multiple injections, led to the selection of the Thermo Fisher Siltek Metal Liner (1 x 2.75 x 120mm) and Thermo Fisher Scientific Trace Gold Dioxin capillary column (12 m x 0.25 mm x 0.1 μm) for analysis of samples across all matrices. A column length of 12 m was selected as optimal, as a trade off between reductions in chromatographic resolution against adequate signal intensity of OBDF, the most thermally labile compound in the analyte set. Unlike traditional targeted HRMS analyses approaches conducted by magnetic- sector based instrumentation, analysis on the GC Q Exactive posed additional chromatographic challenges. Ion intensities of target analytes when measured Full- Scan

mode suffer significant suppression when baseline total ion counts (TIC) over analyte elution RTs are present above ~10^8 counts. This issue is principally due to ion trap saturation and subsequent analyte competition for injection to the orbital trap for analysis. Consequentially, chromatographic temperature profiles needed to be fine tuned to ensure that target analytes did not elute simultaneously with chromatographic interferences, such as siloxane peaks from the use of silicone-based vial cap liners or other contaminants co- extracted during sample clean up procedures.

2.5.2.1 Sediments, Breast Milk and PM_{10}: Optimised Gas Chromatography Method.

F1 and F2 sample fractions from sediments and breast milk as well as the PM_{10} samples were subjected to the identical chromatographic procedure described below:

Samples (2 µL) were introduced to the column by PTV injector operating in splitless mode. A programmed temperature of injection of 120 °C followed by a ramp profile from 150 °C to 320 °C at 14.5 °C sec^{-1} was employed to ensure minimal degradation of thermally labile analytes. Splitless time of 2 min was deemed sufficient to elute all target compounds from the injection liner before a split flow of He at 50 mL min^{-1} was introduced to begin the cleaning phase. Separation was conducted on a Thermo Fisher Scientific Trace Gold Dioxin capillary column (12 m x 0.25 mm x 0.1 µm) with a constant He flow of 1.3 mL min^{-1} and an initial temperature of 120 °C held for 3 min before ramping to 250 °C at 6.5 °C/min. A second ramp from 250 °C to 305 °C at 8 °C/min held for 7 min was used to ensure elution of all target compounds.

2.5.3 Mass Spectrometric Detection.

Fraction 1 (non- planar) samples were analysed in Selected Ion Monitoring (SIM) Mode. SIM mode was selected for the analysis of PBDEs and NBFRs in sediments and breast milk samples due to the comparatively smaller quantity of target analytes present in this fraction. Further all target analytes present in F1 fractions were present in calibration standards, for which retention times were

established and the analysis of homologue group total concentrations, consisting of unidentified compounds was not required. Fraction 2 (planar) sediment, breast milk and the PM_{10} samples (provided to the authors) were analysed in Full- Scan ion acquisition mode. This mode was selected specifically due to the large number of known and unknown target compounds likely present in samples of this fraction. Detection methods for F1 and F2 are described separately.

2.5.3.1 Mass Resolution Selection.

High resolution analysis is critical for the MS detection of trace organic contaminants, increasingly so for halogenated compounds present at low concentrations. Resolving power is directly related to the selectivity of analyses as increased analytical resolution provides additional certainty for target analyte conformation. Mass resolution above nominal mass is achieved by traditional GC/HRMS (magnetic sector) instrument by means of physically restricting the transmission of the ion beam generated immediately post acceleration. Accordingly, increased mass resolution by traditional analytical approaches reduces analyte signal intensities and therefore restricts the maximum practical resolution to ~20K (10 % Valley). Analytical resolution of analysis by FTICR MS or orbital trap measurements does not decrease the transmission or sensitivity of measurements performed, however does restrict the maximum scan rate achievable considerably. Accordingly, the resolution of analysis, for the analytical method developed here was determined by selecting the highest value possible, to resolve the greatest number of potential interferences while maintaining a scan rate sufficient to provide an adequate number of measurement points across analyte peaks. This differed with respect to the intensity of the analysed peak, however in all cases was found to provide a number of scans sufficient for adequate statistical representation of peaks at a resolution of 60K, which was selected for all analyses conducted here.

2.5.3.2 Sediment and Breast Milk (Fraction 1) Optimised Targeted SIM MS Method.

Fraction 1 (non- planar) sediment and breast milk samples were analysed for target PBDEs and NBFRs by Targeted- SIM mode acquisition. Data was by acquired the instrument from 3 - 26 min RT using positive EI ionisation of 70 eV (50 µA) at a source temperature of 280 °C. A resolution of 60K FWHM was selected for the analysis with an AGC target of 5 $x10^4$ ions with automatically regulated Maximum Ion Injection Times and Microscans set to 1. These settings resulted in a scan rate of between 5- 8 scan sec^{-1} which was positivity related to the intensity of the selected ion. This produced between 18- 28 scans $peak^{-1}$, based on an average peak base width of 3 sec (0.05 min RT), well above that required to achieve adequate statistical relevance (generally agreed to be ~9 measurement points $peak^{-1}$). The Targeted- SIM analysis was multiplexed (MSX count= 2) and conducted over an m/z range of 245- 900 u, to ensure monitoring of the mono- deca-BDE quantification and ratio ions, with an isolation window of ± 12 u sufficient to acquire both native target analytes as well as their respective $^{13}C_{12}$ labelled internal standards within single SIM windows. No exclusion or lock masses were included in this analysis.

2.5.3.3 Sediment, Breast Milk (Fraction 2) and PM_{10}: Optimised Full Scan MS Method.

Fraction 2 (planar) sample fractions as well as atmospheric particulate samples were analysed in Full- Scan Mode over an acquisition period from 2- 26 min RT. As was the case in the analysis of the F1 non-planar fraction samples, molecular ionisation was conducted in positive mode at 70eV (50 µA) with a source temperature of 280 °C. For this analysis, an MS lock Mass of 429.0897 (column bleed) was selected for the maintenance of accurate mass calibration over the analysis run- time. Analyte acquisition was conducted in 3 separate Full Scan RT windows, differing in the mass ranges acquired over these windows. All analyses were conducted at 60k FWHM resolution, with 2 Microscans, an AGC Target of 1 $x10^6$ counts and Automatic Ion Injection Times. Scans were conducted over 245- 600 u from RT= 2.0- 15 min, 280- 900 u (RT= 15- 18 min) and 750- 1200 u from

RT= 18- 26 min. These ranges were selected to capture not only the target compounds in the data set, but also the M+[PBDE] base peaks for confirmation of the exclusion of their interference. Mass ranges of acquisition were narrowed in the later RT ranges to reduce background interference and enhance the sensitivity of the less intense hepta- and octa- PBDD/Fs peaks.

2.5.4 Data Handling and Analysis.

Data analysis including quantification and confirmation of analytes was conducted in Target Quan v.3.2.1 (Thermo Scientific). Data visualisation and ion mass simulations were conducted using the Thermo Scientific Xcalibur software package v.3.1.66.1.

2.6 Analyte Confirmation, Quantification and QA/QC Protocols.

Protocols for quantification, confirmation as well as QA/QC processes differed depending upon the analysis method employed. Sediment and breast milk samples of both F1 and F2 fractions were quantified by the isotope dilution method and accordingly native target analytes were confirmed against their respective internal standards. PM_{10} samples were semi- quantitatively assessed for PBDD/Fs using an external calibration only and were not subject to the confirmation procedure employed for the sediment or breast milk samples. Accordingly, descriptions of analytical procedures for each approach are described separately.

2.6.1 Sediment and Breast Milk: Analyte Confirmation, Quantification and QA/QC Protocols.

2.6.1.1 Analyte Calibration.

Calibration lines (5 point) were generated from a series of primary calibration standard solutions for PBDEs and NBFRs (Wellington BFR- CVS- CS1- 5), PBDD/Fs (CIL- EDF 4507- CS1- 5), PCDD/Fs and dl-PCBs (CIL- EDF 4143- CS1- 7). A PXDD/F calibration series (5 point) of containing native target congeners was prepared with the addition of $^{13}C_{12}$ labelled 2,4,6,8- TBDF (CIL- EDF 4510) for internal standardisation of all PXDD/Fs. While not strictly appropriate, alternatives were not available at the time of analysis. Analyte calibration was performed prior to the injection of sample as well as at the conclusion of analysis runs to assess instrumental performance. Each calibration series was constructed through the linear regression of analyte: IS peak area ratios vs. known analyte concentrations present in calibration solutions. R^2 values and regression RSDs were assessed as indicators of calibration line linearity and suitability. Relative response factors RRFs were calculated for each analyte. RRF relative standard deviations in excess of 10 % were deemed unsuitable for quantification and required re-injection prior to sample quantification.

2.6.1.2 Analyte Quantification.

Target analyte congeners and internal standards present in calibration solutions were quantified against corresponding areas of quantification ions (QM) as measured within a mass tolerance window of 10 ppm (i.e. ± 5ppm) from simulated compound mass spectra. PBDEs of substitution order greater than 4 (exclusive) were quantified against their corresponding $[M^+ - 2Br]$ ions as these were observed to be the highest intensity mass fragments observed across full scan spectra. PBDD/Fs were also subject to the same ion selection criteria as PBDEs. PXDD/Fs, and NBFRs were quantified against [M+] theoretical ion intensities which in these cases were observed as the most intense spectral beam in their 1^o ion cluster. Analyte quantification was conducted by Equation: 2.1.

Eq: 2.1 $$. Conc_{a-i} = \frac{(A_{QM_{a-i}} \times SpAmt_{IS})}{A_{QM_{Std-i}} \times RF_{a-i}} \times \frac{V_{smp}}{M_{smp}}$$

Where: $Conc_{a\text{-}i}$ refers to the concentration of analyte- *i*, A_{QM} refers to the QM peak areas of the analyte (a- *i*) and its corresponding internal standard (Std- *i*). $SpAmt_{IS}$ is the specified amount of internal standard present, and $RF_{a\text{-}i}$ is the Average Response Factor for the analyte a-*i* as calculated from the corresponding analytes' calibration curve (conducted as a non- weighted linear regression of native: internal standard area ratios using Eq 2.1 also, and substituting 1 for the RF value of recovery standards vs. internal standard peaks and omitting the final quotient). V_{sap} and M_{smp} here refer to the volume of the sample extract injected and the mass of the sample extracted. Here M_{smp} can be on a whole weight, DW, lw or OC basis depending on the concentration required.

2.6.1.3 Procedural Blanks.

Method blanks consisting of 6 g anhydrous Na_2SO_4 were incorporated into each analysis batch consisting of 12 samples (inclusive) and treated analogously to those containing samples. The presence of target analytes in method blanks was assessed. No instances of blank contamination were observed in any of the analyses performed.

2.6.1.4 Internal Standard Recoveries.

Recoveries of internal standards spiked prior to extraction were calculated for all compound groups in all samples across the entire data set. Internal standard recoveries were calculated by Equation: 2.2.

Eq: 2.2. $$Recovery_{IS-i}\,(\%) = \frac{\left(100 \times \frac{M_{meas_{IS-i}}}{M_{Specf_{IS-i}} \times M_{Smp}}\right)}{V_{Smp}}$$

Where: recovery $_{(IS\text{-}i)}$ in % corresponds to that of the recovery of Internal Standard (*i*), $M_{meas\ (IS\text{-}i)}$ is the measured mass corresponding to the measurement of the internal standard on a per injection basis by Eq. 2.1, $M_{specf\ (IS\text{-}\ i)}$ is the specified amount of IS (*i*) added to the sample pre- extraction, M_{smp} and V_{smp} refer to the mass of the sample extracted and its corresponding extract volume respectively.

2.6.1.5 Limits of Detection and Quantification.

Instrument Detection Levels (IDLs) were calculated from the data pertaining to the lowest calibration point in each series using Equation 2.3.

Eq: 2.3. $$IDL_{a-i} = \left(\frac{\sum Noise_{a-i} \times SpAmt_{IS-i}}{\sum Height_{Is-i} \times RF_{a-i}}\right) \times \left(\frac{V_{smp}}{M_{smp}}\right)$$

Where: IDL is the instrument detection limit concentration of analyte (*i*), ∑noise refers to the noise height measured at 6 equidistant points around the analyte peak (*i*) using the ICIS INCOS method [92], $SpAmt_{IS-i}$ and $\sum Height_{IS-i}$ refer to the specified amount of the internal standard used for the quantification of analyte (*i*) and the corresponding sum of their respective QM and RM peak heights respectively. RF_{a-i} refers to the calculated response factor for the native analyte (*i*) and V_{smp} and M_{smp} are the sample extract volume and sample mass respectively. IDLs are displayed in Tables 2.4- 2.6).

Sample Detection Limits (SDLs) were calculated from IDL values for each analyte in each sample analysed by Equation 2.4. Method Detection Limits (MDLs) were calculated as for SDL, using averaged % IS recoveries and (SS) sample quantities.

Eq: 2.4 $$SDL_{a-i} = \frac{IDL_{a-i} \times V_{smp}}{V_{inj} \times SS} \times \frac{100}{\%\ IS\ Recovery}$$

Where SDL is the individual compound detection limit of (i) exclusive to the sample analysed. IDL is the instrument detection limit (as previously defined) V_{smp}, V_{inj} and SS refer to final extract volume, the volume injected for analysis and SS the quantity of material sampled. IS Recovery is also as previously defined.

2.6.1.6 Chromatographic Assessment.

To provide a basis to monitor and control isobaric interferences arising from incomplete sample fractionation chromatographic conditions including sample introduction and chromatographic temperature profiles were standardised for the analysis of both F1 (non- planar) and F2 (planar) sample fractions. Injection port and oven temperature profiles were optimised to prevent the co-elution of all known target analytes present in the calibration solutions of all compound classes, as well as to ensure target analytes did not co- elute with interfering signals derived from the presence

of contaminate peaks, present in samples or calibration standards. To ensure this, mid- point calibration standards of each compound class were analysed and assessed prior to the introduction of samples to the instrument for analysis.

2.6.2 Isobaric Interferences and Target Analyte Conformation Protocol.

The co-elutions of contaminants isobaric with target analytes has the potential to produce quantification errors and lead to false positive confirmations. Identification and control of isobaric interferences in the quantification of low abundant analytes is especially crucial, as QM analyte peaks are often present at intensities many orders of magnitude lower than their respective interference. The majority of identified interferences acting upon the analytes targeted in these analyses were controlled by the high resolving power of the analytical procedure. Despite this, a range unresolved interfering compound ions still remain present. Many, due to structural similarities and the presence of substituted halogens, produce ion fragmentation patterns indistinguishable from target analytes through the use of QM- RM ratios alone. This leaves chromatographic separation and the monitoring of compounds known to produce interferences, as the primary methods for their control. Accordingly a survey of compounds with the potential for interference with the target compound sets analysed here was conducted. Accurate mass simulations of 1° ion clusters of a range of these compounds were performed, ions reordered and monitored to ensure exclusion from target compound concentrations reported. The full-scan ion monitoring mode afforded by the GC Q Exactive provided for the recording of all ions present across acquisition time and m/z scan ranges. Scan ranges defined for analysis were purposely broad to record ion clusters of interfering contaminants and control of these was conducted through manual inspection and exclusion of all target analytes observed to chromatographically co- elute with respective isobaric interfering contaminants.

For the exclusion of PBDE interference with PBDFs in the analysis, the protocol developed by Donnelly et al., 1987 was utilised. For this, confirmation of PBDF analyte peaks is provided by the monitoring of confirmatory $[PBDF\text{-}COBr^{\bullet}]^{+}$ ions. The formation of which is considered to occur in the ionisation of PBDFs exclusively. Accordingly, PBDF target analytes were only qualified for quantification when the presence of their respective $-COBr^{\bullet+}$ ion was demonstrated.

Confirmation of target analytes for quantification required the following:

1. RRF RSD of less than 10 % must be present for native analyte peaks across all calibration points before samples are to be quantified.
2. Internal standard recovery must be demonstrated within 50- 110 %
3. QM peak presence at a S:N > 5.
4. Analyte elution within ± 2 s of its corresponding internal standard, or where a corresponding internal standard is not present, elution within ± 2 s of its specified retention time as observed in calibration standards.
5. QM and RM analyte peaks must be present at within ± 5 ppm of theoretical values and analysed at a resolving power not less than 60K FWHM.
6. QM:RM peak area ratios must be observed within ± 15 % with respect to values observed in calibration standards.
7. Confirmation of congener identity can only be confirmed when target peak is present at > 50 % baseline separation from other target peaks.
8. QM and RM analyte peaks must be visibly confirmed to elute in the absence of known isobaric interferences.
9. PBDF analyte peaks must demonstrate the presence of their respective $-COBr^{\bullet+}$ confirmation ion within ± 20 %.

2.6.3 PM_{10}: PBDD/F Analysis Procedures, QA/QC Protocols and Method Validation.

Analysis of PBDD/Fs was conducted semi-quantitatively against a 5 point external calibration on a Thermo Scientific GC Q Exactive HRMS against known native concentrations contained in Cambridge Isotope Laboratories' (CIL) EDF-5407 PBDD/F calibration series. QC standards (CIL EDF- 5407-3 mid range calibration standard) were employed for method error determinations bracketing 1 in 3 samples injected. Method blank samples were not provided to the authors for analysis and recovery determinations were not possible as the samples were not spiked with appropriate recovery standards. Three calibration lines for each of the 14 native PBDD/F congeners contained in the standard calibration series (CIL EDF- 5407) were generated; at the beginning of the analysis batch, the middle and upon conclusion of the analysis series. No significant statistical differences in concentrations of individual congeners between calibration lines conducted throughout the analysis series were observed (Student's t-test 2-sided; $p< 0.05$). Calibration line equations were averaged and subsequently used for PBDD/F quantification. In all cases R^2 values were above 0.9990 accept for the averaged OBDF and OBDD calibration lines which returned regression coefficients of 0.9974 and 0.9983 respectively. Congener specific averaged calibration line linearity (R^2) and RSD (n=3) values are displayed in Table 2.3.

Measurement error, presumed to be predominantly due to instrument drift and syringe volume imprecision occurring over the period of analysis was estimated by the use of a QC standard (CIL EDF 5407-3; mid range calibration standard), injected after every third sample. This standard was selected as concentrations therein most closely resembled those observed in the initial 3 samples injected. Concentrations of native congeners contained in the QC injections were treated as unknowns and subjected to identical numerical quantification as were the congeners quantified in the air samples analysed. Mean values obtained for each congener across all 4 QC injections were found to be statistically similar to the mean values of their respective counterparts analysed in the

derivation of the calibration curves (Student's t-test 2-sided $p < 0.05$). Accuracy and precision of the measurements was determined by calculating mean concentration differences obtained by repeated measurements of the QC standard against known values contained therein (accuracy) and by calculating the mean relative error obtained from those QC injections (precision), and are expected to be representative of errors associated with sample quantification as well as to be indicative of overall method certainty and reproducibility. Congener specific accuracy of the method along with individual QC congener concentrations are displayed in table 2.3. QC concentration deviation showed no systematic error with respect to time, suggesting instrument drift was negligible over the period of analysis. Method accuracy, here represented by relative mean error (%) was in all cases below 20% except for HxBDF and OBDF which yielded reproducibility to within 20.6 and 31.7 % respectively and was thought predominantly but not entirely attributable to inter-sample injection volume variability and inconsistent PBDD/F on-column degradation, especially in the case of thermally labile higher brominated congeners. Non- 2,3,7,8 substituted PBDD/F congeners were expected to be far more prevalent in air samples analysed. These congener composite totals were calculated against calibration points where both slopes and offsets were averaged from all similarly substituted congeners present in calibration standards used. For example total sample HxBDD content was analysed vs. the average of all three calibration lines for the co-eluted 1,2,3,4,7,8+ 1,2,3,6,7,8- HxBDD (averaged slope= 137745×X, averaged offset= -304671; n= 3) combined with the averaged slope and offset for the 3 calibration lines of 1,2,3,7,8,9- HxBDD (averaged slope= 61493.4×X, averaged offset= -192844; n= 3) yielding the calibration line for total HxBDD of Y= -248757.5+ 99619.2×X; (n= 6). This calculation yielded a calibration line between those calculated for individual HxBDD congeners.

2.6.3.1 IDL, SDL and MDL Determinations.

Instrument detection limits were defined as the concentration of and individual target native compound sufficient to produce a S:N ratio of 3:1. Values for IDL calculations were composed as composite averages of individual congeners present in the lowest concentration point across the 3 calibration lines composed for quantification. Sample detection limits used were calculated via Eq: 2.4, with SS values corresponding to the volume of normalised air sampled (here ranging from 1502 - 1563 Nm^3). % IS recovery in this case was not determined empirically for the PBDD/Fs analysed as ISs were not utilised in this investigation (external calibration). A value of 80 % was assumed as this was determined for the PCDD/Fs analysed in these samples (further data not available to the authors). MDL values were compiled from target compound IDLs and were calculated as for SDL substituting individual air masses with the average air mass sampled across all sampling sites (1529 Nm^{-3}) MDLs for individual PBDD/F congeners in the data set and are displayed in Table 2.3. Composite SDLs for the determination of total congener detection limits where more than one congener was present in the CIL-EDF-5407 calibration were averaged and used accordingly.

Table 2.3: Quality Assurance, Calibration data and Instrumental and Method Detection Limits pertaining to the screening of PBDD/Fs in air samples.

	Quality Assurance and Control							Calibration and Limits of Quantification			
	Standard	QC-1	QC-2	QC-3	QC-4	Mean ±SD	Accuracy %	Linearity (R^2)	RSD (n= 3)	IDL (pg μL^{-1})	MDL (fg Nm^{-3})
Dioxins											
2,3,7,8-TBDD	2.00	2.3	2.1	2.2	2.1	2.2± 0.1	17.7	0.9999	**10.11**	**0.05**	**0.26**
Total TBDD	2.00	2.3	2.1	2.2	2.1	2.2± 0.1	17.7	0.9999	**10.11**	0.05	**0.26**
1,2,3,7,8-PeBDD	4.00	3.6	3.8	3.7	3.7	3.7± 0.1	18.1	0.9997	**6.72**	0.03	**0.14**
Total PeBDD	4.00	3.6	3.8	3.7	3.7	3.7± 0.1	18.1	0.9997	**6.72**	0.03	**0.14**
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD [a]	24.00	25.1	23.9	23.7	24.3	24.2± 0.6	11.0	0.9996	**7.02**	0.03	**0.16**
1,2,3,7,8,9-HxBDD	12.00	11.1	10.8	11.6	10.5	11.0± 0.5	18.5	0.9995	**9.82**	0.03	**0.16**
Total HxBDD	36.00	36.2	34.7	35.3	36.5	35.6± 0.8	11.0	0.9995	**8.56**	0.03	**0.16**
1,2,3,4,6,7,8-HpBDD	15.00	15.8	16.9	15.4	16.7	16.2± 0.7	18.0	0.9996	**7.16**	0.06	**0.31**
Total HpBDD	15.00	15.8	16.9	15.4	16.7	16.2± 0.7	18.0	0.9996	**7.16**	0.06	**0.31**
OBDD	20.00	19.2	19.0	23.7	18.6	20.1± 2.4	1.6	0.9983	**5.04**	0.13	**0.70**
Furans											
2,4,6,8-TBDF	4.00	4.2	4.1	4.4	4.5	4.3± 0.2	17.6	0.9997	**3.64**	0.01	**0.07**
2,3,7,8-TBDF	4.00	4.4	4.6	4.0	3.8	4.2± 0.4	15.0	0.9999	**7.92**	0.01	**0.05**
Total TBDF	8.00	7.8	8.7	8.4	8.3	8.3± 0.4	13.6	0.9998	**6.01**	0.01	**0.06**
1,2,3,7,8-PeBDF	8.00	8.9	9.0	7.7	5.5	7.8± 1.6	12.8	0.9996	**7.15**	0.08	**0.39**
2,3,4,7,8-PeBDF	8.00	8.5	8.5	7.4	5.4	7.5± 1.5	16.9	0.9997	**6.76**	0.07	**0.38**
Total PeBDF	16.00	17.4	17.5	15.1	10.9	15.2± 3.1	14.8	0.9996	**7.00**	0.07	**0.39**
1,2,3,4,7,8-HxBDF	12.00	13.5	14.3	13.5	11.8	13.3± 1.1	20.6	0.9999	**6.54**	0.10	**0.51**
Total HxBDF	12.00	13.5	14.3	13.5	11.8	13.3± 1.1	20.6	0.9999	**6.54**	0.10	**0.51**
1,2,3,4,6,7,8-HpBDF	15.00	15.5	15.0	14.7	16.2	15.4± 0.7	12.4	0.9997	**6.51**	0.08	**0.43**
Total HpBDF	15.00	15.4	15.1	14.7	17.0	15.5± 1.0	13.6	0.9997	**6.51**	0.08	**0.43**
OBDF*	20.00	13.3	14.8	11.7	14.9	13.7± 1.5	31.7	0.9974	**1.15**	0.87*	**4.55***

Standard column refers to certified concentrations as listed present in the CIL-5408 CS-3 Calibration solution

% accuracy is calculated as the relative error between concentrations quantified in QC injections (CIL- 5407 CS-3) vs. known concentrations present (column 1) as a surrogate for method accuracy.

IDL based on the concentration of native compound at an S:N = 3 with an injection of 2 µL. MDLs are based on average air volume sampled (1529 Nm^{-3}) and recover of 80%.

*OBDF calculated from 3 calibration points only. IDL and MDL are likely reduced due to the IDL and MDL methods utilised and may not reflect actual detection limits.

2.6.3.2 Isobaric Interferences and PBDF Congener Confirmations.

Several methods were employed to negate the potential influence of isobaric interferences in the quantification of analyte peaks. PBDEs potentially present in fraction 3 air samples not adequately fractionated during cleanup were of main concern. The presence of PBDEs in samples analysed was conducted by several approaches. For 2,3,7,8- substituted congeners RT matching to within ± 0.1 min was achieved across all QC's and calibration points for all congeners analysed and was therefore stipulated as the first requirement for 2,3,7,8- PBDD/F congener confirmation in samples. Secondly, 2,3,7,8-PBDF RTs were compared with RTs of PBDEs injected under identical chromatographic conditions. For this purpose the Wellington BFR-CS3 standard containing 41 native PBDE congeners was injected. 2,3,7,8-PBDD/Fs eluting without baseline separation from the $[\text{-4BrBDE}]^+$ potentially interfering peaks were not confirmed. However, due to the nature of the samples, the presence of a multitude of non-2,3,7,8 substituted PBDD/Fs were expected to be present in vastly higher concentrations and were also expected to elute over a relatively larger RT range. As standards of these compounds were not available, the potential for RT matching was not feasible. In this case additional confirmation requirements were utilised. Firstly, all confirmed composite congener mass traces were compared against those for relevant interfering PBDE congeners, injected externally under identical chromatographic conditions. In cases were interfering PBDE peaks were present as identified by the presence of peaks in [M+BDE] mass traces of samples, quantification was excluded over the entire RT range for which PBDEs interactions would be plausible (see Figure 2.10- PBDF Quantification Exclusion Zone). An example of this confirmation strategy is displayed in Figure 2.10 This process was conducted for all PBDF congeners in all air samples analysed.

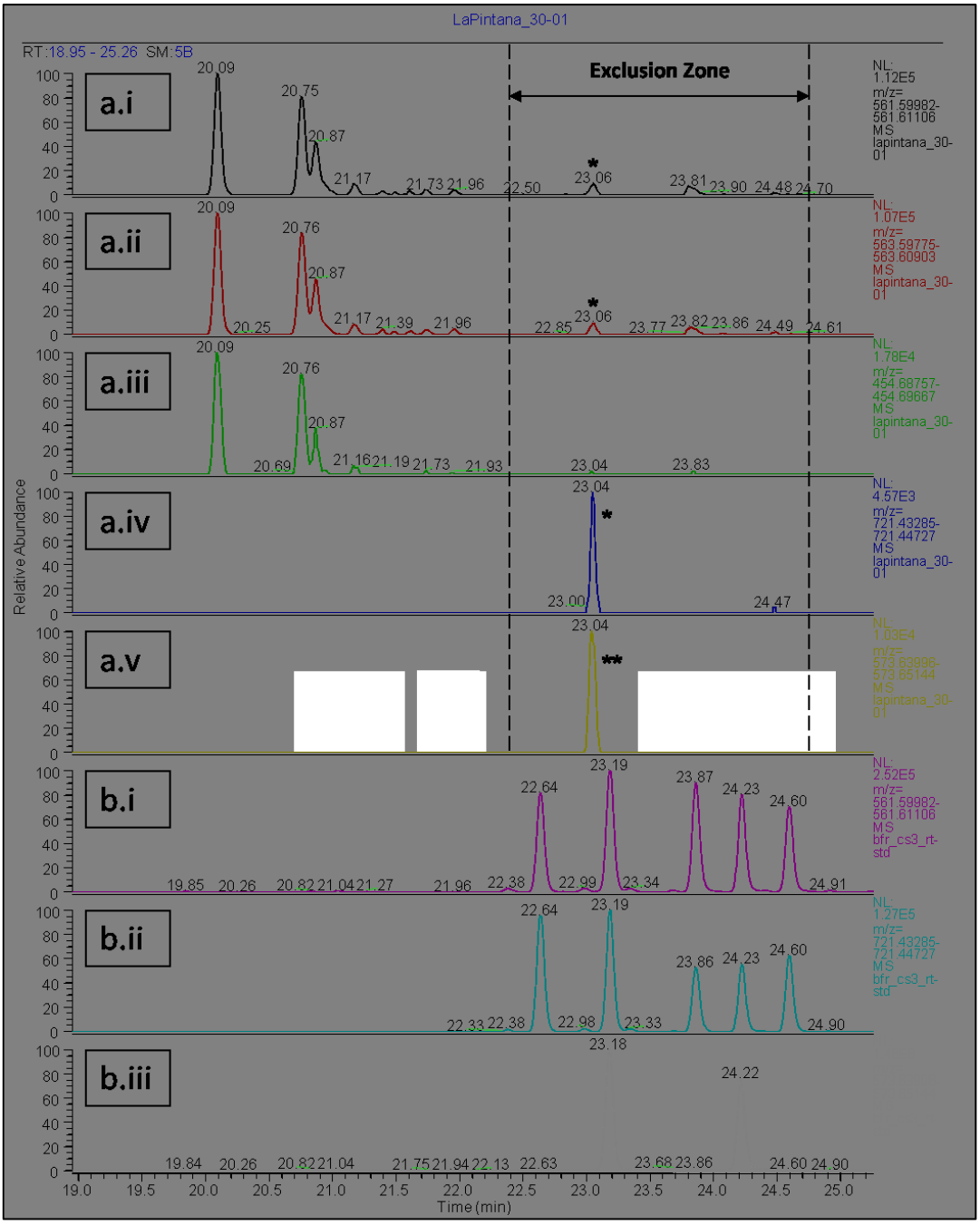


Figure 2.10: Monitored mass traces for the confirmation of PeBDFs in air sample LaPintana 30-01. Mass traces (a.i) to (a.v) are extracted from the injection of sample LaPintana 30-01. Traces (b.i) to (b.iii) pertain to an external injection of Wellington BFR-CS3 conducted under identical chromatographic conditions. Traces (a.i) and (a.ii) are extracted ion chromatograms for the PeBDF Quantification ([QM-PeBDF]) and Ratio ions ([RM-PeBDF]) respectively. (a.iii) shows the mass trace of the $[PeBDF\text{-}COBr^{\bullet}]^{+}$ 'confirmation' ion. Chromatogram (a.iv) traces the mass of the $[M+HpBDE]^{+}$ ion exclusive to the presence of interfering native HpBDEs, which was confirmed by the presence of its counterpart $^{13}C_{12}$-HpBDE standard in (a.v). (b.i) through (b.iii) show the RTs of potential PeBDF isobaric interferences as monitored on the [QM-PeBDF] mass trace, the HpBDE native base peak $[M+ HpBDE]^{+}$ and its counterpart $^{13}C_{12}$-HpBDE ion respectively in the BFR-CS3 standard. The figure also shows the presence of a PeBDF quantification exclusion zone within which PeBDFs peaks present in air samples are excluded from quantification due to uncertainty of interference from HpBDEs. Examples of these are denoted on the figure with asterisks and are likely derived from BDE-183 not sufficiently fractionated during sample cleanup. Confirmation is provided in (a.v) with the denotation of **'s next to a peak believed to be composed of ions originating from the $^{13}C_{12}$-BDE-183 cleanup standard spiked prior to sample extraction. Analysis was conducted in all cases at 60,000 mass resolution and reported at ±10 ppm mass deviation.

2.7 Sediment and Breast Milk: Method Evaluation and Validation.

Instrumental validation was performed by assessment of calibration lines and multiple calibration standard injections. Method validation incorporating an assessment of the extraction and clean- up procedure was performed by multiple extraction and analysis of the NIST Certified Standard Reference Material, SRM 1944: New York/ New Jersey Waterway Sediment. In total, 7 SRM samples were analysed consisting of 1 batch of 5 samples + 1 procedural blank and the addition of 1 SRM to each of two sediment extraction batches. PBDEs and PBDD/Fs were quantified in all 7 SRMs analysed, with PXDD/Fs quantified in only 2 instances. PCDD/Fs and dl- PCBs were not determined in SRM samples.

2.7.1 Instrumental Accuracy and Reproducibility.

An assessment of instrumental method suitability, including confirmation of calibration linearity, and instrumental accuracy and reproducibility was conducted by the injection of calibration standards. Calibration standards provided appropriate concentration ranges for the measurement of BFRs (0.25- 1000 pg μL^{-1}), PCDD/Fs and dl- PCBs (0.03- 60 pg μL^{-1}) in the samples, however for PBDD/Fs and PXDD/Fs several measurements were conducted above and below the calibration ranges of 0.1- 500 pg μL^{-1} (PBDD/Fs) and 0.05- 1000 pg μL^{-1} (PXDD/Fs). In these cases linearity of the calibration function was assumed. Calibration line linearity was assessed by inspection of 10 separately injected calibration series performed on different occasions throughout the periods of sample analysis. Results pertaining to the average linearity of calibration sequences (n=10/ compound group) are displayed in Tables 2.4- 2.6. Results showed consistent R^2 values for all target analytes > 0.999 and were accordingly deemed satisfactory. Relative response factor RSDs were also inspected across these calibration series and in all cases were observed to be below 10 %, except for 1,2,3,4,6,7,8-HpBDD which was observed at 14.50 %. Averaged calibration slope gradients for PXDD/F analytes were also calculated to provide an indication of method sensitivity as defined by the change in

observed concentration with respect to change in observed analyte: internal standard area ratio (R_A). Average sensitivity of the PXDD/F instrumental method for each analyte is displayed in Table 2.6. Slope values for these compounds were revealed to be on the order of 10^{-3} indicating that small changes in R_A values produced large effects on analyte concentrations. While these values were deemed suitable for analysis, reducing the concentration difference between the TBDF internal standard (5 pg μL^{-1}) with respect to the PXDD/F target analytes (0.05- 1 pg μL^{-1}) across the calibration series in retrospect would have served to increase PXDD/F instrumental sensitivity. The difference in calibration line gradient with respect to that of the other compound sets analysed is illustrated in the presentation of representative calibration curves of individual compounds from other target analyte classes in Figure 2.11.

To assess instrumental accuracy and reproducibility of measurements a series of calibration standards were injected and treated as unknown sample injections. Accordingly, these were subject to identical QA/QC and data handling procedures as outlined in Section 2.5. For this assessment multiple sequential injections of high and low point calibration standards were performed. By injecting low followed by high calibration levels assessment of analyte carryover, injection port and detection robustness could be performed. The results of these analyses formed the basis of analyte method accuracy for those compounds not present in the Standard Reference Material as represented by the absolute relative error (%) calculated from the difference between mean concentrations observed (n= 10) and their respective stated concentration in calibration standards at the levels assessed (Tables 2.4- 2.6). Instrumental reproducibility was here defined at both calibration levels assessed by the standard deviation (1 SD, n= 10) of the mean concentrations observed. Instrumental accuracy across the 39 individual PBDE analytes assessed ranged from 0.11–14.89 % observed for BDE- 205 and BDE- 196 respectively at CS-1 concentration level and 0.04- 9.24 % for BDE- 138 and BDE- 30 in the high point injections respectively. Elevated deviations (decreased

accuracy) were generally observed for the target PBDD/F compounds in the analysis and ranged from 3.0- 22.6 % the latter attributed to the low abundance signal received for OBDD in the low calibration level injections. Accuracy was observed to increase for the PBDD/Fs in the multiple injection of the CS-4 high point calibration standard with all congeners showing relative error < 10 %, with the exception once more of OBDD which was recorded at a value of 16.2 %. The CS-4 calibration standard level was selected here for PBDD/F assessment as excessive ion source fouling would be expected across the sequential injection of 10 CS-5 level standards. PXDD/F analyte instrumental accuracy of < 10 % relative error was observed for all congeners at the CS- 1 concentration level of 50 fg (on column) apart from the 2-Br-7,8-CDD congener at 10.3 %. Accuracy decreased overall at the 1 pg levels however remained < 11 % for all congeners.

Reproducibility (1SD) at n= 10 injections was observed on a range of between 2- 3 orders of magnitude lower than analyte concentrations at both calibration points for all compounds in the data set, with the exceptions of the higher brominated BDEs (BDE -205 to -209) and the octa-substituted PBDD/Fs (Tables 2.4- 2.6). PCDD/Fs, dl-PCBs and NBFRs were also subject to an identical instrumentation validation process and returned values in all cases within the ranges of those reported here, and were accordingly not individually tabulated for display.

Instrumental detection limits for analysis as defined by Eq: 2.3 were calculated for each analyte in the target set and displayed in Tables 2.4-2.6. These were deemed suitable for the analysis based on previously quantified environmental levels.

Table 2.4: PBDE and NBFR Method Validation Data.

	CS-1-Conc±SD (n=10)	CS-1 Value	Rel. % Error	CS-5 Conc±SD (n=10)	CS-5 Value	Rel. % Error	Linearity (n=10)	RRF RSD (%)	IDL (pg inj.$^{-1}$)	MDL (pg g^{-1} dw)	SRM (ng g^{-1} dw)	SRM Ref. Values
BDE-7	0.25±0.03	0.25	0.44	104.59±3.59	100	4.59	0.99998	0.86	0.02	0.9	0.761±0.039	
BDE-10	0.25±0.03	0.25	0.89	101.86±2.28	100	1.86	0.99983	6.86	0.04	1.0	0.028±0.011	
BDE-15	0.26±0.01	0.25	5.33	105.08±1.12	100	5.08	0.99999	4.33	0.01	0.4	0.603±0.063	
BDE-17	0.26±0.01	0.25	3.56	108.61±1.96	100	8.61	0.99998	5.58	0.01	6.4	0.533±0.032	
BDE-28	0.26±0.02	0.25	4.00	106.75±1.07	100	6.75	0.99999	4.02	0.01	5.7	**0.333±0.012**	**0.26±0.24***
BDE-30	0.26±0.02	0.25	3.56	109.24±1.64	100	9.24	0.99993	6.21	0.01	7.4	<0.007	
BDE-47	0.52±0.03	0.5	4.89	205.74±1.30	200	2.87	0.99998	2.42	0.01	9.3	**1.485±0.327**	**1.72±0.28**
BDE-49	0.54±0.05	0.5	7.33	203.94±2.36	200	1.97	0.99991	4.25	0.02	31.5	**1.069±0.312**	**1.24±0.55***
BDE-66	0.54±0.02	0.5	7.78	209.14±1.69	200	4.57	0.99997	7.19	0.02	18.1	**1.867±0.36**	**0.13±0.08***
BDE-71	0.56±0.04	0.5	5.50	205.57±1.56	200	2.78	0.99995	1.27	0.03	24.4	1.235±0.24	
BDE-77	0.55±0.04	0.5	5.36	206.15±1.58	200	3.07	0.99995	1.75	0.01	6.7	0.525±0.11	
BDE-85	0.50±0.02	0.5	0.89	208.03±2.18	200	4.02	0.99995	8.29	0.05	6.2	0.602±0.15	
BDE-99	0.53±0.02	0.5	6.67	205.04±0.65	200	2.52	0.99990	6.12	0.02	4.8	**1.703±0.032**	**1.98±0.26**
BDE-100	0.52±0.02	0.5	3.11	209.04±1.04	200	4.52	0.99996	2.37	0.01	2.8	**0.402±0.081**	**0.447±0.027**
BDE-119	0.52±0.05	0.5	3.11	211.01±1.31	200	5.50	0.99972	3.07	0.03	5.0	0.501±0.14	
BDE-126	0.52±0.03	0.5	3.11	209.61±1.10	200	4.81	0.99999	4.85	0.02	2.7	0.676±0.45	
BDE-138	0.51±0.04	0.5	2.00	200.08±2.14	200	0.04	0.99997	3.83	0.02	12.0	0.219±0.05	
BDE-139	0.50±0.02	0.5	0.22	195.73±2.78	200	2.14	0.99992	4.19	0.02	11.7	1.366±0.42	
BDE-140	0.51±0.02	0.5	0.22	192.53±2.61	200	3.74	0.99998	1.72	0.02	10.9	0.577±0.18	
BDE-153	0.58±0.04	0.5	7.83	205.07±0.79	200	2.54	0.99998	6.04	0.02	9.0	**6.402±0.503**	**6.44±0.37**
BDE-156	0.45±0.04	0.5	10.44	188.26±3.87	200	5.87	0.99984	6.51	0.01	10.4	0.388±0.05	
BDE-171	1.13±0.07	1	12.89	408.31±4.07	400	2.08	0.99961	6.17	0.03	5.9	4.169±0.156	
BDE-180	1.13±0.09	1	13.00	412.98±4.53	400	3.25	0.99978	4.07	0.03	6.6	**31.932±2.608**	**31.8±0.10**
BDE-183	1.06±0.06	1	6.33	419.26±4.7	400	4.81	0.99981	0.84	0.01	2.7	5.592±0.102	
BDE-184	1.07±0.07	1	6.89	407.61±1.77	400	1.90	0.99987	7.72	0.01	3.1	1.393±0.373	
BDE-191	1.04±0.05	1	3.56	397.64±2.70	400	0.59	0.99925	4.44	0.02	3.4	4.973±0.877	

	CS-1 Conc±SD (n=10)	CS-1 Value	Rel. % Error	CS-5 Conc±SD (n=10)	CS-5 Value	Rel. % Error	Linearity (n=10)	RRF RSD (%)	IDL (pg inj.$^{-1}$)	MDL (pg g^{-1} dw)	SRM (ng g^{-1} dw)	SRM Ref. Values
BDE-196	1.15±0.06	1	14.89	394.12±2.69	400	1.47	0.99994	3.83	0.01	6.0	**2.363±0.245**	**1.15±0.06**
BDE-197+201[1]	1.99±0.16	2	10.33	804.64±5.78	800	0.58	0.99982	0.84	0.01	8.1	22.304±0.221	
BDE-203	1.10±0.07	1	10.00	410.14±2.19	400	2.54	0.99949	7.72	0.01	13.8	23.476±2.787	
BDE-204	1.06±0.09	1	6.00	407.44±6.50	400	1.86	0.99988	4.44	0.02	18.5	24.133±1.872	
BDE-205	1.00±0.11	1	0.11	417.21±8.89	400	4.30	0.99992	3.57	0.04	32.7	4.042±1.14	
BDE-206	2.61±0.21	2.5	4.40	1010.78±11.03	1000	1.08	0.99992	8.44	0.05	76.8	**6.401±0.128**	**6.2±1.0**
BDE-207	2.34±0.23	2.5	6.40	1032.42±8.37	1000	3.24	0.99981	1.88	0.03	58.0	22.606±2.006	
BDE-208	2.78±0.22	2.5	11.20	1022.33±5.09	1000	2.23	0.99978	4.07	0.04	65.7	3.299±0.552	
BDE-209	2.73±0.27	2.5	9.20	970.77±12.97	1000	2.92	0.99964	9.39	0.60	149.6	**108.813±18.132**	**93.5±4.4**

*CS-i-Conc±SD refers to mean the concentration of (n= 10) injections (pg µL^{-1}) ± 1SD. CS-i Value is the 'known' concentration reported in the CS-i calibration level standard, Rel. % Error corresponds to the relative error associated with the corresponding mean measurement (%) as a proxy for method accuracy. Linearity is the averaged R^2 observed for the slope of (n= 10) calibration lines. RSD (%) represents the relative standard deviation observed for the Relative Response Factors (RRFs) observed from the injection of (n= 10) calibration series. IDL (pg injection^{-1}) as calculated from Eq. 2.3 and MDL (pg g^{-1}dw) as calculated by Eq. 2.4 for the quantification of SRM- 1944 (6 g) samples. SRM column refers to the mean±1SD concentration of the respective target analyte observed across (n= 7) SRM- 1944 sediment measurements. SRM Ref. Values refer to the reported certified concentrations±1SD of corresponding analytes present in the SRM samples, here: * refers to additional values not certified by NIST reported in Lynch et al. 2007.*

[1]*Chromatographic co-elution.*

Table 2.5: PBDD/F Method Validation Data.

	CS-1 Conc±SD (n=10)	CS-1 Value	Rel. % Error	CS-4 Conc±SD (n=10)	CS-4 Value	Rel. % Error	Linearity (n=10)	RRF RSD (%)	IDL (pg inj.$^{-1}$)	MDL (pg g^{-1} dw)	SRM (pg g^{-1} dw)
Dioxins											
2,3,7,8-TBDD	0.09±0.01	0.1	6.00	10.83±0.11	10	8.26	0.999997	7.36	0.01	0.03	<0.03
Total TBDD							0.999986	7.36	0.01	0.02	2.27±0.04
1,2,3,7,8-PeBDD	0.21±0.01	0.2	7.29	18.77±0.1	20	6.18	0.999988	8.18	0.02	0.05	<0.05
Total PeBDD							0.999987	7.13	0.02	0.17	<0.17
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD[1]	1.27±0.03	1.2	5.42	121.43±0.62	120	1.19	0.999973	2.61	0.09	0.24	<0.24
1,2,3,7,8,9-HxBDD	0.53±0.03	0.6	12.17	54.38±0.77	60	9.37	0.999946	4.18	0.09	0.13	<0.13
Total HxBDD							0.999980	2.69	0.09	0.13	<0.13
1,2,3,4,6,7,8-HpBDD	0.59±0.05	0.75	21.04	74.98±0.57	75	0.03	0.999989	14.50	0.10	0.43	<0.43
Total HpBDD							0.999992	14.34	0.10	0.43	<0.43
OBDD	0.78±0.03	1	22.64	116.65±1.37	100	16.65	0.999999	5.95	0.96	0.22	14.15±2.06
Furans											
2,3,7,8-TBDF	0.22±0.01	0.2	10.00	21.29±0.12	20	6.45	0.999997	4.92	0.01	0.01	0.61±0.07
Total TBDF							0.999911	9.29	0.01	0.03	22.48±1.08
1,2,3,7,8-PeBDF	0.39±0.02	0.4	3.00	39.94±0.53	40	0.15	0.999840	1.96	0.05	0.18	0.65±0.15
2,3,4,7,8-PeBDF	0.36±0.02	0.4	9.50	38.97±0.21	40	2.59	0.999850	2.49	0.04	0.18	<0.18
Total PeBDF							0.999053	7.99	0.05	0.15	155.11±19.08
1,2,3,4,7,8-HxBDF	0.52±0.04	0.6	12.76	60±0.72	60	0.01	0.999980	7.93	0.09	0.13	6.66±0.26
Total HxBDF							0.999989	7.97	0.09	0.12	217.46±11.61
1,2,3,4,6,7,8-HpBDF	0.86±0.05	0.75	14.80	75.5±0.48	75	0.66	0.999982	5.71	0.13	0.46	139.78±3.92
Total HpBDF							0.999995	7.60	0.13	0.46	139.96±3.62
OBDF	n.d	1	n.d	98.79±4.2	100	1.21	0.999972	0.20	2.26	2.50	<2.5
∑PBDD/F$_{2,3,7,8}$											**155.12±3.43**
∑PBDD/F											**551.43±30.25**
TEQ PBDD/F (Lb)											**2.15±0.05**
TEQ PBDD/F (Ub)											**2.27±0.01**

[1] Chromatographic co-elution: See Table 2.4 for column descriptions. CS-4 used in place of CS-5 to prevent excessive ion source fouling.

Table 2.6: PXDD/F Method Validation Data.

	CS-1 Conc±SD (n=10)	CS-1 Value	Rel. % Error	CS-5 Conc±SD (n=10)	CS-5 Value	Rel. % Error	Linearity (n=10)	Slope (m)	RRF RSD (%)	IDL (pg inj.$^{-1}$)	MDL (pg g^{-1} dw)	SRM (pg g^{-1} dw)
Dioxins												
2-Br-7,8-CDD	0.045±0.003	0.05	10.25	0.932±0.043	1	6.82	0.999310	1.212	4.10	0.005	0.005	2.381±0.175
Total Br-2CDDs	0.048±0.004	0.05	4.74	1.101±0.03	1	10.06	0.998354	1.198	5.34	0.005	0.005	0.914±0.035
2-Br-3,7,8-CDD	0.049±0.003	0.05	1.29	0.961±0.016	1	3.89	0.999743	1.084	5.81	0.003	0.007	0.241±0.004
Total Br-3CDDs	0.049±0.003	0.05	1.93	0.958±0.029	1	4.23	0.999680	1.201	5.44	0.002	0.003	1.084±0.123
2,3-Br-7,8-CDD	0.048±0.002	0.05	3.62	0.934±0.036	1	6.63	0.999714	1.542	1.93	0.002	0.004	0.008±0.002
Total 2Br-2CDDs	0.049±0.002	0.05	1.66	0.953±0.051	1	4.73	0.999590	1.524	4.59	0.002	0.004	0.999±0.102
1-Br-2,3,7,8-CDD+ 2-Br-1,3,7,8-CDD[1]	0.102±0.003	0.1	1.74	1.783±0.113	2	10.83	0.999831	1.148	7.10	0.005	0.005	<0.0054
2-Br-3,6,7,8,9-CDD	0.107±0.004	0.1	7.15	1.889±0.185	2	5.55	0.999284	1.460	7.67	0.002	0.005	0.933±0.203
Total Br-5CDDs	0.053±0.004	0.05	5.15	1.043±0.056	1	4.32	0.999616	1.171	4.57	0.002	0.004	0.139*
Furans												
2-Br-7,8-CDF	0.05±0.002	0.05	0.28	0.921±0.016	1	7.94	0.999584	1.561	5.04	0.001	0.003	0.626±0.156
Total Br-2CDFs	0.049±0.002	0.05	2.23	0.901±0.016	1	9.94	0.999997	1.753	2.31	0.003	0.003	3.388±0.143
2-Br-6,7,8-CDF+ 3-Br-2,7,8-CDF[1]	0.106±0.003	0.1	6.07	1.809±0.044	2	9.53	0.999545	1.701	5.17	0.001	0.003	0.342±0.034
Total Br-3CDFs	0.108±0.003	0.1	7.79	1.839±0.343	2	8.06	0.999556	1.928	5.98	0.004	0.003	1.483±0.087
1-Br-2,3,7,8-CDF	0.05±0.001	0.05	0.08	1.019±0.039	1	1.89	0.999347	1.786	3.96	0.002	0.003	0.070*
Total Br-4CDFs	0.05±0.001	0.05	0.38	1.014±0.039	1	1.42	0.999877	1.827	4.46	0.002	0.003	1.185±0.022
∑PXDD$_{2/3,7,8}$												**2.630±0.177**
∑PXDF$_{2/3,7,8}$												**1.004±0.141**
∑PXDD/F$_{2/3,7,8}$												**3.634±0.036**
∑PXDD												**5.448±0.365**
∑PXDF												**6.056±0.208**
∑PXDD/F												**11.504±0.573**

See Table 2.4 for column descriptions. Concentrations SRM values indicate the mean and 1SD concentrations of (n= 6) samples analysed. Slope (m) refers to the slope of the calibration functions: Δ Area Ratio [QM(Analyte): QM (Int.Std)] x 10^{-3} fg^{-1} µL^{-1}. SRM concentration values reported here represent the first such reporting of these compounds in SRMs.

[1] Chromatographic co-elution.

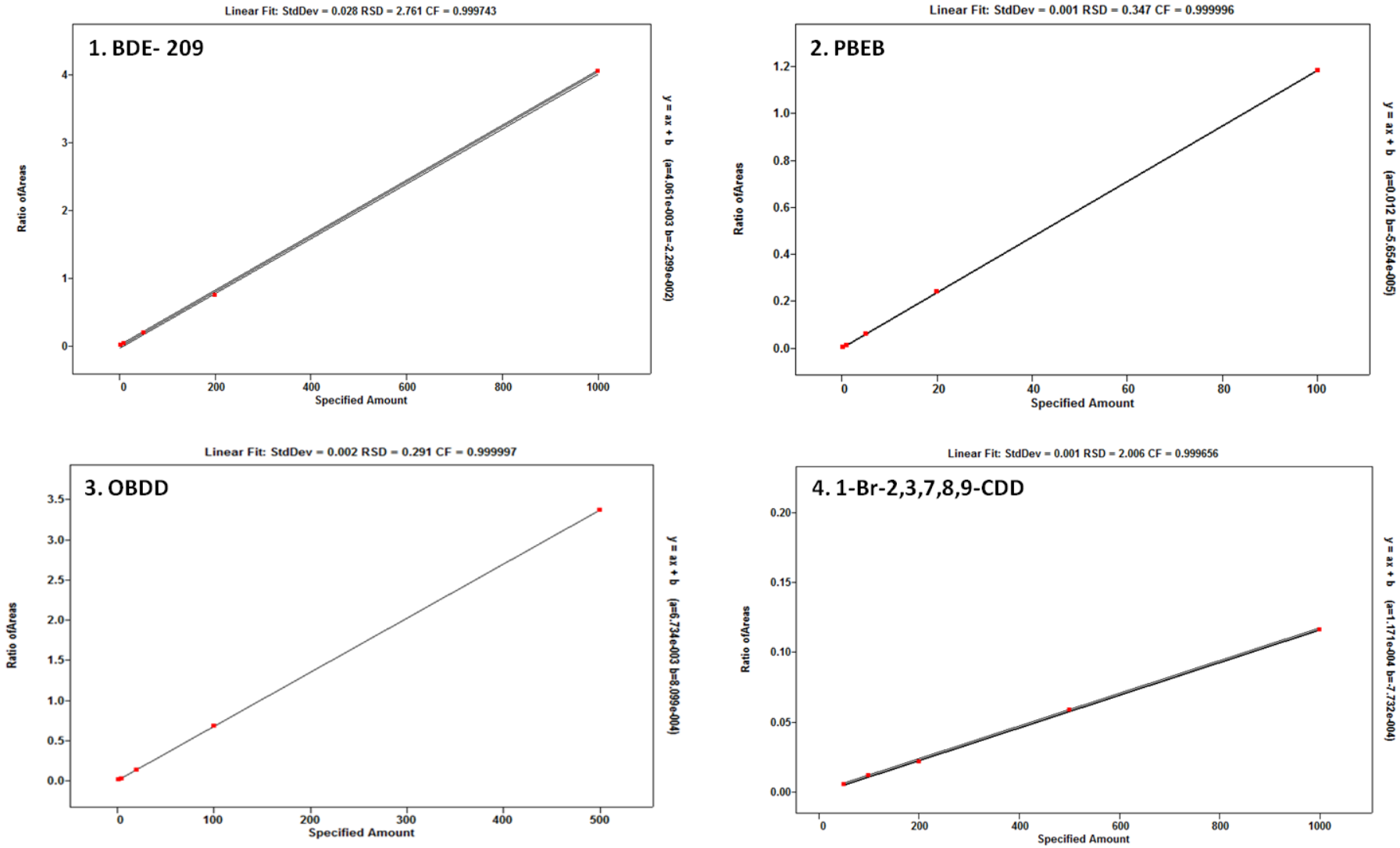


Figure 2.11: Typical calibration lines, showing (x- axis) calibration concentration range, and (y-axis) analyte: labelled internal standard peak area ratios for: 1. BDE-209, 2. PBEB, 3.OBDD and 4. 1-Br-2,3,7,8,9CDD.

2.7.2 Analytical Method Performance.

2.7.2.1 Extraction, Purification and Fractionation.

Validation of the wet chemical procedures for both sediment and breast milk samples employed here, as well as the analytical procedure were conducted on the basis of adequate recoveries of internal standard compounds, effective removal of background matrix, and suitability of the non/ planar fractionation. Recoveries for all target analyte internal standards ranged between 50- 110 %, with the exception of OBDD and OBDF which were recorded on several occasions at 40 % and were indicated as such where reported. These observed recovery values were deemed acceptable for these analyses. Sample purification and fractionation procedures, provided sample extracts with sufficiently reduced background interference to produce clear analyte signals for all targets and was therefore also deemed suitable. Sample fractionation procedures were validated by matching the RTs of each analyte peak against those generated by analysis of calibration standard solutions. In no case investigated were specific F2 analyte peaks observed above limits of detection in F1 samples or procedural blanks. The converse was also observed for F1 analytes in F2 sample fractions, with some exceptions described in Section 2.7.3. This assessment was made by the analysis of 5 SRM injections analysed prior to the extraction and analysis of the samples discussed in the results chapters of this report.

2.7.2.2 Sediment: Method Detection Limits, Accuracy and Reproducibility.

Method detection limits were calculated for all target analytes for the analysis of SRM sediments according to Eq: 2.4. Average dry weight sample quantities were used in the calculations and analyte MDLs expressed in pg g^{-1} dw are displayed in Tables 2.4- 2.6. Method trueness determinations were made based on mean target analyte concentration (dw basis) deviations between observed concentrations of target analytes and NIST reported certified values, with some (non- certified) additions from inter-laboratory studies reported in Lynch et al. 2007. Fortification experiments to

assess method trueness for those compounds without certified values was not conducted, primarily due to the lack of available native standards and certifiably clean starting materials. Trueness, as a method to assess the uncertainty associated in the comparison of replace measurements was calculated by the standard method (ERM, 2005) as described by Poma et al. 2016. This calculation accounts for the degree of accuracy as well as reproducibility involved in concentration comparisons and yields a value (U), percent trueness at a 95 % statistical confidence. Trueness values for the comparison of certified reference PBDE values and concentrations observed in measurements here ranged from 79- 109 %, well within established guideline values (ERM, 2005). No statistically significant differences (Student's t-test, 2 sided, $p>0.05$) were observed between the measured and NIST certified values or those provided by Lynch et al. 2007. Reproducibility of PBDE congener measurements as defined by the 1SD values of mean measurements (n =7) ranged over values at 1 order of magnitude lower than mean concentrations observed, again with the exception of BDE-205, for which instrumental reproducibility also suffered. Accordingly, it can be assumed that the reduced method reproducibility of this congener is due to instrumental, rather than a wet- chemical clean up associated error. Method reproducibility for PBDD/F and PXDD/F analytes quantified in SRMs were also observed over a range lower than 1 order of magnitude of analyte concentrations and accordingly deemed satisfactory (Tables 2.4- 2.6).

2.7.2.3 Breast Milk: Method Detection Limits, Accuracy and Reproducibility.

Sample and method detection limits for analytes measured in breast milk samples were calculated from the IDL values also used for the determination of sediment MDL values. Accordingly, breast milk MDLs differed only by the amount of sample analysed and the internal standard recoveries observed. All recoveries of analyte internal standards were approximately identical to those observed for sediments, indicating suitability of the extraction and clean up method developed and accordingly returned suitably similar MDL values as those observed for sediments and therefore are not tabulated here. Accuracy and reproducibility measurements were not able to be performed for

this matrix due to the lack of available standardised sample material and the prohibitive costs associated with the fortification of matrix with labelled internal standards.

2.7.3 Monitoring and Control of Analyte Isobaric Interferences.

The protocol developed for the chromatographic control and monitoring of isobarically interfering ions is described in Section: 2.6.2. Here interferences, potentially contributing to quantification errors and false positive confirmations is described separately for F1 and F2 sample fractions.

2.7.3.1 F1: (non- Planar Fraction) PBDE and NBFR Interferences.

Inter- homologue group interferences are commonly observed in the analysis of PBDEs, as thermal de-bromination of higher substituted congeners results in ion clusters identical to those of their lower brominated counterparts. The extent of analyte degradation can be significantly reduced by appropriate chromatographic optimisation. Further, the use of standardised retention time indices and chromatographic temperature profiles can also ensure that homologue groups elute over sufficiently distinct RT ranges as to negate the potential of quantification errors, as was employed here. Isobaric interferences have been previously identified to occur between PBDE congener QM [M-2Br and -4Br] ions and others contributed from the presence of some PCBs, PCTs (polychlorinated terphenyls) and PCNs (polychlorinated naphthalenes). Interfering ions from these compound groups were all calculated to be sufficiently mass resolved at resolutions >25K (10 % valley, ~50K FWHM) well below the resolution at which PBDEs were analysed (60K FWHM) here. PBDFs interfering ions however, remained non- resolved throughout the analysis. Control of PBDF interferences was conducted through the standardisation of chromatographic conditions for all identified congeners contained in the calibration standards of both compound classes. This was carefully adjusted to ensure that interfering PBDF congeners would elute separately from those of PBDEs and accordingly not induce interference. PBDF congeners present in calibration standard

solutions (n= 7) in this method did not control for interferences derived from the presence of 'unknown' congeners for which calibration standards were not available. However, given the far lower ambient concentrations at which PBDFs are present (typically on the order of 10^{-4}- 10^{-6} lower), quantification errors associated with the inclusion of PBDF ions to PBDE QM peak areas is likely to result in concentration deviations of less than 1 % and accordingly were considered negligible.

2.7.3.2 F2: (Planar Fraction) Dioxin and Furan Interferences.

A literature search as well as ion fragmentation simulations of a range of halogenated environmental contaminants with the potential to induce ion interferences with the range of target compound classes analysed here was conducted. Interactions investigated included ([Interference- Target Analyte Group]): [PXB- PBDF]; [PCT- PBDF]; [PCB- PXDD]; [PBDE- PBDF], and were found to be mostly mass resolvable at the resolution of analysis, with the notable exceptions of [PCB- PXDD]; and [PBDE- PBDF]. Baseline mass separation of interfering PCB ions from the analyte peaks of PXDD requires the impractical resolution of ~2 x10^6. The potential isobaric effect was reduced as much as was possible by the appropriate selection of PXDD QM peaks pertaining to those where the extent of PCB interference was minimised. PXDD ion selection and the extent of potential interference induced from the presence of PCBs in PXDD ion traces is illustrated in Figure 2.12. Figure 2.12 shows the simulated accurate mass interference at the resolution of analysis (60K FWHM) between the Hx-CB and 1-Br-3CDD ion clusters. These congeners were chosen for display as an exemplar pair for the interaction occurring across all corresponding congeners in these compound classes. Figure 2.12- A shows the simulated ion intensities for Hx- CB and 2.11- B for mono-Br-3ClDD. The inset on the figure is an illustration of the extent of the interference between the M+ 9 Hx- CB ion at 365.83347 Da (Figure 2.12-A.i.) and the M+ 3 (QM) mono-Br-3ClDD ion at 365.84413 Da (Figure 2.12- B.i.). As can be seen in the inset figure, the interaction occurs mainly due to the presence of an additional unresolved M+ 10 Hx- CB ion as well as the M+ 9 Hx- CB ion, which is approximately 90 % resolved at the resolution of the measurements. This represents a 'worst case' scenario for interference which

given the interaction takes place between very low relative intensity PCB ions and PXDDs is, as mentioned, not likely to induce quantification errors sufficiently high to substantially effect PXDD quantification. Despite PCBs likely being present at far greater concentration than PXDDs in the data set, their interference was deemed to be sufficiently negligible upon concentrations under the selected instrumental procedure. An additional validation was none the less conducted, to investigate whether chromatographic restrictions may have prevented this interference from occurring. For this, the most intense ions for all PCBs were monitored across all samples, and inspected for chromatographic co- elution with PXDD targets for which potential interference may occur. It was revealed that, despite the reduced chromatographic resolution of this analysis (12 m capillary column) PCBs were not in any case observed to elute over RT ranges where target PXDDs were quantified. An example of this is illustrated in Figure 2.13, again for the potential interference between Hx- CB and mono-Br-3CDD in sediment from S3 Holt Hall Lake shows PCBs not eluting over RT ranges in which PXDDs were quantified.

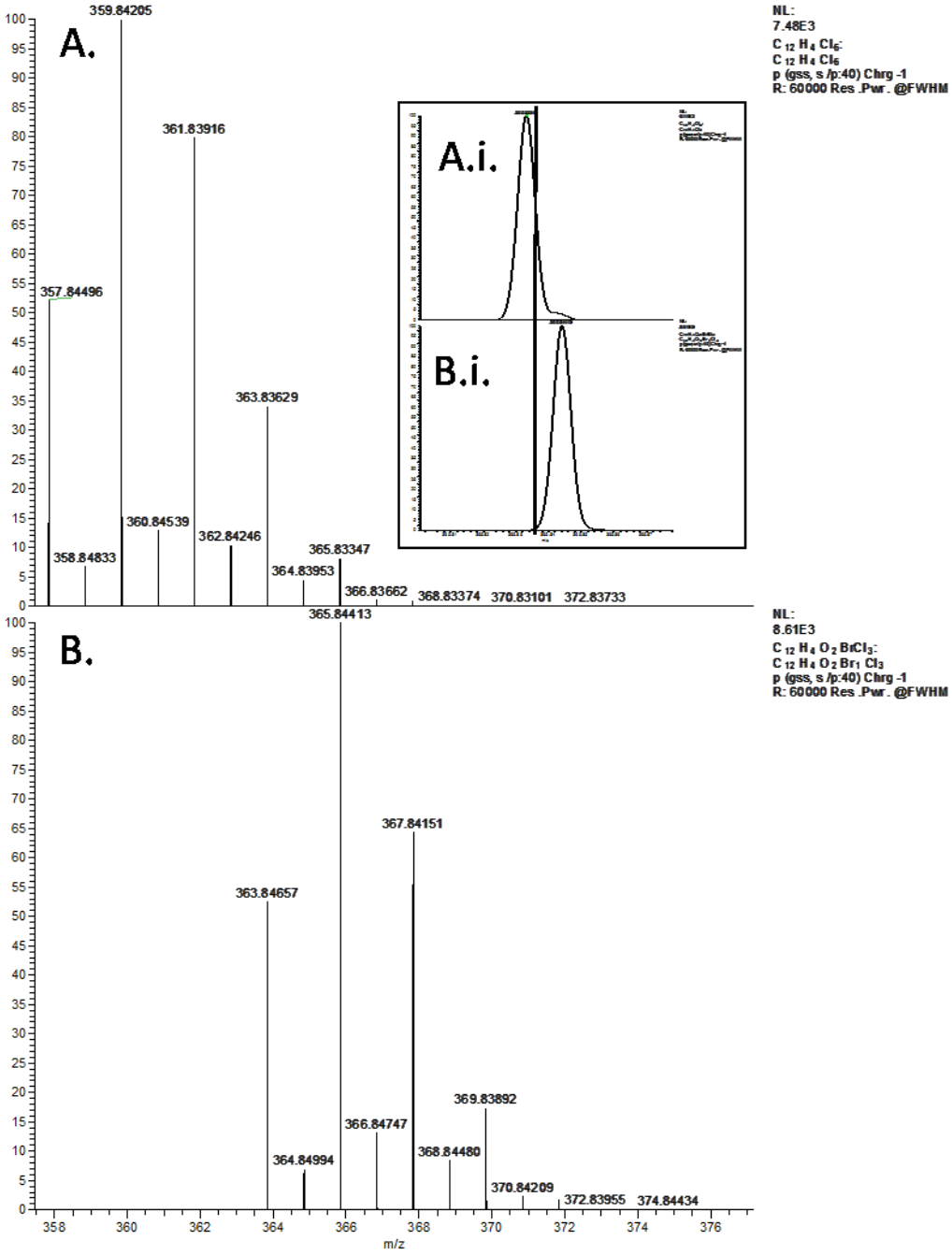


Figure 2.12: Isobaric interference at m/z 365.8 Da observed between [M+9]/[M+10] Hx- CB ions at 365.83347 Da (A) and the [M+3] (QM) mono-Br-3ClDD ion at 365.84413 Da (B) at a simulated resolving power of 60K FWHM. Inset in A.i are the [M+9]/[M+10] Hx- CB ions with those of the [M+3] (QM) mono-Br-3ClDD in B.i.

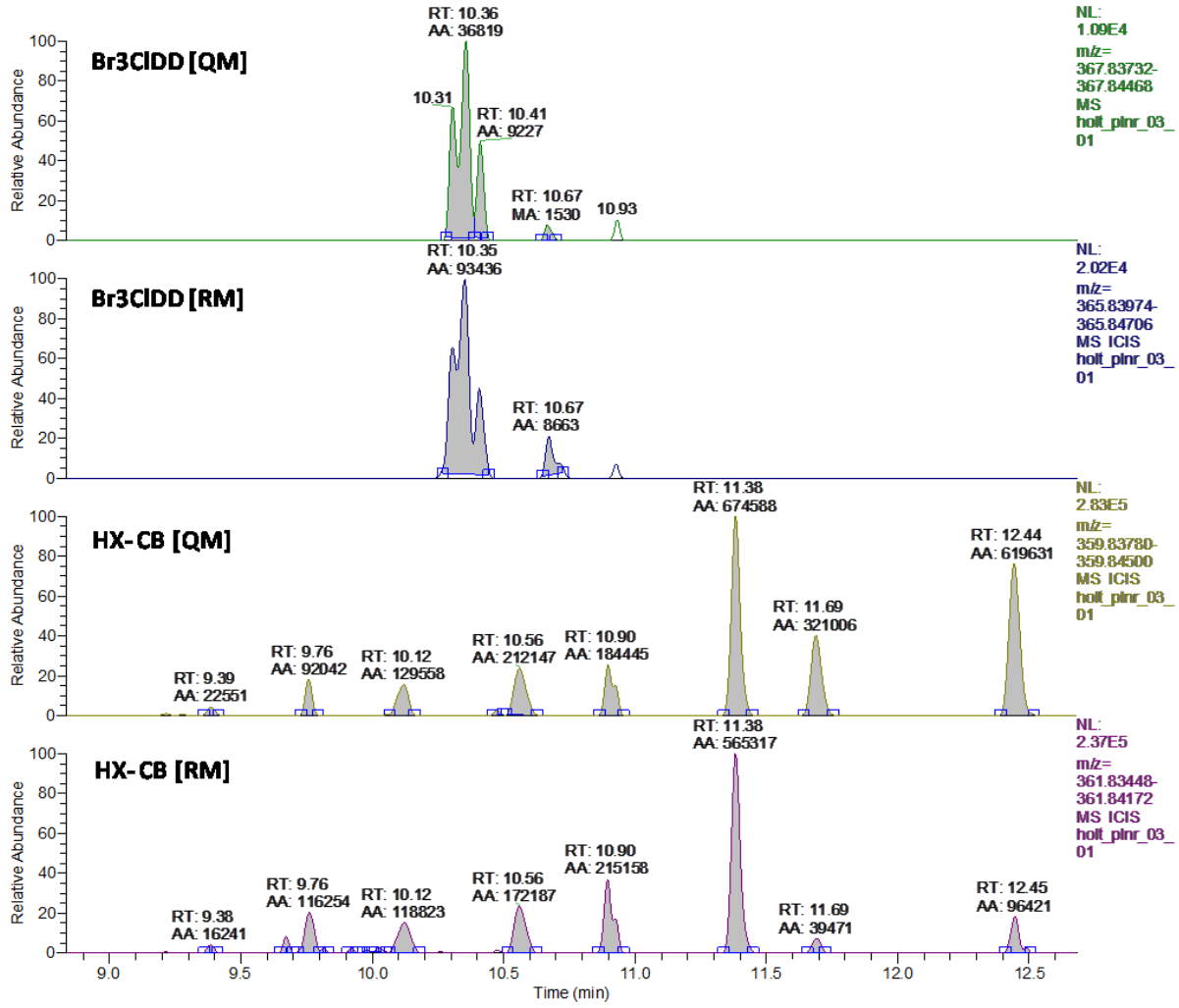


Figure 2.13: Extracted ion chromatograms of mono-Br-3ClDD QM and RM as well as the 1st (QM) and 2nd (RM) most intense ion masses for Hx- CB as measured in sediment radiometrically dated to 1999, sampled at S3 Holt Hall Lake. The lack of chromatographic co-elution between the mono-Br-3ClDDs and the isobaric interfering Hx-CB lead to confirmation of the mono-Br-3ClDD peaks shown.

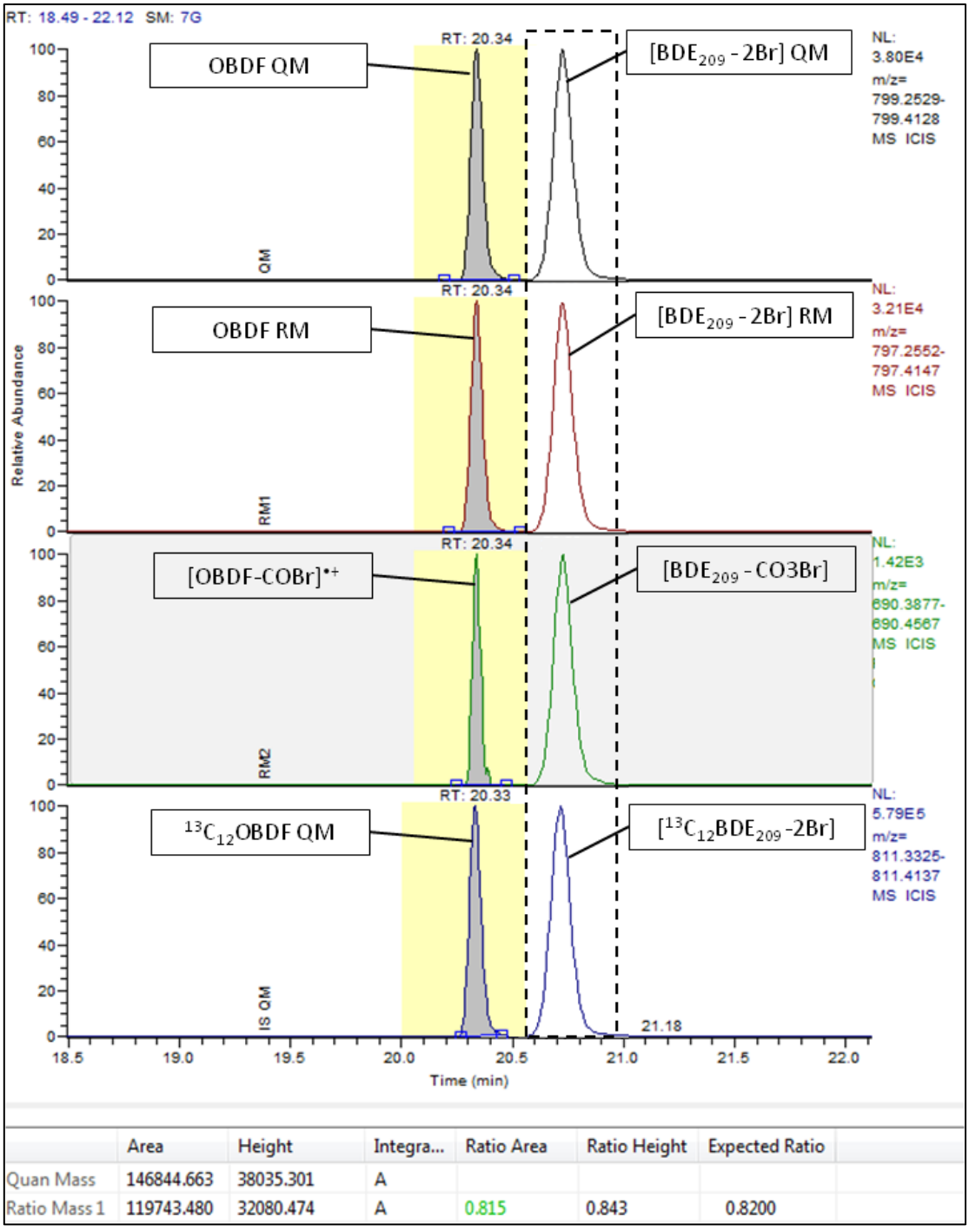
2.7.3.3 Additional PBDF Confirmation.

Isobaric interference occurring between $[\text{-4Br-BDE}]^+$ ions and QM PBDF ions represent a special case of ion interaction. In virtually all observed interactions a theoretical resolution exists for which the complete resolving of interferences can occur. This however, is not the case for the ion interaction of PBDE- PBDF, as -4Br- BDE accurate masses are essentially identical to those of their respectively substituted PBDFs. This is predominantly due to the structural similarities shared between these compound classes. Several approaches, beyond retention time matching of native PBDFs with their corresponding $^{13}C_{12}$ -labelled standard and RM ratio standardisation to within ± 15 %, have been developed which include the wet chemical separation employed in the sample clean up here, as well as the monitoring of additional MS confirmatory peaks. Donnelly et al., 1987 first proposed the inclusion of either $[\text{PBDF- COBr}^{\bullet}]^+$ or $[\text{PBDF-2Br}]^{+\bullet}$ as the formation of the $[\text{PBDF- COBr}^{\bullet}]^+$ was considered restricted to formation by the ionisation of PBDFs alone. Therefore, it was concluded by Donnelly et al. and further included in more contemporary studies of PBDF environmental contamination (Hagberg 2009) that the presence of this ion provided a sufficient basis for PBDF confirmation in the absence of PBDE interference. However, here with the technological advantages provided by the Full Scan analysis performed on the GC Q Exactive platform, we have observed that this excluded ion trace is also populated by the presence of an unidentified ion derived from the EI+ ionisation (70 eV) of PBDE congeners. Figure 2.14 shows an example of the peak confirmation approach for OBDF present in breast milk samples analysed here following the Donnelly et al. 1987 confirmation approach. From top down, the figure shows the QM, RM, $[\text{OBDF- COBr}^{\bullet}]^+$ confirmation, and $^{13}C_{12}$- OBDF QM extracted ion chromatograms measured at the resolution of analysis (60K FWHM) shaded by yellow. Not shaded and enclosed in the dashed box are the identical extracted ion chromatograms (XIC) from an external injection of BDE- 209 conducted under identical chromatographic conditions. In the XIC displayed third from the top is that corresponding to the $[\text{OBDF- COBr}^{\bullet}]^+$ confirmation ion. Observed is the presence of an additional peak derived from the ionisation of BDE- 209 (believed to be a meta-stable $[BDE_{209}\text{- CO3Br}]^+$). The presence of this peak in

the OBDF confirmation XIC indicates that while the formation of the $[PBDF\text{-}COBr^{\bullet}]^{+}$ may well be restricted to PBDFs, the presence of this restricted peak in the ion spectra of PBDE invalidates this approach for PBDF analyte confirmation. Accordingly, we propose an alternative procedure for confirmation of PBDFs where confirmation is achieved only via demonstration of the absence of the [M+BDE]. An example of this extended validation protocol is displayed in Figure 2.10 for PM_{10} samples analysed and was conducted for all sediment and breast milk PBDF confirmations. In this example, we show the exclusion of PeBDF quantification ion peaks eluting over RT space potentially occupied by interfering hepta- BDEs. Also, we show the presence of hepta- [M+ BDE] peaks not adequately removed by sample fractionation (not conducted by the authors). As chromatographic conditions were standardised between F1 and F2 samples, PBDF quantification exclusion zones were incorporated across all measurements and PBDFs reported for all samples.

In summary, isobaric interferences arising from a multitude of exogenic compounds in XICs of target analytes were assessed and controlled for by the incorporation of the following procedures:

1. The inclusion of an additional fraction process in the wet chemical purification of samples analysed.
2. The judicious selection of target analyte QM and RM ion masses.
3. Selection of instrumental resolution of sufficient resolving power as to mass resolve the vast majority of interfering ions.
4. Standardisation of chromatographic procedures employed for both sample analyte fractions
5. Manual visual inspection and verification of chromatographic separation of interferences not completely mass resolved.
6. The development of an alternative assessment procedure for the confirmation of PBDFs not relying on confirmation by the presence of $[PBDF\text{-}COBr^{\bullet}]^{+}$ but rather confirmation through the absence of the [M+BDE] parent ion.



	Area	Height	Integra...	Ratio Area	Ratio Height	Expected Ratio
Quan Mass	146844.663	38035.301	A			
Ratio Mass 1	119743.480	32080.474	A	0.815	0.843	0.8200

Figure 2.14 OBDF accurate mass traces showing Quantification, Qualification, additional confirming ([OBDF-COBr•]+and $^{13}C_{12}$OBDF internal standard Quantification Ions. Ratio Area corresponds to the abundance ratio of the Quantification and Qualification OBDF chromatograms with the Expected Ratio corresponding to the theoretical OBDF ratio by isotope simulation. BDE-209 interfering peaks (taken from separate injection of Wellington BFR-CS3 standard) are shown boxed and overlaid. 690.3877-690.4567 mass trace shows the presence of an unconfirmed meta-stable BDE-209 fragment ion suspected to be derived from [BDE209- CO3Br]+

Chapter 3 Concentrations, Temporal and Spatial Trends of PBDE, PBDD/F and PXDD/F Contamination in Radiometrically Dated English Fresh Water Sediments.

3.1 Synopsis:

In this chapter we describe and contrast concentrations of PBDEs, PBDD/Fs and PXDD/Fs observed in individual slices of radiometrically dated sediment cores sampled by the authors from 3 different UK fresh water lakes. These concentrations in conjunction with their associated deposition date provide for the first time, a basis for which PBDE contamination can be plausibly assessed for association with PBDD/Fs and PXDD/Fs by analysis of temporal trends. The PXDD/F data reported here represents the first temporal trends for these compounds to be reported in scientific literature to date. Results and analytical assessment of these data are provided in the following sections.

3.2 Sampling Strategy.

Sediment core sampling was conducted at 3 sites across England, UK: S1- Edgbaston Pool, S2- Wake Valley Pond and S3- Holt Hall Lake. Details of sampling procedures, locations and physical characteristics are described in Chapter 2 (2.2.1). As is also more fully described in Chapter 2, sediments cores collected from these 3 locations were analysed for differing target compound sets. S1 Edgbaston Pool was analysed for PBDEs, selected NBFRs and PBDD/Fs, while S2 (Wake Valley Pond) and S3 (Holt Hall Lake) were additionally investigated for the presence of PXDD/Fs. Concentration data generated were used to construct contaminant input chronologies to benthic sediments over a period from 1935 to 2015, with a temporal resolution of between 5– 10 years. Contaminants quantified in this study were derived from individual sediment slices pertaining to the year of sedimentation as revealed from ^{210}Pb radiometric dating (Section 2.3.1.1). Chronologies derived here are contrasted against a previously established PBDE temporal trend established from

the same sampling locations [82]. The Yang et al study established for the first time temporal trends of PBDEs as observed in pooled (5 yearly homogenised core slices) UK sediments dating from 1954 to 2009. Here, with the use of novel, highly sensitive and selective analytical procedures developed during the course of this study we were able to enhance the temporal resolution by deriving quantification data from single core slices pertaining to radiometrically dated individual years of deposition. We also expanded the target set of PBDEs to include a more comprehensive investigation of higher brominated -hepta, -octa and -nona substituted congeners. Additionally quantified in this study are concentrations of the 13 individual 2,3,7,8- substituted and total congener PBDD/Fs, known to be trace level contaminants of PBDE commercial mixtures as well as eight 2/3,7,8 substituted and total homologue group PXDD/Fs, compounds strongly suspected as products derived from the incineration of materials containing BFRs [93]. All concentration data presented in the following sections is reported on a total organic carbon (OC) basis unless otherwise indicated.

In total 10 core slices were selected for analysis from each site corresponding to a sedimentation date ranging from 1935 to 2015 (surface sediment), with the exception of Core 1 from S1 Edgbaston which was comprised of 11 samples of sediment, radiometrically dated to the identical time period. The following sections are dedicated to expanding the currently established PBDE chronologies as well as describing and contrasting these with any temporal trends which may become apparent from the quantification of the additional aforementioned compound groups present in the sediments analysed.

3.3 BFR Contaminant Trends in English Fresh Water Lakes.

3.3.1 Concentrations, Temporal and Spatial Distribution of BFRs.

Tables 3.1- 3.3 show the concentrations of target PBDEs (n= 35) analysed from sediments sampled in this study, as well as concentrations previously established by Yang et al (2016) at S1 Edgbaston Pool, S2 Wake Valley Pond and S3 Holt Hall Lake respectively. All data in this section is quantified on an OC basis unless otherwise described. Figure 3.1 shows composite PBDE congener concentration trends with respect to sedimentation date at the 3 sites sampled.

Table 3.1: Concentrations of target PBDEs (ng g^{-1} OC, unless otherwise specified) in analysed sediment from S1- Edgbaston Pool.

	2015	2012	2009	2004	1999	1993	1985	1977	1969	1954	1935
BDE-7	0.177	<0.003	0.091	0.008	0.003	<0.003	0.004	<0.003	<0.003	<0.003	<0.003
BDE-10	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
BDE-15	0.331	0.434	0.264	0.222	0.254	<0.003	0.180	0.021	0.020	<0.003	<0.003
BDE-17	0.157	0.081	0.105	<0.002	0.029	0.012	0.092	<0.002	<0.002	<0.002	<0.002
BDE-28	0.607	0.383	0.249	0.213	0.186	0.130	0.175	0.014	0.013	<0.002	<0.002
BDE-30	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
BDE-47	4.056	2.222	1.888	2.010	2.052	1.725	<0.003	0.164	0.301	0.171	0.028
BDE-49	2.163	0.692	0.449	0.479	0.450	0.527	<0.279	<0.279	<0.279	<0.279	<0.279
BDE-66	0.815	0.582	0.493	0.415	<0.005	0.167	<0.005	<0.005	<0.005	<0.005	<0.005
BDE-71	0.094	<0.007	<0.007	0.034	<0.007	<0.007	<0.007	0.041	<0.007	<0.007	<0.007
BDE-77	0.060	0.049	0.034	<0.002	0.014	0.019	<0.002	<0.002	<0.002	<0.002	<0.002
BDE-85	0.136	0.058	0.092	0.153	0.190	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
BDE-99	8.910	5.850	4.508	4.135	4.615	1.915	2.752	0.256	0.237	<0.004	0.046
BDE-100	1.562	1.020	0.688	0.630	0.667	0.312	0.394	0.035	0.036	<0.002	<0.002
BDE-119	<0.009	0.101	0.370	0.265	0.177	0.039	0.153	<0.009	<0.009	<0.009	<0.009
BDE-126	0.152	<0.004	0.063	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
BDE-138	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
BDE-139	<0.002	<0.002	<0.002	0.295	<0.002	<0.002	<0.002	0.052	<0.002	<0.002	<0.002
BDE-140	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.046	<0.001	<0.001	<0.001
BDE-153	0.778	0.191	0.275	0.208	0.219	0.079	0.709	0.037	<0.001	<0.001	<0.001
BDE-156	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
BDE-171	0.391	<0.045	<0.045	0.539	0.180	0.172	0.081	<0.045	<0.045	<0.045	<0.045
BDE-180	1.689	<0.055	<0.055	<0.055	<0.055	<0.055	0.278	<0.055	<0.055	<0.055	<0.055
BDE-183	2.458	2.134	2.967	2.914	2.894	1.332	4.923	0.292	0.206	<0.017	0.033
BDE-183 (dw)	0.939	0.817	1.062	0.922	0.917	0.416	1.489	0.088	0.058	<0.007	0.008
BDE-183 (Yang et al)			5.45	2.87	4.40	6.09	6.72	4.62	1.43	<0.04	
BDE-184	0.756	0.176	0.235	0.242	0.045	<0.021	0.035	<0.021	<0.021	0.052	<0.021

	2015	2012	2009	2004	1999	1993	1985	1977	1969	1954	1935
BDE-196	2.050	0.760	1.569	0.891	0.706	1.134	1.723	0.324	0.262	0.133	<0.005
BDE-197+201*	<0.013	1.260	2.293	1.201	0.772	0.920	1.378	0.358	0.285	<0.013	<0.013
BDE-203	<0.020	1.807	3.169	1.758	1.052	1.075	1.147	0.360	<0.020	<0.020	<0.020
BDE-204	1.887	0.350	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018
BDE-205	71.835	<0.119	126.695	142.785	56.533	17.982	18.023	2.423	1.758	0.907	0.380
BDE-206	80.153	44.892	43.254	70.463	38.890	25.418	9.869	1.488	0.929	0.689	0.278
BDE-207	47.732	27.832	<0.050	47.408	25.163	21.809	4.846	0.824	0.625	0.398	<0.050
BDE-208	325.611	375.129	304.992	230.419	208.710	156.505	136.551	46.021	49.444	12.223	3.723
BDE-209	124.396	143.647	109.193	72.928	66.142	48.875	41.303	13.818	13.894	3.578	0.970
BDE-209 (dw)	2.050	0.760	1.569	0.891	0.706	1.134	1.723	0.324	0.262	0.133	<0.005
BDE-209 (Yang et al)			351	251	207	135	120	89.5	53.1	19.6	
∑PBDE (n)	557.56 (25)	467.38 (22)	496.91 (23)	508.79 (24)	344.37 (23)	231.91 (21)	183.94 (20)	52.95 (18)	54.34 (13)	14.57 (7)	4.49 (6)
∑PBDE (dw)	213.01	178.97	177.90	161.03	109.13	72.42	55.64	15.90	15.27	4.27	1.17
∑PBDE (Yang et al)			370.55	260.02	217.72	145.62	132.26	96.89	56.14	19.6	
$\sum PBDE_{tri\text{-}hexa}$ (n)	19.49 (12)	11.23 (11)	9.22 (12)	8.84 (11)	8.60 (10)	4.93 (10)	4.28 (6)	0.65 (8)	0.59 (4)	0.17 (1)	0.07 (2)
$\sum PBDE_{tri\text{-}hexa}$ (dw)	19.49	11.23	9.22	8.84	8.60	4.93	4.28	0.65	0.59	0.17	0.07
$\sum PBDE_{tri\text{-}hexa}$ (Yang et al)			14.1	6.15	6.32	4.53	5.54	2.77	1.61	<0.03	
$\sum PBDE_{di\text{-}nona}$	231.95	92.26	191.91	278.37	135.66	75.40	47.39	6.93	4.91	2.35	0.76
$\sum PBDE_{di\text{-}nona}$ (dw)	88.61	35.33	68.71	88.10	42.99	23.55	14.33	2.08	1.38	0.69	0.20
$\sum PBDE_{hepta\text{-}nona}$	211.95	80.59	182.34	269.30	126.80	70.48	42.93	6.26	4.30	2.18	0.69
$\sum PBDE_{hepta\text{-}nona}$ (dw)	80.97	30.86	65.28	85.23	40.19	22.01	12.98	1.88	1.21	0.64	0.18
$\sum PBDE_{(a)}$	18.41	10.89	8.47	8.04	8.19	4.79	3.41	0.47	0.59	0.17	0.07
$\sum PBDE_{(b)}$	16.83	9.84	7.63	7.70	7.97	4.54	3.15	0.55	0.57	0.17	0.07

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section (2.6.3.1) for detailed description of SDL derivation.

[a,b] refer to BDE congeners -17, -28, -49, -47, -66, -100, -99, -85 and -153 quantified on an OC and dw basis respectively.

Yang et al values correspond to those previously reported from the same location as presented in Yang et al, 2016.

Table 3.2: Concentrations of target PBDEs (ng g^{-1} OC, unless otherwise specified) in analysed sediment from S2- Wake Valley Pond.

	2015	2009	2005	1999	1993	1985	1977	1965	1954	1935
BDE-7	0.040	<0.001		<0.001	0.070		<0.001	<0.001	<0.001	<0.001
BDE-10	<0.001	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001	<0.001
BDE-15	0.017	<0.001		0.015	0.016		0.003	<0.001	<0.001	<0.001
BDE-17	0.063	0.003		0.009	0.020		<0.001	<0.001	0.003	<0.001
BDE-28	0.076	0.034		0.055	0.044		0.005	<0.001	0.029	<0.001
BDE-30	<0.001	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001	<0.001
BDE-47	1.250	0.663		0.569	0.480		0.119	0.181	0.847	0.308
BDE-49	0.164	0.123		0.272	0.115		0.002	<0.003	0.043	<0.004
BDE-66	0.089	0.030		0.061	0.089		0.002	<0.001	<0.003	<0.002
BDE-71	0.015	<0.003		0.307	0.130		<0.003	<0.003	0.518	<0.005
BDE-77	0.009	<0.001		<0.001	0.003		<0.001	<0.001	<0.001	<0.001
BDE-85	0.056	0.005		0.011	0.040		<0.001	<0.001	<0.002	<0.002
BDE-99	1.188	0.798		0.859	0.831		0.080	<0.001	0.091	<0.002
BDE-100	0.233	0.136		0.134	0.101		0.009	<0.001	<0.004	<0.001
BDE-119	0.069	<0.002		<0.002	<0.002		<0.002	<0.002	<0.004	<0.003
BDE-126	<0.001	<0.001		<0.001	<0.001		<0.001	<0.001	<0.002	<0.002
BDE-138	0.014	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001	<0.001
BDE-139	0.021	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001	<0.001
BDE-140	0.007	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001	<0.001
BDE-153	0.205	0.126		0.222	0.232		0.024	<0.001	<0.001	<0.001
BDE-156	<0.001	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001	<0.001
BDE-171	<0.002	<0.002		<0.002	<0.002		<0.002	<0.002	<0.003	<0.003
BDE-180	0.052	<0.002		<0.002	<0.002		<0.002	<0.002	<0.003	<0.003
BDE-183	0.173	0.145		0.148	0.133		0.048	<0.0002	<0.0002	<0.0002
BDE-183 (dw)	0.584	0.567		0.536	0.508		0.169	<0.001	<0.001	<0.001
BDE-183 (Yang et al)		0.63	0.58	0.53	0.50	0.44	0.33	<0.12	<0.12	
BDE-184	0.055	0.012		0.038	0.018		<0.001	<0.001	<0.002	<0.001

	2015	2009	2005	1999	1993	1985	1977	1965	1954	1935
BDE-196	0.824	0.714		0.426	0.367		0.129	0.019	<0.005	<0.004
BDE-197+201*	0.537	0.360		0.327	0.339		0.074	<0.005	<0.009	<0.008
BDE-203	0.804	0.496		0.251	0.371		0.085	0.034	<0.012	<0.011
BDE-204	<0.011	<0.012		<0.011	<0.012		<0.011	<0.012	<0.021	<0.019
BDE-205	3.754	1.301		1.458	0.639		<0.009	<0.009	<0.016	<0.015
BDE-206	3.552	2.207		1.359	1.438		0.271	<0.007	<0.012	<0.011
BDE-207	2.592	1.672		0.874	1.069		0.091	<0.008	<0.014	<0.013
BDE-208	42.209	45.590		31.940	19.535		14.960	<0.162	<0.282	<0.255
BDE-209	12.498	11.617		8.849	5.122		4.264	<0.042	<0.042	<0.042
BDE-209 (dw)	0.824	0.714		0.426	0.367		0.129	0.019	<0.005	<0.004
BDE-209 (Yang et al)		32.9	17.9	27.0	15.6	19.4	17.3	2.5	<0.13	
∑PBDE (n)	59.08 (29)	55.23 (19)		39.90 (21)	26.57 (23)		16.02 (15)	0.23 (3)	1.53 (6)	0.31 (1)
∑PBDE (dw)	17.49	14.07		11.05	6.97		4.57	0.06	0.24	0.05
∑PBDE (Yang et al)		35.96	19.84	30.08	17.79	21.18	18.38	2.54	<0.13	
$\sum PBDE_{tri\text{-}hexa}$ (n)	3.46 (15)	1.92 (9)		2.50 (10)	2.09 (11)		0.24 (7)	0.18 (1)	1.53 (6)	0.31 (1)
$\sum PBDE_{tri\text{-}hexa}$ (dw)	1.02	0.49		0.69	0.55		0.07	0.05	0.24	0.05
$\sum PBDE_{tri\text{-}hexa}$ (Yang et al)		2.43	1.36	2.55	1.69	1.34	0.75	<0.01	<0.01	
$\sum PBDE_{di\text{-}nona}$	2.16	5.12	7.02	2.76	11.97	6.27	10.2	4.31	4.56	4.73
$\sum PBDE_{di\text{-}nona}$ (dw)	5.00	2.46		2.20	1.84		0.30	0.06	0.24	0.05
$\sum PBDE_{hepta\text{-}nona}$	13.36	7.72		5.44	4.86		0.82	0.05	<0.021	<0.021
$\sum PBDE_{hepta\text{-}nona}$ (dw)	3.96	1.97		1.51	1.28		0.23	0.01	<0.003	<0.003
$\sum PBDE_{(a)}$	3.33	1.92		2.19	1.95		0.24	0.18	1.01	0.31
$\sum PBDE_{(b)}$	0.98	0.49		0.61	0.51		0.07	0.05	0.16	0.05

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section (2.6.3.1) for detailed description of SDL derivation.

[a,b] refer to BDE congeners -17, -28, -49, -47, -66, -100, -99, -85 and -153 quantified on an OC and dw basis respectively.

Yang et al values correspond to those previously reported from the same location as presented in Yang et al, 2016.

Table 3.3: Concentrations of target PBDEs (ng g^{-1} OC, unless otherwise specified) in analysed sediment from S3- Holt Hall Lake.

	2015	2009	2004	1999	1993	1985	1977	1969	1954	1935
BDE-7	0.009	0.014	0.021		<0.001	<0.001		<0.001	0.001	0.001
BDE-10	<0.001	<0.001	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001
BDE-15	0.019	0.025	0.022		0.007	0.037		0.015	0.006	0.003
BDE-17	0.049	0.062	0.044		0.027	0.012		0.012	0.010	0.007
BDE-28	0.046	0.086	0.059		<0.002	0.029		0.025	0.015	0.012
BDE-30	<0.002	<0.002	<0.002		<0.002	<0.002		<0.002	<0.002	<0.001
BDE-47	0.748	1.455	1.024		0.821	0.446		0.186	0.109	0.078
BDE-49	0.397	0.736	0.635		1.009	0.239		0.104	0.010	0.003
BDE-66	0.091	<0.003	<0.004		<0.004	0.053		0.042	<0.004	<0.003
BDE-71	<0.004	0.037	<0.005		0.769	0.179		<0.005	<0.005	<0.004
BDE-77	0.004	0.006	0.002		<0.002	<0.002		<0.002	<0.002	<0.001
BDE-85	0.046	0.101	0.068		<0.002	0.037		0.002	<0.002	<0.001
BDE-99	1.215	2.439	1.913		1.943	0.939		0.235	0.032	0.026
BDE-100	0.253	0.524	0.430		0.157	0.143		0.026	<0.001	0.005
BDE-119	0.027	0.015	0.007		<0.002	<0.002		0.021	<0.001	<0.001
BDE-126	<0.001	<0.001	<0.001		<0.001	<0.001		<0.001	<0.001	<0.001
BDE-138	0.013	0.044	0.019		<0.003	<0.003		<0.003	<0.003	<0.002
BDE-139	0.013	0.024	0.012		<0.003	<0.003		<0.003	<0.003	<0.002
BDE-140	0.002	0.003	0.003		<0.003	<0.003		<0.003	<0.003	<0.002
BDE-153	0.202	0.467	0.390		0.132	0.176		0.015	0.002	<0.002
BDE-156	<0.002	<0.002	<0.002		<0.003	<0.003		<0.003	<0.002	<0.002
BDE-171	0.007	0.042	<0.002		<0.002	<0.002		<0.002	<0.002	<0.001
BDE-180	0.024	0.044	0.040		<0.002	<0.002		<0.002	<0.002	<0.001
BDE-183	0.432	0.737	0.759		0.368	0.372		0.061	0.008	<0.001
BDE-183 (dw)	0.148	0.212	0.204		0.076	0.075		0.012	0.002	<0.0001
BDE-183 (Yang et al)		0.59	1.40	0.51	0.57	0.51	<0.12	<0.12		
BDE-184	0.034	0.049	0.047		<0.001	0.013		<0.001	<0.001	<0.001

	2015	2009	2004	1999	1993	1985	1977	1969	1954	1935
BDE-196	0.302	0.394	0.309		<0.002	0.056		0.011	<0.002	<0.001
BDE-197+201*	0.435	0.730	0.610		<0.002	0.248		0.047	0.003	<0.002
BDE-203	0.579	0.629	0.458		<0.004	0.276		0.048	0.005	<0.002
BDE-204	0.838	0.824	0.689		<0.005	0.157		0.025	<0.004	<0.003
BDE-205	<0.006	<0.006	<0.007		<0.008	<0.008		<0.007	<0.007	<0.005
BDE-206	2.205	2.856	2.211		0.074	0.475		0.036	<0.015	<0.010
BDE-207	2.447	3.375	2.737		0.581	0.551		0.114	<0.011	<0.008
BDE-208	2.072	2.726	2.128		0.288	0.293		0.056	0.010	<0.009
BDE-209	35.041	28.947	22.356		22.061	11.153		1.158	<0.637	<0.435
BDE-209 (dw)	12.026	8.306	5.993		4.560	2.326		0.316	<0.1492	<0.1492
BDE-209 (Yang et al)		26.7	19.4	9.45	13.6	7.97	2.52	3.53		
∑PBDE (n)	47.58 (29)	47.39 (28)	37.03 (27)		28.24 (13)	15.89 (21)		2.24 (20)	0.21 (13)	0.13(10)
∑PBDE (dw)	20.63	18.89	13.86		6.91	4.15		0.67	0.09	0.17
∑PBDE (Yang et al)		33.15	25.87	15.13	17.95	10.95	3.58	4.17		
$\sum PBDE_{tri\text{-}hexa}$ (n)	3.11 (14)	6.00 (14)	4.61 (13)		4.86 (7)	2.25 (10)		0.67 (10)	0.18 (6)	0.13 (6)
$\sum PBDE_{tri\text{-}hexa}$ (dw)	1.29	3.74	4.4	1.86	8.74	4.45	7.37	2.19	2.16	3.7
$\sum PBDE_{tri\text{-}hexa}$ (Yang et al)		5.86	5.07	5.17	3.78	2.47	1.06	0.64		
$\sum PBDE_{di\text{-}nona}$	12.54	18.44	14.68		6.18	4.73		1.08	0.21	0.13
$\sum PBDE_{di\text{-}nona}$ (dw)	4.31	5.33	3.96		1.32	0.99		0.23	0.05	0.03
$\sum PBDE_{hepta\text{-}nona}$	9.40	12.41	10.03		1.31	2.44		0.40	0.03	0.00
$\sum PBDE_{hepta\text{-}nona}$ (dw)	3.23	3.56	2.69		0.27	0.49		0.08	0.01	0.00
$\sum PBDE_{(a)}$	3.05	5.87	4.56		4.09	2.07		0.65	0.18	0.13
$\sum PBDE_{(b)}$	1.05	1.69	1.22		0.85	0.42		0.13	0.04	0.03

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section (2.6.3.1) for detailed description of SDL derivation.

[a,b] refer to BDE congeners -17, -28, -49, -47, -66, -100, -99, -85 and -153 quantified on an OC and dw basis respectively.

Yang et al values correspond to those previously reported from the same location as presented in Yang et al, 2016.

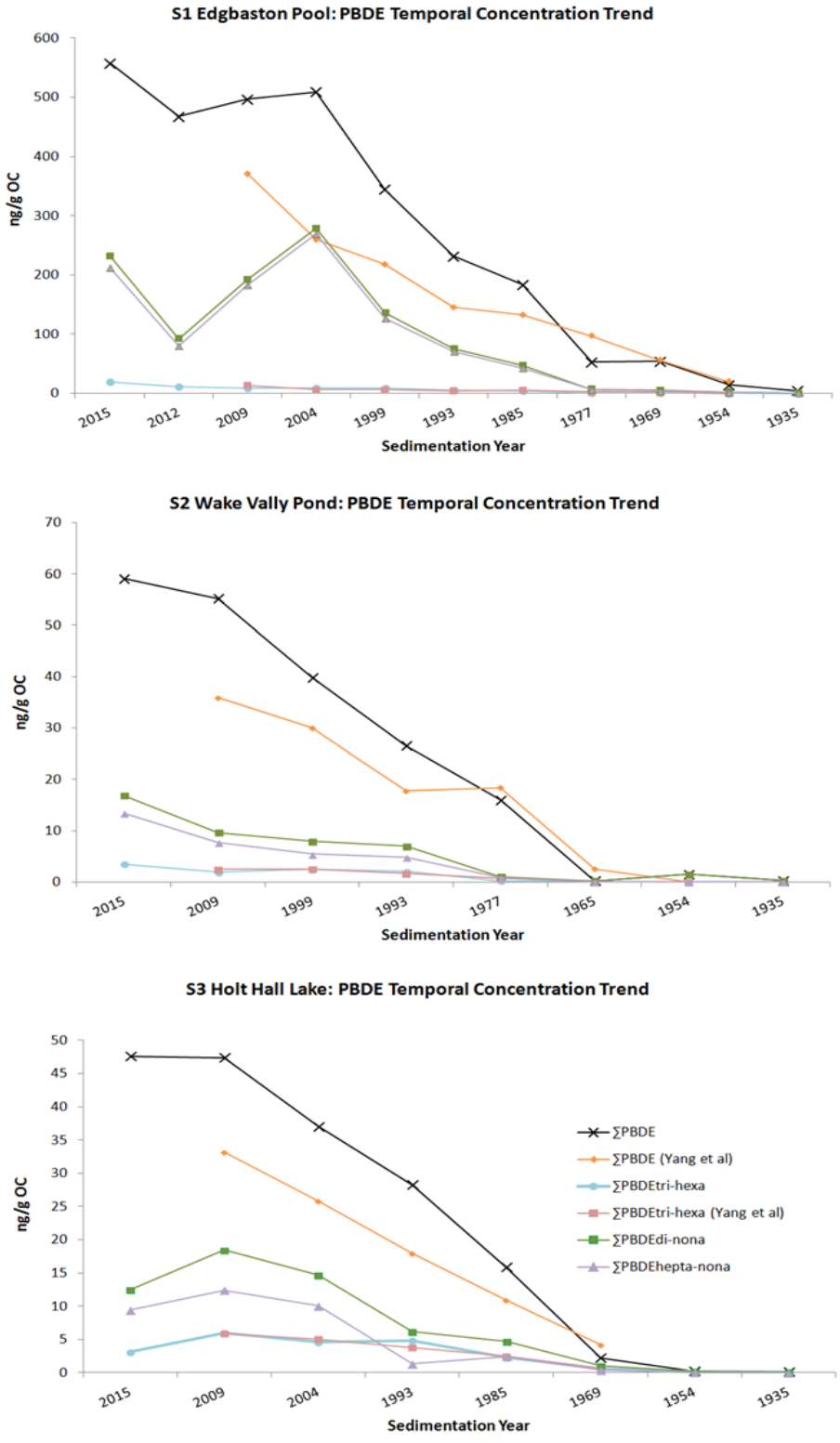


Figure 3.1: Temporal trends of composite PBDE in ng g^{-1} OC as quantified in sediments taken at S1- 3. Yang et al data was taken from Yang et al 2016 for corresponding sampling locations and sedimentation year.

∑PBDE trends across all three sites showed reasonable congruence with those previously reported by Yang et al, 2016 with appreciable concentrations (2× MDL) appearing in sediments from the mid-1960s to approximately 1970. All sites showed a trend of increase continuing relatively steadily to 2015 levels with noticeable exceptions at S1 Edgbaston Pool, which showed a decline in ∑PBDE concentration over the period of 2004- 2012 (508.79- 467.38 ng g^{-1} OC) before continuing to increase to its maximum value (557.56 ng g^{-1} OC) observed in the data set in the 2015 sample. Wake Valley Pond ∑PBDE concentrations, unlike those at S1 Edgbaston Pool were observed to increase linearly at a rate of ~1.3 ng g^{-1} OC y^{-1} over the period of 1965 to 2009 before reducing to ~0.64 ng g^{-1} OC y^{-1} from 2009 to reach the maximum observed ∑PBDE concentration at this site of 59.08 ng g^{-1} OC in 2015. ∑PBDE concentration trends at S3 were also observed to plateau after 2009 (∑PBDE= 47.39 ng g^{-1} OC) with an increase of just 0.19 ng g^{-1} observed between the 2009 and 2015 sample. This slight increase was attributed almost entirely to BDE- 209, which increased from 28.95- 35.04 ng g^{-1} OC over this period, during which time the vast majority of other analysed congeners were in decline with $\sum PBDE_{di\text{-}nona}$ concentrations falling by 31 % from 18.44- 12.54 ng g^{-1} OC.

Substantial differences were observed in ∑PBDE concentrations between site specific data sets with comparison to those observed previously, with all post- 1977 ∑PBDE concentrations quantified here, exceeding those reported in Yang et al. This was attributable principally to the additional number of congeners analysed in this study, for the most part belonging to those of bromination order –hepta and above, and specifically to the relative contribution of higher brominated congeners to ∑PBDE totals. $\sum PBDE_{hepta\text{-}nona}$ relative contributions to ∑PBDE concentrations followed a consistent pattern of temporal increase across all sites, ranging on average from 13.3 % to 27.1 % (3 site average % value) from 1977 to 2004 respectively, approximately equal to the ∑PBDE concentration difference observed between data sets during this period. The presence of elevated nona- BDE congeners in UK sediment chronologies is not without precedent, in 2010 Vane et al reported averaged contributions

of 11 % to total weight PBDEs as sampled in cores from the Clyde River Estuary [38]. While the presence of nona- BDE contamination in sediments is expected, given these congeners constitute between 0.3- 8 % to the total weight of deca-BDE commercial mixtures [16,94] the magnitude observed here and in the Vane et al data set, highlight the need for continued inclusion of these congeners to future investigations of ∑PBDE contamination.

$\sum PBDE_{tri\text{-}hexa}$ values and trends showed remarkable agreement with those observed in the Yang et al data set across all sites and showed slight elevations in the more recently deposited sediments at S1 and S2, increasing by 26.9 % (11.23- 19.49 ng g^{-1} OC) at S1 and 35.7 % (1.92- 3.46 ng g^{-1} OC) between 2009 and 2015 respectively. The extension of the temporal scale from 2009- 2015 has confirmed, in contrast to the observations of Yang et al, that $\sum PBDE_{tri\text{-}hexa}$ trends are in not as yet in decline at these sites. $\sum PBDE_{tri\text{-}hexa}$ concentrations over the same period were, however observed to decline in the years following the Yang et al assessment at S3, by 48.1 % from 6.00- 3.11 ng g^{-1} OC (2009-2015). Differences in the direction of these trends is indicative of the degree of inter-site trend heterogeneity and the extent to which localised factors such as population density and degree of urbanisation/industrialisation influence observed contaminant fluxes.

BDE- 183 concentration trends were observed to be reasonably consistent with those previously reported in Yang et al 2016 for sites S2 and S3 however deviated significantly in concentration and direction at S1 (Figure 3.2). Differences in concentrations between data sets are as yet currently unexplained however, may be due to the sample pooling and homogenisation procedure employed by Yang et al which was not conducted here. The more up to date temporal trends at S1 conducted in this study revealed clear reductions in BDE- 183 sediment contamination from 2009 to 2015 with steady concentrations at S2 and slight reductions at S3 apparent over the same period respectively,

which is suggestive of the effectiveness of legislative restrictions on the use of the Octa-BDE commercial formulation which came into effect in Europe in 2004 [95]. This congeners slowed response to legislative regulations, as observed at S2 and S3, is troubling as it is likely the result of continued environmental release from a sizeable residual PBDE reservoir in waste streams or products remaining in use throughout the UK.

Reflective of continued usage patterns of commercial BDE formulations in the UK over the temporal scale of the sediment chronology, BDE- 209 was not surprisingly the most abundant single BDE congener observed in all samples. BDE- 209 concentration chronologies are illustrated in Figure 3.1 across the 3 sites as the difference between the $\sum PBDE_{di\text{-}nona}$ and ∑PBDE trends presented. Across all sites BDE- 209 showed steady increases from its appearance in sediment deposited from ~1954 onwards. These data are consistent with the findings of Yang et al which also reported no obvious levelling off trend in concentrations of this congener at these sites.

As was concluded in Yang et al, ∑PBDE trends observed at the 3 sites analysed here were generally consistent with the vast majority of observations reported in Western Europe, N America and Asia. Almost all chronologies observed rapid increase immediately post onset of quantifiable concentrations, with onset years ranging from the mid-1940s in N America [96] to the beginning of the 1970s at sites in Switzerland [97], with varying direction and magnitude of trends in surface layers reported from inter-core comparisons within individual studies. A most notable and recent example, showed vast differences in the direction and magnitude of ∑PBDE trends at surface layers across 6 cores taken at sites sampled along a 10 km section of the Inner Clyde Estuary, UK [38], with 2 surface layer trends indicating sustained temporal ∑PBDE increases, and 4 showing decreasing or constant contamination trends. Variations in surficial sediment trend magnitude and direction were

also observed in a study by Zegers et al (2003) where increasing trends were identified in surface layers in 2 of 3 cores analysed. This difference however, is likely attributable to the large geographical distance and vastly different environmental conditions between the locations of sampling [40]. ∑PBDE concentration trend magnitude and direction was however, somewhat more definitively demonstrated in a set of 6 cores taken from the Great Lakes region (surface layer deposition dated to 2002), where steady increases were observed at surface layers in 5 of the 6 cores sampled [96] as well as in a set of 3 cores from Tokyo Bay, Japan sampled in 2002. This site, despite reporting increasing ∑PBDE trends, noted the negative trend of $\sum PBDE_{di\text{-}nona}$ from the mid-1990s with increasing BDE- 209 concentrations responsible for the observed overall PBDE increases [70].

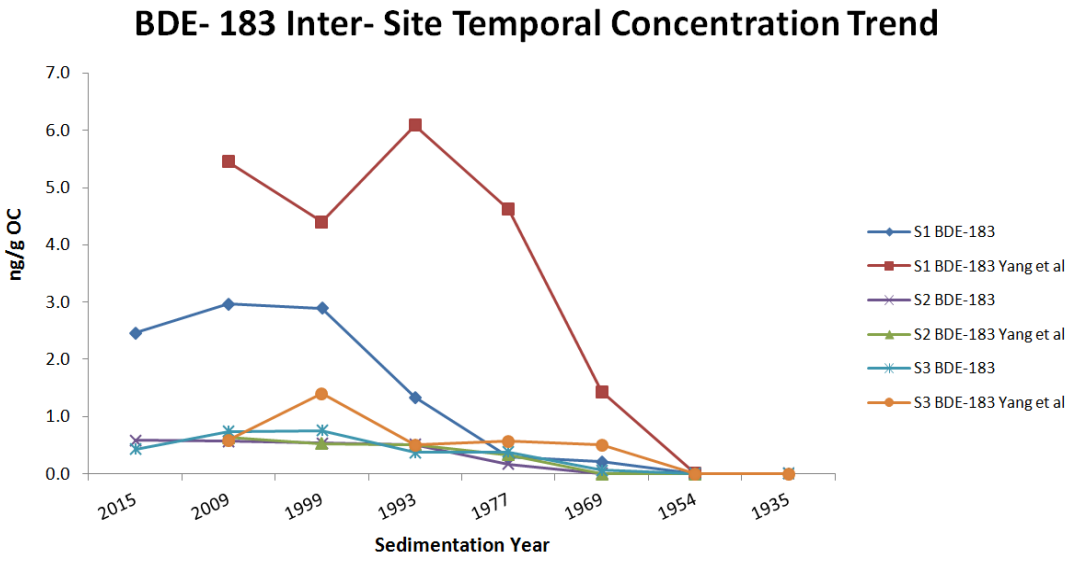


Figure 3.2: Inter- site sediment BDE- 183 concentrations in ng g^{-1} OC quantified at S1 Edgbaston Pool, S2 Wake Valley Pond and S3 Holt Hall Lake with comparison to concentrations previously observed at these sites in Yang et al 2016.

3.4 PBDD/F Contaminant Trends in Sediments from English Fresh Water Lakes.

3.4.1 Concentrations, Temporal and Spatial Distribution of PBDD/Fs.

To evaluate the presence and categorise the temporal distribution of brominated dioxin and furan contamination at these sites, vertical profiles of sediments were sampled, radiometrically dated and analysed for thirteen 2,3,7,8- substituted PBDD/Fs as well as homologue composite totals for tetra- through hepta- substituted PBDD/Fs. The presence of the 2,4,6,8- substituted $^{13}C_{12}$TBDF in both calibration and cleanup standards permitted the individual quantification of this compound and it was therefore included in the target analyte set. Analysis of PBDD/Fs was performed on identical sample material as were PBDEs, eliminating effects associated with sample homogenisation and inconsistent extraction and clean-up procedures (Chapter 2.3).

Tables 3.4- 3.6 show the concentrations of PBDD/Fs analysed from sediment core samples taken across the 3 sites in this study. All data in this section is quantified on a per OC basis unless otherwise described. All data from samples listed in Tables 3.4- 3.6, met the requirements for positive identification and quantification as outlined in Section 2.6, with the exception of S3- 1993, which suffered from low recovery of internal standards, and higher than usual background counts. This sample despite being included in data tables for the purpose of reporting SDLs did not yield conclusive PBDD/F results.

The following sections are dedicated to describing the concentrations, composition and temporal trends of PBDD/F present in the sediment profile at the sampling sites as well as establishing the extent and presence of relationship between these and those of the PBDEs described in the preceding sections.

Table 3.4: Concentrations of target PBDD/Fs (pg g^{-1} OC, unless otherwise specified) in analysed sediment from S1- Edgbaston Pool.

	2015	2012	2009	2004	1999	1993	1985	1977	1969	1954	1935
Dioxins											
2,3,7,8-TBDD	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
Total TBDD	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
Total TBDD (dw)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
1,2,3,7,8-PeBDD	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32
Total PeBDD	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32
Total PeBDD (dw)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD*	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32
1,2,3,7,8,9-HxBDD	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32
Total HxBDD	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32
Total HxBDD (dw)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
1,2,3,4,6,7,8-HpBDD	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96
Total HpBDD	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96
Total HpBDD (dw)	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19
OBDD	<1.33	<1.33	<1.33	<1.33	<1.33	<1.33	<1.33	<1.33	<1.33	<1.33	<1.33
OBDD (dw)	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42
Furans											
2,4,6,8-TBDF	27.45	18.15	2.61	5.59	6.95	2.23	<0.23	<0.23	<0.23	<0.23	<0.23
2,3,7,8-TBDF	<0.14	5.90	0.47	0.49	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Total TBDF	171.47	175.42	31.12	55.53	17.16	6.88	<0.21	0.40	<0.21	<0.21	<0.21
Total TBDF (dw)	65.51	67.17	11.14	17.58	5.44	2.15	<0.07	0.12	<0.07	<0.07	<0.07
1,2,3,7,8-PeBDF	<2.48	33.83	<2.48	<2.48	<2.48	<2.48	<2.48	<2.48	<2.48	<2.48	<2.48
2,3,4,7,8-PeBDF	<2.42	16.54	<2.42	<2.42	<2.42	<2.42	<2.42	<2.42	<2.42	<2.42	<2.42
Total PeBDF	5635.09	3975.82	3706.18	3563.99	2594.31	1515.47	416.76	113.78	3.50	<3.32	<3.32
Total PeBDF (dw)	2152.83	1522.45	1326.88	1128.00	822.15	473.27	126.06	34.16	0.98	<1.05	<1.05

	2015	2012	2009	2004	1999	1993	1985	1977	1969	1954	1935
1,2,3,4,7,8-HxBDF	244.26	215.43	292.27	<3.42	<3.42	14.09	<3.42	<3.42	<3.42	<3.42	<3.42
Total HxBDF	8478.68	7874.84	6884.82	9145.01	6431.20	2740.81	1301.49	165.77	<3.45	<3.45	<3.45
Total HxBDF (dw)	3239.20	3015.50	2464.90	2894.40	2038.09	855.93	393.67	49.77	<1.09	<1.09	<1.09
1,2,3,4,6,7,8-HpBDF	4339.18	3498.87	3775.51	3334.50	1783.53	1715.29	915.10	248.21	11.18	<0.59	<0.59
Total HpBDF	4339.18	3990.19	3778.00	3334.50	1793.29	1715.29	915.10	248.21	11.27	<6.29	<6.29
Total HpBDF (dw)	1657.74	1527.96	1352.60	1055.37	568.30	535.67	276.80	74.53	3.17	<1.99	<1.99
OBDF	<10.38	<10.38	<10.38	<10.38	<10.38	<10.38	<10.38	<10.38	<10.38	<10.38	<10.38
OBDF (dw)	<3.29	<3.29	<3.29	<3.29	<3.29	<3.29	<3.29	<3.29	<3.29	<3.29	<3.29
$\sum PBDD_{2,3,7,8}$	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
$\sum PBDF_{2,3,7,8}$	4583.4	3770.6	4068.2	3335.0	1783.5	1729.4	915.1	248.2	11.2	<0.14	<0.14
$\sum PBDF_{2,3,7,8+2,4,6,8}$	4610.9	3738.3	4070.9	3340.6	1790.5	1731.6	915.1	248.2	11.2	<0.14	<0.14
$\sum PBDD/F_{2,3,7,8}$	4583.4	3770.6	4068.2	3335.0	1783.5	1729.4	915.1	248.2	11.2	<0.14	<0.14
∑PBDD	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
∑PBDF	18624.4	16016.3	14400.1	16099.0	10836.0	5978.5	2633.4	528.2	14.8	<0.14	<0.14
∑PBDD/F	18624.4	16016.3	14400.1	16099.0	10836.0	5978.5	2633.4	528.2	14.8	<0.05	<0.05
WHO05-TEQ PBDD/F (Lb)	67.82	63.10	67.03	33.39	17.84	18.56	9.15	2.48	0.11	0.00	0.00
WHO05-TEQ PBDD/F (Ub)	68.53	63.65	67.72	34.13	18.59	19.27	9.90	3.23	0.86	0.76	0.76
$\sum PBDD_{2,3,7,8}$ (dw)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
$\sum PBDF_{2,3,7,8}$ (dw)	1751.1	1443.9	1456.5	1055.5	565.2	540.1	276.8	74.5	3.1	<0.04	<0.04
$\sum PBDF_{2,3,7,8+2,4,6,8}$ (dw)	1761.5	1450.8	1457.4	1057.3	567.4	540.8	276.8	74.5	3.1	<0.04	<0.04
$\sum PBDD/F_{2,3,7,8}$ (dw)	1751.1	1443.9	1456.5	1055.5	565.2	540.1	276.8	74.5	3.1	<0.04	<0.04
∑PBDD (dw)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
∑PBDF (dw)	7115.3	6133.1	5155.5	5095.3	3434.0	1867.0	796.5	158.6	4.2	<0.07	<0.07
∑PBDD/F (dw)	7115.3	6133.1	5155.5	5095.3	3434.0	1867.0	796.5	158.6	4.2	<0.05	<0.05
WHO05-TEQ dw PBDD/F (Lb)	25.91	24.16	24.00	10.57	5.65	5.80	2.77	0.75	0.03	0.00	0.00
WHO05-TEQ dw PBDD/F (Ub)	26.34	24.33	24.43	11.01	6.09	6.23	3.21	1.19	0.47	0.44	0.44

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of SDL derivation.

Table 3.5: Concentrations of target PBDD/Fs (pg g^{-1} OC, unless otherwise specified) in analysed sediment from S2- Wake Valley Pond.

	2015	2009	2005	1999	1993	1985	1977	1965	1954	1935
Dioxins										
2,3,7,8-TBDD	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Total TBDD	<0.06	<0.06	<0.06	0.61	<0.06	1.80	<0.06	<0.06	<0.06	<0.06
Total TBDD (dw)	<0.02	<0.02	<0.02	0.17	<0.02	0.49	<0.02	<0.02	<0.02	<0.02
1,2,3,7,8-PeBDD	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17
Total PeBDD	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17
Total PeBDD (dw)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD*	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41
1,2,3,7,8,9-HxBDD	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41
Total HxBDD	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41
Total HxBDD (dw)	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
1,2,3,4,6,7,8-HpBDD	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37
Total HpBDD	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37	<1.37
Total HpBDD (dw)	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43
OBDD	2.20	2.24	<0.44	<0.44	0.69	<0.44	<0.44	<0.44	<0.44	<0.44
OBDD (dw)	0.65	0.57	<0.14	<0.14	0.18	<0.14	<0.14	<0.14	<0.14	<0.14
Furans										
2,4,6,8-TBDF	21.51	10.85	10.28	9.48	6.57	6.76	0.60	<0.09	<0.09	<0.09
2,3,7,8-TBDF	0.93	<0.05	0.53	<0.05	1.39	0.82	1.36	<0.05	<0.05	<0.05
Total TBDF	109.77	76.86	95.00	80.06	43.45	42.83	5.63	1.55	5.39	<0.03
Total TBDF (dw)	32.50	19.58	24.98	22.18	11.39	11.71	1.60	0.41	0.82	<0.03
1,2,3,7,8-PeBDF	<0.57	<0.57	<0.57	<0.57	<0.57	<0.57	3.17	<0.57	<0.57	<0.57
2,3,4,7,8-PeBDF	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56
Total PeBDF	483.52	280.69	260.89	247.00	68.76	72.30	10.96	<0.48	<0.48	<0.48
Total PeBDF (dw)	143.16	71.52	68.60	68.43	18.03	19.76	3.13	<0.15	<0.15	<0.15

	2015	2009	2005	1999	1993	1985	1977	1965	1954	1935
1,2,3,4,7,8-HxBDF	<0.42	<0.42	5.65	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42
Total HxBDF	441.77	222.52	205.33	101.67	61.58	39.77	10.25	<0.37	<0.37	<0.37
Total HxBDF (dw)	130.80	56.70	53.99	28.17	16.15	10.87	2.92	<0.12	<0.12	<0.12
1,2,3,4,6,7,8-HpBDF	233.74	107.04	106.57	21.66	16.75	<1.44	<1.44	<1.44	<1.44	<1.44
Total HpBDF	234.06	110.17	109.13	21.72	16.75	<1.44	<1.44	<1.44	<1.44	<1.44
Total HpBDF (dw)	69.30	28.07	28.70	6.02	4.27	<0.46	<0.46	<0.46	<0.46	<0.46
OBDF	399.08	265.30	<4.69	<4.69	<4.69	<4.69	<4.69	<4.69	<4.69	<4.69
OBDF (dw)	118.16	67.60	<1.49	<1.49	<1.49	<1.49	<1.49	<1.49	<1.49	<1.49
$\sum PBDD_{2,3,7,8}$	2.2	2.2	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
$\sum PBDF_{2,3,7,8}$	633.7	372.3	112.7	21.7	18.1	0.8	4.5	<0.05	<0.05	<0.05
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$	655.2	383.2	123.0	31.1	24.7	7.6	5.1	<0.05	<0.05	<0.05
$\sum PBDD/F_{2,3,7,8}$	635.9	374.6	112.7	21.7	18.8	0.8	4.5	<0.05	<0.05	<0.05
∑PBDD	2.2	2.2	<0.06	0.6	0.7	1.8	<0.06	<0.06	<0.06	<0.06
∑PBDF	1668.2	955.5	670.3	450.5	190.5	154.9	26.8	1.5	5.4	<0.05
∑PBDD/F	1670.4	957.8	670.3	451.1	191.2	156.7	26.8	1.5	5.4	<0.05
WHO05-TEQ PBDD/F (Lb)	2.55	1.15	1.68	0.22	0.31	0.08	0.23	0.00	0.00	0.00
WHO05-TEQ PBDD/F (Ub)	3.12	1.73	2.21	0.79	0.88	0.66	0.79	0.58	0.58	0.58
$\sum PBDD_{2,3,7,8}$ (dw)	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
$\sum PBDF_{2,3,7,8}$ (dw)	187.6	94.9	29.6	6.0	4.8	0.2	1.3	<0.01	<0.01	<0.01
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$ (dw)	194.0	97.6	32.3	8.6	6.5	2.1	1.5	<0.01	<0.01	<0.01
$\sum PBDD/F_{2,3,7,8}$ (dw)	188.3	95.4	29.6	6.0	4.9	0.2	1.3	<0.01	<0.01	<0.01
∑PBDD (dw)	0.7	0.6	<0.02	0.2	0.2	0.5	<0.02	<0.02	<0.02	<0.02
∑PBDF (dw)	493.9	243.5	176.3	124.8	49.8	42.3	7.6	0.4	0.8	<0.03
∑PBDD/F (dw)	494.6	244.1	176.3	125.0	50.0	42.8	7.6	0.4	0.8	<0.02
WHO05-TEQ dw PBDD/F (Lb)	0.76	0.29	0.44	0.06	0.08	0.02	0.07	0.00	0.00	0.00
WHO05-TEQ dw PBDD/F (Ub)	0.94	0.48	0.61	0.24	0.26	0.21	0.25	0.19	0.19	0.19

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of SDL derivation.

Table 3.6: Concentrations of target PBDD/Fs (pg g^{-1} OC, unless otherwise specified) in analysed sediment from S3- Halt Hall Lake.

	2015	2009	2004	1999	1993	1985	1977	1969	1954	1935
Dioxins										
2,3,7,8-TBDD	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Total TBDD	<0.06	0.36	0.59	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Total TBDD (dw)	<0.02	0.10	0.16	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1,2,3,7,8-PeBDD	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Total PeBDD	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54
Total PeBDD (dw)	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD*	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39
1,2,3,7,8,9-HxBDD	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39	<0.39
Total HxBDD	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28
Total HxBDD (dw)	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
1,2,3,4,6,7,8-HpBDD	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38
Total HpBDD	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40
Total HpBDD (dw)	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
OBDD	<0.70	4.34	6.63	<0.70	<0.70	<0.70	<0.70	<0.70	<0.70	<0.70
OBDD (dw)	<0.22	1.25	1.78	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22
Furans										
2,4,6,8-TBDF	55.40	33.34	33.84	13.93	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
2,3,7,8-TBDF	0.87	1.28	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Total TBDF	250.98	149.28	180.71	79.93	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28
Total TBDF (dw)	86.15	42.85	48.46	18.73	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
1,2,3,7,8-PeBDF	0.99	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
2,3,4,7,8-PeBDF	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
Total PeBDF	393.13	442.99	351.71	188.19	<0.32	<0.32	<0.32	<0.32	<0.32	<0.32
Total PeBDF (dw)	134.94	127.16	94.32	44.09	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

	2015	2009	2004	1999	1993	1985	1977	1969	1954	1935
1,2,3,4,7,8-HxBDF	8.30	<0.28	5.60	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28
Total HxBDF	487.32	788.13	492.64	303.87	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38
Total HxBDF (dw)	167.27	226.24	132.11	71.19	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
1,2,3,4,6,7,8-HpBDF	249.24	489.05	288.33	77.83	<0.65	<0.65	<0.65	<0.65	<0.65	<0.65
Total HpBDF	296.01	490.22	288.54	78.02	<0.56	<0.56	<0.56	<0.56	<0.56	<0.56
Total HpBDF (dw)	101.61	140.72	77.38	18.28	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
OBDF	<2.51	<2.51	<2.51	<2.51	<2.51	<2.51	<2.51	<2.51	<2.51	<2.51
OBDF (dw)	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
$\sum PBDD_{2,3,7,8}$	<0.05	4.3	6.6	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
$\sum PBDF_{2,3,7,8}$	259.4	490.3	293.9	77.8	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$	314.8	523.7	327.8	91.8	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
$\sum PBDD/F_{2,3,7,8}$	259.4	494.7	300.6	77.8	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
∑PBDD	<0.06	4.7	7.2	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
∑PBDF	1427.4	1870.6	1313.6	650.0	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28
∑PBDD/F	1427.4	1875.3	1320.8	650.0	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
WHO05-TEQ PBDD/F (Lb)	3.44	5.02	3.44	0.78	0.00	0.00	0.00	0.00	0.00	0.00
WHO05-TEQ PBDD/F (Ub)	3.70	5.32	3.72	1.08	0.31	0.31	0.31	0.31	0.31	0.31
$\sum PBDD_{2,3,7,8}$ (dw)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
$\sum PBDF_{2,3,7,8}$ (dw)	89.0	140.7	78.8	18.2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$ (dw)	108.1	150.3	87.9	21.5	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
$\sum PBDD/F_{2,3,7,8}$ (dw)	89.0	142.0	80.6	18.2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
∑PBDD (dw)	<0.02	1.3	1.9	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
∑PBDF (dw)	490.0	537.0	352.3	152.3	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
∑PBDD/F (dw)	490.0	538.3	354.2	152.3	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
WHO05-TEQ dw PBDD/F (Lb)	1.18	1.44	0.92	0.18	0.00	0.00	0.00	0.00	0.00	0.00
WHO05-TEQ dw PBDD/F (Ub)	1.26	1.53	1.01	0.28	0.09	0.09	0.09	0.09	0.09	0.09

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of SDL derivation.

3.4.2 Concentrations, Temporal and Spatial Distribution of PBDDs.

PBDDs, composed of 7 individual 2,3,7,8- substituted congeners (including 1 chromatographic co-elution; Tables 3.4- 3.6, Section 2.6.1.6) as well as total (tetra- hepta) homologue group concentrations were quantified across the sampling sites. Observations of PBDD congeners at concentrations >MDLs were scarce and were entirely composed of OBDD and other unidentifiable non-2,3,7,8 tetra substituted PBDDs. Of the 31 samples analysed, ∑PBDDs composed of unidentifiable non- 2,3,7,8 substituted compounds were, however present in appreciable concentrations across the entire data set and ranged from 7.2- 0.6 pg g^{-1} OC, the maximum, present in sediment deposited in 2007 at S3, and the minimum value in the range from the 1999 sample at S2 respectively. OBDD was the dominant congener in all cases where ∑PBDDs were observed (Tables 3.4- 3.6), and given the elevated MDLs calculated for OBDD in S1 samples (<3.29 pg g^{-1} OC), it is entirely likely that OBDD is present in these sediments also, albeit at concentrations which were not quantifiable in this investigation and likely only in upper-layer sediments as was revealed at S2 and S3. The relative lack of observable PBDDs with respect to PBDFs has been well documented previously in the few studies available in literature focusing on PBDD/F contamination of surface sediments [98], atmospheric and bulk particulate deposition in Japan [67] and South America (Section 5.4), biological matrices (Section 4.6), Ericson Jogsten et al. 2010) as well as PBDD/F congener profiles of emissions from industrial and municipal waste incinerators (Wang *et al.*, 2010). Analysis of BDE commercial formulations revealed that for those mixtures analysed (n= 5), PBDDs were not present at concentrations exceeding LOQs [54]. PBDDs were however detected at levels 25000 times higher than their respective PBDF counterparts in Baltic Sea sponges (*Ephydatia fluviatili*), lending evidence to formation by natural processes [64]. In the handful of studies where PBDDs have positively been identified in ambient environmental matrices, concentrations are in all cases comparatively low with respect to quantified furans, were almost always dominated by tetra substituted congeners and do not tend to show concentration correlations with PBDEs, PBDFs, or PCDD/Fs leading most studies to conclude that PBDD environmental contamination is derived from

sources distinctly different to those of PBDF [67,69] and were accordingly not further explored in the context of this study.

3.4.3 PBDF Concentrations, Spatial Distributions and Comparisons.

Brominated furans were ubiquitously observed in sediment samples analysed from all 3 sites and tended to show higher concentrations in surficial sediments, following a declining trend with respect to sedimentation year. Peak ∑PBDF concentrations by site were highest at S1, with 18.624 ng g^{-1} OC (7.115 ng g^{-1} dw) observed in 2015 dated sediment, followed by S3 with 1.875 ng g^{-1} OC (0.537 ng g^{-1} dw, 2009) and S2 with a maximum ∑PBDF concentration of 1.670 ng g^{-1} OC (0.494 ng g^{-1} dw) observed in the 2015 dated slice. For the most part 2,3,7,8- substituted congeners correlated well with ∑homologue totals, despite being present at significantly reduced concentrations, however were observed to follow a different site maximum concentration pattern as observed for ∑PBDFs with S1 > S2> S3 in terms of maximum $\sum PBDF_{2,3,7,8}$ concentrations with 4.583 ng g^{-1} OC (1.751 ng g^{-1} dw) present at S1 in the 2015 sample, 0.639 ng g^{-1} OC (0.188 ng g^{-1} dw) at S2 in 2015 and 0.490 ng g^{-1} OC (0.141 ng g^{-1} dw) at S3 (2009).

Table 3.7 shows comparative values as reported in soils and surficial sediments from a variety of locations. Important to note is that the vast majority of these studies report ∑PBDD/F concentrations derived exclusively from 2,3,7,8- substituted congeners. Our maximum reported values for 2,3,7,8-congener total ∑PBDF (essentially identical to $\sum PBDD/F_{2,3,7,8}$ in these samples) show $\sum PBDD/F_{2,3,7,8}$ contamination at surficial sediment layers at S1, S2 and S3 to be slightly elevated in comparison to the majority of previously reported values from other urban rivers and lakes [65,101], marine sediments in Asia [102–105], yet lower than those from Sweden (Dang 2009 in Lundstedt 2016). Our values were also consistently below previous reported concentrations observed from soils at e-waste recycling and handling sites, and from fire affected soils in N America [76] and Sweden

(Lundstedt 2012 in Lundstedt, 2016). In perhaps the only previously reported data set of PBDD/F sediment trends, Goto et al in 2017 reported ∑PBDD/F as total homologue values from a set of 8 marine sediment cores and 5 additional surface samples taken from Tokyo Bay in 2002 [69]. Values reported at surface showed large spatial variability and ranged from 0.066- 0.002 ng g^{-1} dw, considerably lower than the ∑PBDD/F concentrations observed at surface in our data set. This, however was expected, and is likely a result of dilution and mixing effects arising from the sampling of sediments in a far larger water body. ∑PBDE concentrations and trends were also reported in Goto et al. and are contrasted with our data set in the following sections.

Table 3.7. Total concentration of PBDD/Fs, PCDD/Fs and PBDEs in soil and sediments in various environments.

	ΣPBDD/F	ΣPCDD/F	ΣPBDE	Reference
	(ng/g, dw)	(ng/g, dw)	(ng/g dw)	
Fresh water sediments				
S1-Edgbaston, UK (2015)	**7.115**		**213.01**	**This Study**
S3- Holt, UK (2009)	**0.537**		**18.89**	**This Study**
S2- Wake, UK (2015)	**0.494**		**17.49**	**This Study**
Rural/urban lakes, Sweden	0.44-0.54	0.97-2.4		Hagberg et al. (2005a)
Urban river, Sweden	0.41-1.7	0.31-2.0	29-62	Lundstedt (2012)
Rural lake Sweden	0.082-0.085	1.3-1.9	4.4-16	Lundstedt (2012)
Urban lake, China	0.00048-0.0057	0.056-0.35		Zhou et al. (2012)
Pond and stream, Sweden (fire affected)	0.061-8.7	0.013-2.1	0.73-150	Lundstedt (2012)
Stream at dump site, Peru	0.012-0.074	0.021-0.17	3.7-6.1	Naturvårdsverket (2011)
Lake, industr. Area, Thailand	0.037-1.5	0.27-180	3.4-58	Naturvårdsverket (2011)
Marine sediments				
Coastal, Hong Kong/Korea	nd.-0.46	0.23-6.3		Terauchi et al. (2009)
Cores, Tokyo Bay, Japan	0.0052-0.070	0.55-36	10-78050	Choi et al. (2003a)
Coastal, Osaka, Japan	0.0041-0.077	1.98-17.4	8.0-352	Ohta et al. (2002)
Coastal, Osaka, Japan – also cores	0.0024-0.59	0.50-12	53-910	Takigami et al. (2005)
Coastal and offshore, Sweden	0.050-10			Dang (2009)
Rural Soil				
Lanna, Sweden	0.028-0.054	0.0052-0.068	0.065-1.3	Lundstedt (2012)
Urban soil				
Umeå and Norrköp., Sweden	0.0011-0.22	0.0092-0.97	0.18-66	Lundstedt (2012)
Bangalore and Chennai, India	0.0060-0.31	0.045-1.4		Ramu et al. (2008)
Kyoto, Japan	0.28	0.54		Hayakawa et al. (2004)
Industr. area, China	nd.-0.43	0.045-0.71	2.03-269	Ma et al. (2008, 2009);
Industr., Thailand	0.019-0.16	0.40-1.0	1.8-13	Naturvårdsverket (2011)
Dump site, Peru	0.0086-0.32	0.031-1.3	3.6-92	Naturvårdsverket (2011)

3.4.4 Temporal Distribution of PBDFs and Relation with PBDEs.

Temporal trends of ∑PBDF, $\sum PBDF_{2,3,7,8}$ and ∑PBDEs observed at all 3 sites are displayed in Figure 3.3. ∑PBDF trends across sites all followed the same basic profile of increase post initial detection with respect to time, as was observed for ∑PBDEs. However, the temporal increase in ∑PBDFs was not as large in magnitude, nor as rapid in onset as was seen for ∑PBDEs. Attempts to statistically describe temporal ∑PBDF trends in terms of concentration 'doubling time', a common metric describing the time required for concentrations to double [106], could not be performed on these data, as slopes of $\ln(x)_i$ where $(x)_i$ represents ∑PBDF concentration at time (*i*) were not sufficiently linear, a requirement for the calculation of the first order rate constants used for doubling time calculations. Interestingly, the appearance of a temporal lag was present at all sites, between the onset of ∑PBDE concentrations and those of ∑PBDF, which, assuming the ∑PBDF temporal trends are principally driven by, or are in concert with those of ∑PBDE may indicate that concentrations required several years to reach levels >MDLs and be quantified accordingly. ∑PBDF concentrations first appeared in sediment at quantifiable concentrations (and subsequently remained so) at S1 in 1969, with a concentration of 3.5 pg g^{-1} OC, at S2 in 1954 at a concentration of 5.4 pg g^{-1} OC, however were not observed conclusively at S3 until 1999. It is possible however, that concentrations >MDLs were present in the 1993 sample, however this was not adequately quantified and suffered with low recoveries of $^{13}C_{12}$-labelled internal standards. Observation of PBDF in all samples and at all sites post onset, suggests that PBDF contamination at these sites has been widespread since initial detection.

As mentioned, following onset temporal ∑PBDF trends remained positive in magnitude across all sites until the period of 2004- 2009 where a decrease from 16.1- 14.4 ng g^{-1} OC was observed at S1. Following this decline, concentrations continued to rise at an increased rate to the values observed in the most recent sample taken at the benthic surface in 2015 (18.6 ng g^{-1} OC). Interestingly, this

feature was also present in the ∑PBDE temporal trend observed at S1 during the same period of sedimentation, and is clearly seen in trends displayed in Figure 3.3. The ∑PBDF temporal trend at S2 remained in steady increase from onset and was also observed to increase in magnitude with respect to time in the later deposited sediments. These trends are suggestive of increased PBDF contamination fluxes in recent years and accordingly warrant continued monitoring. S3 however, did not display the same trends as observed at S1 and S2, with indications of a decline in ∑PBDF fluxes to sediments occurring in the most recently deposited sediments there. This reduction in slope magnitude was also observed in ∑PBDE concentrations over the period of 2009 to 2015, with a rise of only 0.7 ng g^{-1} OC, in comparison to the increase of 10.36 ng g^{-1} OC, observed over the preceding sample period (2004- 2009). However indicative of a declining ∑PBDF contamination trend, it is important to note that this was established by the analysis of a single composite data point and therefore requires additional analysis of later deposited sediment (outside the scope of this study) before a trend decline can be adequately confirmed.

Spearman's rank correlation tests were performed to assess the presence of and extent of correlations between ∑PBDE and ∑PBDF observed in the data sets. Spearman's correlation coefficients (ρ) of 0.79, 0.78 and 0.71 were calculated between data sets from S1, S2 and S3 respectively. In cases where PBDF concentrations were <SDL, 0.5 x SDL was assumed. All relationships were found to be positive in magnitude and significant at a 95 % confidence interval with p values in all cases < 0.05, when compared against the appropriate critical values.

Correlations were re-evaluated after the removal of data points for which ∑PBDF concentration was <SDL. On doing so, the significance of the correlation was observed to decrease, lowering the confidence associated with the analysis. Despite this decrease in p value caused by the removal of

data points, S1 and S2 still yielded a significant correlation at 95 % confidence, this was not the case, however, for the S3 correlation, where the removal of 6 of the 10 data points resulted in a non-statistically significant correlation ($p > 0.05$). Accordingly entire data sets with concentrations <SDL assumed at 0.5x SDL was considered valid for the characterisation of the relationship in trends between ∑PBDE and ∑PBDF concentrations. This, given the vast body of established evidence linking PBDF formation from PBDE precursors, is an expected result, and indeed was recently established by Goto et al in a Japanese marine sedimentation chronology of PBDF contamination. In this study, positive and statistically significant correlations between PBDE and PBDF contamination (average ρ= 0.69, n= 3, $p< 0.05$) where observed in Osaka Bay [69]. The extent to which these values are correlated however, remains somewhat surprising, as the high ρ values observed in correlations across each site here, suggests a relatively consistent concentration ratio between ∑PBDE and ∑PBDF. This ratio, which appears to differ spatially, remains temporally constant over the time scale of this investigation, and strongly suggests that PBDF contamination does not take place in the absence of PBDE fluxes at these sites. This is a surprising result and lends indication to the assumption that despite the multitude of vastly different physical processes known to result in the emission of PBDFs to the environment, at these sites, in the absence of further data on concentrations of other phenolic BFRs, PBDEs appear to be the principal driver of PBDF contamination.

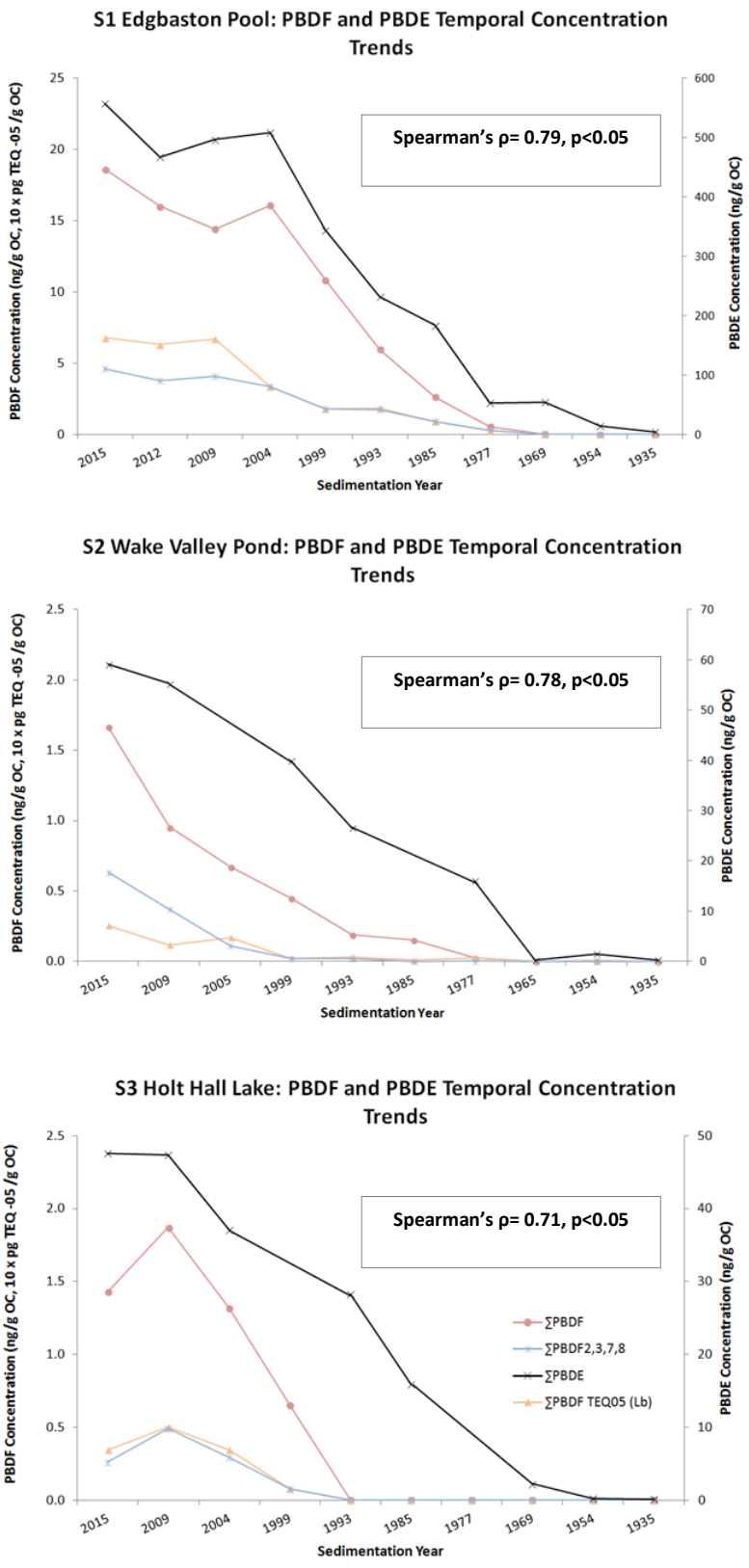


Figure 3.3: ∑PBDF, ∑2,3,7,8- PBDF in ng g^{-1} OC and 10x pg TEQ g^{-1} and ∑PBDE temporal concentration trends from S1 Edgbaston Pool, S2 Wake Valley Pond and S3 Holt Hall Lake. Also represented are site specific Spearman's rank order correlation results as performed between ∑PBDF and ∑PBDE.

To further assess the relationship between PBDF and PBDE contamination, concentration ratios between ∑PBDF and ∑PBDE were calculated for each sample analysed and compared against those measured in several technical BDE formulations as well as from house dusts generated from Japanese (for lack of more relevant local data) televisions known to have been treated with PBDE. Median (range) concentration ratios of 0.029 (2.718×10^{-4}- 0.034, n= 9), 1.03×10^{-4} (2.512×10^{-6}- 1.86×10^{-4}, n= 7) and 0.035 (0.030- 0.040, n= 3) were observed in data derived from S1- 3 respectively. Median PBDF: PBDE concentration ratios obtained in this study were compared against those in PBDE technical formulations [54], PBDE treated television components [55] as well as those reported for marine sediments from Tokyo [69] and Osaka [105] Bays and displayed in Figure 3.4.

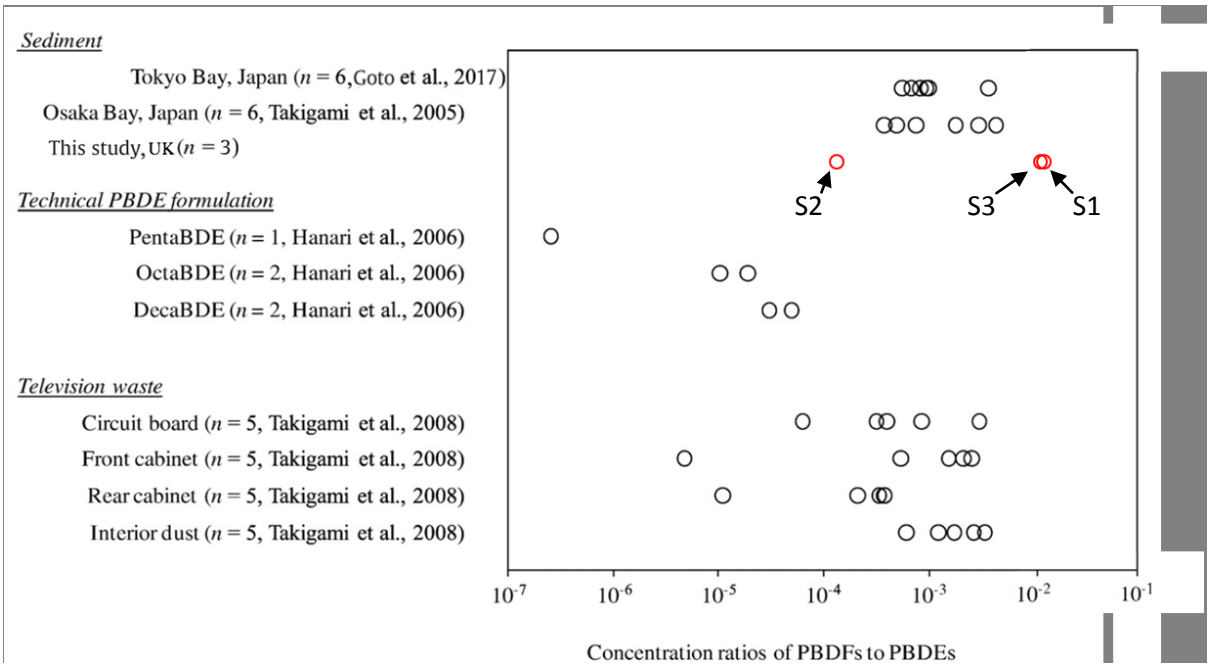


Figure 3.4: Median PBDF: PBDE concentration ratios observed at S1- 3 across all samples in sediment profiles as compared with those of Japanese marine sediment (cores- Goto et al, 2017, and surficial sediments- Takigami et al, 2005), Technical PBDE formulations, and in dusts generated from Japanese televisions treated with PBDE based FRs.

Median ratios obtained across sites sampled in this study essentially bracket those obtained from both sets of Japanese sediment as well as the vast majority of ratios observed in Japanese house dusts. However, our data are consistently elevated with respect to ratios obtained from BDE-technical formulations, indicating that the sediment concentration ratios obtained in UK are not derived exclusively from BDE- technical formulations, but rather from additional formation processes occurring at some stage during the transportation, storage and further treatment of PBDE containing waste streams. The large spatial variation observed in our data set is intriguing, and is likely reflective of differing PBDF sources operating on a more localised scale as compared to the sampling locations in Japan, where contaminant mixing in the larger water bodies of Osaka and Tokyo Bays likely induced a homogenising effect with respect to ratios contributed by the various PBDF sources there. Also interesting, is that despite the large observed inter-site variation in contaminant ratio, ∑PBDE and ∑PBDF trends at all sites remained statistically correlated. This also strongly implies that across the large number of physical and industrial processes leading to the PBDF contamination of the sites studies here, PBDEs are in the vast majority of cases the major driver of PBDF contamination.

3.4.5 PBDD/F Congener and Homologue Profiles.

Homologue group relative concentration profiles and absolute concentrations by sedimentation year for those samples showing concentrations >SDLs were calculated for each site and displayed in Figure 3.5. Homologue contributions were relatively consistent across sites, showing high % contributions of Hexa- and Hepta- BDFs in the vast majority of samples analysed, with variable amounts of Penta- substituted congeners also present. Penta-BDFs were the dominant homologue group observed at S2 from 1977- 2015 with increasing competition from the only instances of OBDF observed across all samples in the data sets at S2 in sediments from 2009 and 2015 at concentrations of 399 pg g^{-1} OC (118 pg g^{-1} dw) and 265 pg g^{-1} OC (67.6 pg g^{-1} dw) respectively. Present in appreciable contributions throughout the sediment profiles at S2 and S3 were TBDFs,

which were observed at S2 over a range of 100- 7.5 % and S3 at 8.3- 18.6 %. TBDF congeners were observed throughout the sediment chronology at S2 and are exclusively represented in samples dated from as far back as 1954 (5.4 pg g^{-1} OC, 0.82 pg g^{-1} dw) and 1965 (1.55 pg g^{-1} OC, 0.41 pg g^{-1} dw). These congener groups represent the earliest recording of PBDF in the sediment chronology from all 3 sites, and do not appear elsewhere >SDL until 1969 at S1.

Congener profile contributions were not observed to change with respect to sedimentation date with such degree of consistency as to be considered a trend, suggesting that despite positive trends in concentration, contamination sources of these compounds has remained relatively consistent over time and accordingly do not reflect any (immediately obvious) changes in commercial BDE or other phenolic FR usage patterns in the UK.

Reports of PBDF homologue profiles in sediment as is the case with other environmental matrices are sparse. Even rarer are homologue profiles composed of non-2,3,7,8 substituted congeners. In a recent report of PBDD/F contamination trends in Japanese marine sediments, Goto et al provided one of the first such data sets. Data presented in that study is broadly consistent with those observed here, and showed a trend of BDF homologue dominance with increasing bromination order [69] which was also shown to be relatively consistent with time. This study also confirmed significant statistical relationships between HpBDFs and BDE- 209 in surface sediments which they concluded was indicative of a relatively recent shift towards the usage of BDE- 209 containing FRs in Japanese consumer products. This trend was not observed in the sediment chronologies analysed in this study with no observable homologue composition trends shown. Comparisons with other data sets in sediments were not possible due to a lack of sufficiently reported data.

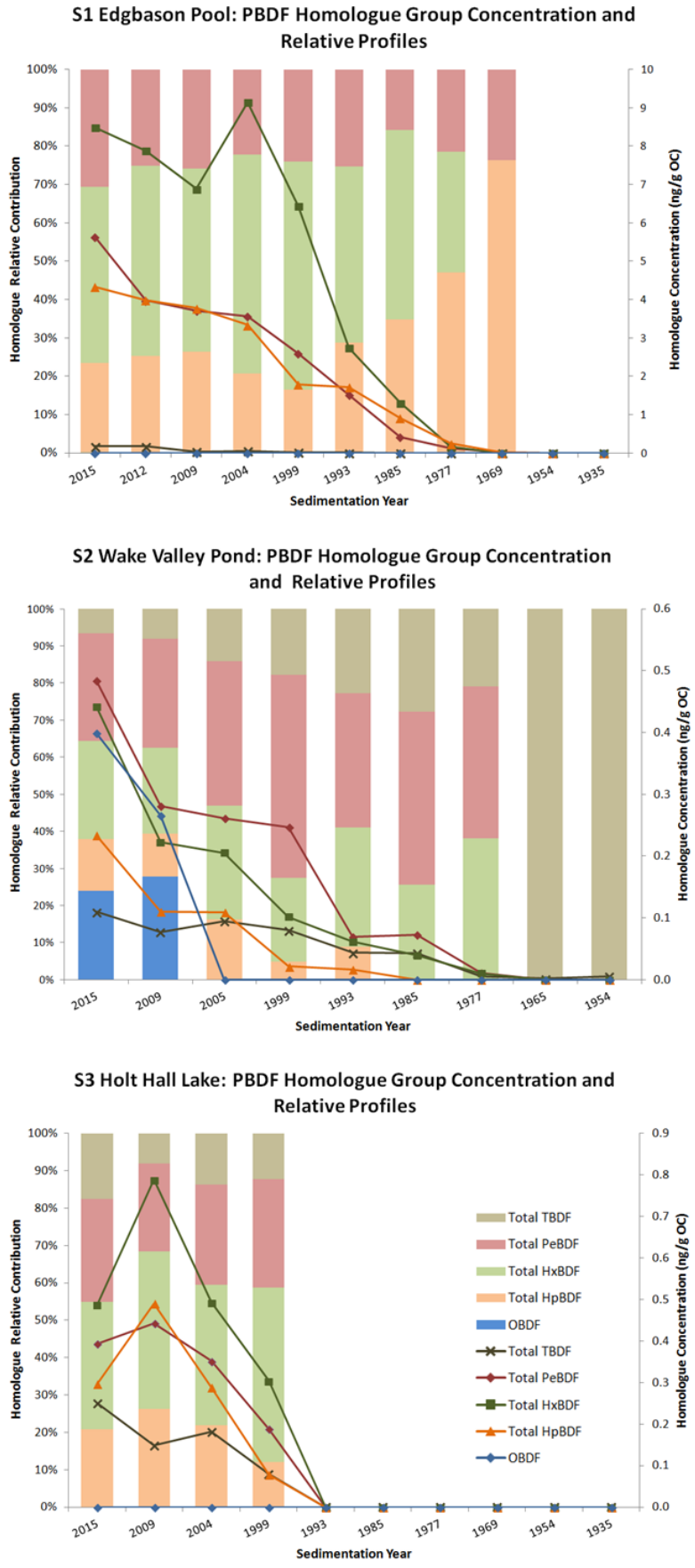


Figure 3.5: PBDF homologue group relative contributions and homologue group concentration profiles at S1 Edgbaston Pool, S2 Wake Valley Pond and S3 Holt Hall Lake.

Hanari et al (2006) in the first observations of PBDD/F by-product contamination in commercial BDE mixes was successful in quantifying and characterising PBDF congener profiles present in 3 different commercial mixes; DE-71, -79 and -83 reported by the manufacturer (Great Lakes Chemical Corporation, West Lafayette, IN, USA) to contain 69, 78 and 82 % Br by mass respectively, indicating that the mixes were likely representative of Penta-, Octa- and Deca- formulations. Results from the Hanari investigation confirmed the absence of PBDD as major by-product constituents of these mixes with all results for PBDDs reported at concentrations below detection limits [54]. PBDF concentrations and relative contributions (in parentheses) are presented in Table 3.8, and graphically represented in Figure 3.6.

PBDF congeners present as unintentional constituents of PBDE commercial mixtures as described by Hanari, show the presence of appreciable quantities of TBDFs and PeBDFs in the commercial Penta-BDE mix DE-71, a pattern of HxBDF> HpBDF/OBDF> PeBDFs> TBDFs in the commercial Octa-BDE formulation, DE-79 and overwhelming OBDF dominance (>95 %) at concentrations in excess of 29 µg/g in the commercial Deca-BDE, DE-83 formulations analysed [54]. These contribution patterns were also reflective of those observed in dusts generated on and around television sets from the 1980s and 1990s known to have been treated with PBDEs [55]. Hagberg et al (2006), in a study designed to indentify homologue contributions of PBDF formed through the photodegradation, of a BDE- 209 commercial formulation (Dow FR-300 BA, Dow Chemical, technical product), was unfortunately, due to analytical constraints, unable to include Hepta- or Octa- substituted PBDFs to the target analyte set. In doing so, they reported very low levels of ∑PBDF in the neat BDE product prior to UV irradiation. Had the authors added the additional Hepta- and Octa- substituted congeners to the analysis, it is probable that the high levels of OBDF as observed in the Hanari et al investigation would have been detected. Post UV irradiation significant formation PBDFs were observed with homologue concentration contributions following a pattern of increase with respect

to bromination [34]. Experiments focused on the observation of congener contribution changes in PBDE profiles during waste incineration processes almost always find increasing contributions of lower brominated species in the post combustion products, a process which has been found to be directly related to combustion efficiency and extent [57]. A general agreement in literature also, suggests that in these processes, homologue contributions of PBDFs undergo a similar shift as observed for PBDEs, favouring the formation of lower brominated PBDF homologues, in accordance with homologue profiles observed in a variety of ambient and flue gas generated particulate matter samples [107,108], [Section 5.4.6]. These studies find HpBDF and TBDF homologue dominance prevalent across different sources, including un/controlled incineration of household waste products known to have been treated with PBDE based FRs. The propensity for the formation of lower substituted PBDFs is supported by statistical thermodynamic theory and as explained by Söderström and Marklund (1999) is primarily due to the presence of an increacing number of binding sites available for halogen substitution, resulting in a larger diversity as well as concentration of lower brominated PBDF congeners [109]. This, as well as increaced thermodynamic stability emparted by reduced dipol moments in lower brominated species, has also been postulated as an explination of this effect, as evidenced by Weber and Kuch in 2003, where significant formation of lower brominated PBDFs was observed during thermal [58] and photolytic [34] degradation. Accordingly, the source of elevated contributions of HpBDFs in our samples is as yet unclear, but can be reasonably assumed to be derived from either the degradation of BDE- 209, debromination of OBDF present as an unintentional by-product of the Deca- BDE commercial formulation, or by other formation processes yet to be described.

Table 3.8: Concentrations in ng/g formulation and homologue relative contributions (%) of PBDF homologue groups present in commercial BDE formulations: DE- 71, -79 and -83 are reflective of the Penta-, Octa- and Deca- formulations by reported Br mass % (Data from Hanari et al 2006).

	DE-71	DE-79	DE-79	DE-83	DE-83
TBDFs	100(38.92)	<100(0)	<100(0)	<100(0)	<100(0)
PeBDFs	157(61.09)	315(1.65)	231(2.21)	<100(0)	<100(0)
HxBDFs	<100(0)	8506(44.33)	4863(46.46)	<100(0)	<100(0)
HpBDFs	<200(0)	4418(23.03)	3657(34.94)	1628(3.29)	1242(4.04)
OBDF	<200(0)	5951(31.02)	1718(16.42)	47978(96.73)	29540(95.97)
Total PBDFs	**257**	**19190**	**10469**	**49605**	**30783**

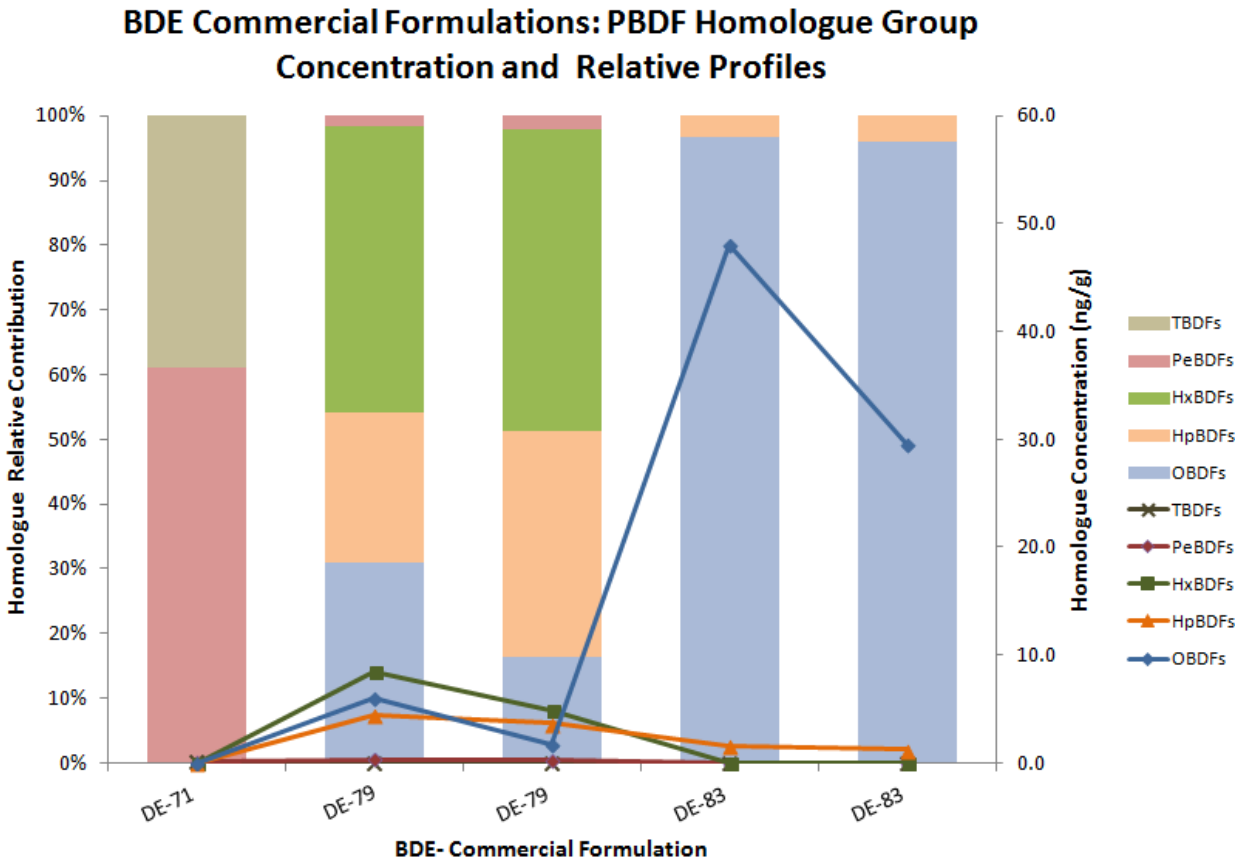


Figure 3.6 Concentrations and relative homologue contributions of PBDFs in commercial BDE- formulations: DE- 71, -79 and -83, reflective of the Penta-, Octa- and Deca- formulations by reported Br mass % (Data from Hanari et al 2006).

For the most part the sediment homologue profiles generated in this study appear to follow the homologue trend established in the majority of atmospheric studies [59] which may indicate atmospheric PBDF sources, however with the lack of local atmospheric levels or homologue profiles, source determination at this point remains speculative. PBDF profiles were shown to broadly reflect (in the absence of OBDF) those profiles established in BDE commercial formulations, and with the identification of strongly correlated ∑PBDE to ∑PBDF trends, sources of PBDFs are likely to reflect those of PBDEs as described in the preceding sections. Profiles observed here however, differ from those reported in the Goto et al (2017) study of Japanese marine sediment, principally by a distinct lack of TBDFs.

TBDFs were observed at S2 (100- 7.5 %) and S3 (8.3- 18.6 %) with complete absence at concentrations >SDL at S1. At S2, TBDFs were observed throughout the sediment chronology and are exclusively represented in samples dated from as far back as 1954 (5.4 pg g^{-1} OC, 0.82 pg g^{-1} dw) and 1965 (1.55 pg g^{-1} OC, 0.41 pg g^{-1} dw). These congener groups represent the earliest recording of PBDF in the sediment chronology from all 3 sites, with all PBDFs recorded at levels below detection until 1969 at S1. Detection of TBDFs at such sections of the sediment chronology can be explained by at least three possible mechanisms: Analytical cross-contamination, TBDF migration to increased depth in the sediment core, or the presence of an additional source to the widespread usage of PBDEs or other phenolic BFRs in the UK. This is indeed a possibility as PBDF formation has been observed in combustion products in the absence of PBDEs or other BFRs due to the presence of other Br containing precursor materials [59]. This, we believe is a reasonable explanation as analytical cross-contamination is unlikely to have occurred due to strict controls over sample handling, and the removal of isobaric interferences during cleanup and MS analysis. These produced no observable concentrations in blank samples analysed. Further support for the positive quantification of TBDFs in these samples are that concentrations observed were in excess of 2 orders

of magnitude higher than respective SDLs, and were not systematically observed in all samples (notable lack of TBDF in S1 samples). TBDF migration to lower sections of the sediment profile, however unlikely, cannot be entirely discounted, as instances of surfactant facilitated transport have been reported, with PCDD/Fs and other highly lipophilic contaminants, with these compounds observed at far greater depth in undisturbed soil profiles than would be otherwise likely in the absence of transportation mechanisms [110].

The confirmation of OBDF in sediment cores despite having been established as a prominent unintentional by-product in commercial Deca-BDE formulations [54], was largely unexpected. This is due principally to the extensive difficulties in analysis, resulting in high limits of detection, as well as thermodynamic instability in ambient matrices. These factors principally, have contributed to the significant lack of environmental data concerning OBDF levels and trends, with this study, to the best of the authors' knowledge, being the first to report confirmed concentrations in virtually any environmental or biological matrix. In the absence of analytical complications, degradation propensity and given the highly similar physico-chemical properties shared between BDE-209 and OBDF, one would expect to observe high concentrations of this compound, ubiquitously in sediments co-contaminated with BDE-209. As explored in the preceding paragraphs, OBDF readily undergoes debromination and further degradation and accordingly, the presence of this compound in the sediment chronology at only 1 of the 3 sites investigated suggests the presence of a further contamination source of PBDFs to S2 exclusively.

Elevated contributions of HpBDFs with respect to other congeners were however, universally observed in the sediment chronologies analysed, especially in samples derived from upper fractions containing the largest concentrations of BDE- 209. These congeners, as explained above, are likely

derived from both the formation of HpBDF from BDE- 209 itself, the reductive dehalogenation of OBDF present as an unintentional by-product in waste streams containing BDE- commercial formulations, both such sources, or from additional contributions as yet unidentified. Goto et al in 2017, report their observations of elevated HpBDF in Japanese marine sediments as a likely result of OBDF degradation. Interestingly however, the HpBDF homologue contribution in our study was in all cases derived almost entirely from 1,2,3,4,6,7,8- HpBDF, with other unidentified congeners contributing less than 0.0001 % to the total homologue concentration total. This observed single congener dominance in sediments was not observed for any other homologue groups and may indicate that in processes inducing the formation of PBDFs, a thermodynamically favoured pathway exists which results in preferential formation of the 1,2,3,4,6,7,8- HpBDF over that of other Hepta-substituted congeners. Wang *et al.* 2009 also reported elevated concentrations of 1,2,3,4,6,7,8-HpBDF in soils contaminated by e-waste recycling procedures in south-eastern China and cites the presence of this specific congener as (first described by Blomqvist, Rosell and Simonson, 2004 Blomqvist, Rosell and Simonson, 2004) a marker for incomplete combustion of electronic equipment treated with BFRs, further strengthening the argument that PBDF contamination is integrally associated with the presence and therefore usage patterns of PBDE based BFRs and their processing in waste streams.

3.4.6 Conclusions Concerning PBDD/F Contamination in English Fresh Water Sediments

Given the weight of evidence including but not limited to:

1. The high degree of statistically significant association observed between PBDE and PBDF trends at all sites in this study ($\rho > 0.71$, in all cases)
2. The level of agreement found between PBDF and PBDE concentrations in these samples and those from dusts derived from products known to have been treated with PBDEs

3. The observation of broadly consistent PBDF homologue profiles to those reported in literature for PBDFs formed from PBDE containing waste streams across a variety of environmentally contaminating processes

We can assert with a reasonable degree of certainty that the increasing use of PBDE containing FRs as well as current-practice waste handling procedures has directly led to increasing PBDF environmental contamination over the spatial and temporal scales investigated here.

3.5 PXDD/F Contaminant Trends in English Fresh Water Lakes.

Unlike the considerable number of sediment and other PBDE chronologies reported in literature, as well as the limited number of PBDD/F sediment chronologies, outside of a handful of measurements determining their ubiquitous presence, the extent of PXDD/F environmental contamination remains unknown. PXDD/F physical, chemical and toxicological profiles have been shown to be at least comparable to those of their brominated and chlorinated analogues [47] and have also been confirmed as incomplete combustion by-products forming in the presence of Br and Cl donors, leading to the postulation that PXDD/Fs and PBDFs share common sources of environmental release [93]. Accordingly their presence as persistent, wide-spread and toxic environmental contaminants is expected. PXDD/F congeners have been positively identified and quantified previously in human breast milk [66], marine and fresh water human food products [113,114], in ambient atmospheric particulate matter [67], and a handful of studies concerning surficial marine sediments [104].

Despite previous assessments, contaminant chronologies of PXDD/F have yet to be established in any environmental matrix and to the best of the authors' knowledge, the proceeding data set stands as the first of its kind generated. The significant analytical challenge of PXDD/F quantification especially in complex environmental matrices such as sediment is the principle factor contributing the paucity of data regarding environmental and biological PXDD/F contamination levels. Briefly,

analytical challenges have previously been due principally to the availability of appropriate reference and internal standard compounds, the presence of the many isobaric interferences from other environmental contaminants including PCBs and PBDEs leading to false positive detections, as well as the large concentration differences between interfering compounds and target PXDD/Fs, differences generally present at concentration ratios of 10^{-5}- 10^{-8} with respect to PCBs and PBDEs (1-100 ng g^{-1} ambient matrix, as compared to 10-100fg g^{-1} ambient matrix as is typical for PXDD/F congener concentrations).

Despite these challenges, the recent availability of appropriate standard solutions and significant advances in high resolution accurate mass analysis platforms has increased compound selectivity substantially and allowed for quantification at resolutions up to 120000 FWHM without a resultant decrease in sensitivity. At resolutions capable of mass resolving the vast majority of interferences, ion cross talk can be considered negligible provided analysis is performed within appropriately stringent QA/QC procedures such as those outlined in section 2.6. The absence of appreciable levels of background noise due to the High Resolution nature of the analysis, the elevated ionisation efficiency of PXDD/Fs as well as increased thermal stability with respect to PBDD/Fs results in large increases in spectral signal intensity for PXDD/Fs over PBDD/Fs. This in turn results in large S/N ratios and accordingly remarkable limits of quantification, as observed for PXDD/F standards in this study which were consistently on the order of 1-10 fg g^{-1} dw (Section 2.7.2.2).

Here we present data generated from 2 of the 3 sediment profiles as described in the previous sections from S2 Wake Valley Pond and S3 Holt Hall Lake. Sediment from S1 Edgbaston was analysed for PXDD/Fs, however it was discovered post extraction that an insufficient quantity of sediment (3 g dw) was extracted for this analysis and accordingly all PXDD/Fs at that site were observed at

concentrations <SDLs. Successful quantification was performed on sediment samples from S2 and S3 where 6 g dw sediment sample was extracted for analysis. Results of these analyses are tabulated in Tables 3.9 and 3.10 and graphically represented in Figures 3.7 and 3.8.

Table 3.9: Concentrations of target PXDD/Fs (pg g^{-1} OC, unless otherwise specified) in analysed sediment from S2 Wake Valley Pond.

	2015	2009	2005	1999	1993	1985	1965	1954
Dioxins								
2-Br-7,8-CDD	0.023	0.158	0.244	0.316	0.394	0.035	0.079	<0.032
Total Br-2CDD	0.729	1.947	1.936	2.689	2.266	3.572	0.801	9.320
Total Br-2CDD (dw)	0.216	0.496	0.509	0.745	0.594	0.976	0.211	1.409
2-Br-3,7,8-CDD	0.081	<0.028	<0.027	0.120	0.216	0.220	0.291	<0.047
Total Br-3CDD	1.447	2.229	2.826	3.790	2.990	3.448	6.157	9.335
Total Br-3CDD (dw)	0.428	0.568	0.743	1.050	0.784	0.942	1.625	1.411
2,3-Br-7,8-CDD	<0.015	<0.017	<0.016	<0.016	<0.017	<0.016	<0.016	<0.029
Total 2Br-2CDD	0.481	0.643	0.874	1.156	1.535	1.753	1.180	4.381
Total 2Br-2CDD (dw)	0.142	0.164	0.230	0.320	0.402	0.479	0.311	0.662
1-Br-2,3,7,8-CDD+2-Br-1,3,7,8-CDD*	<0.018	<0.021	0.369	<0.02	<0.021	<0.02	<0.021	<0.032
Total Br-4CDD	1.691	1.844	2.848	3.751	5.911	4.575	7.019	5.673
Total Br-4CDD (dw)	0.501	0.470	0.749	1.039	1.550	1.250	1.852	0.858
2-Br-3,6,7,8,9-CDD	<0.015	<0.017	<0.016	<0.016	<0.017	<0.016	<0.016	<0.029
Total Br-5CDD	1.040	0.816	3.459	2.161	5.103	7.024	7.522	14.633
Total Br-5CDD (dw)	0.308	0.208	0.909	0.599	1.338	1.920	1.985	2.212
Furans								
2-Br-7,8-CDF	0.774	1.029	0.884	<0.01	2.030	2.730	<0.01	<0.018
Total Br-2CDF	6.929	16.205	16.442	25.631	16.587	25.162	21.513	61.540
Total Br-2CDF (dw)	2.052	4.129	4.323	7.101	4.349	6.877	5.678	9.302
2-Br-6,7,8-CDF+3-Br-2,7,8-CDF*	<0.012	0.229	0.165	0.302	0.654	0.464	0.076	<0.023
Total Br-3CDF	4.280	5.960	6.397	8.440	8.733	9.989	10.684	56.543
Total Br-3CDF (dw)	1.267	1.519	1.682	2.338	2.290	2.730	2.820	8.546
1-Br-2,3,7,8-CDF	0.022	<0.014	0.047	0.042	0.662	<0.012	<0.012	<0.021
Total Br-4CDF	1.464	1.557	2.598	3.632	6.387	5.783	1.986	19.854
Total Br-4CDF (dw)	0.434	0.397	0.683	1.006	1.675	1.581	0.524	3.001

	2015	2009	2004	1999	1985	1977	1969	1954
$\sum PXDD_{2/3,7,8}$	0.105	0.158	0.613	0.436	0.610	0.256	0.370	<0.029
$\sum PXDF_{2/3,7,8}$	0.796	1.258	1.096	0.344	3.346	3.194	0.076	<0.018
$\sum PXDD/F_{2/3,7,8}$	0.901	1.416	1.709	0.779	3.956	3.450	0.446	<0.018
∑PXDD	5.388	7.479	11.943	13.547	17.804	20.371	22.678	43.342
∑PXDF	12.674	23.722	25.437	37.702	31.707	40.934	34.183	137.937
∑PXDD/F	18.062	31.201	37.379	51.249	49.511	61.305	56.862	181.279
$\sum PXDD_{2/3,7,8}$ (dw)	0.031	0.040	0.161	0.121	0.160	0.070	0.098	1.498
$\sum PXDF_{2/3,7,8}$ (dw)	0.236	0.321	0.288	0.095	0.877	0.873	0.076	<0.003
$\sum PXDD/F_{2/3,7,8}$ (dw)	0.267	0.361	0.449	0.216	1.037	0.943	0.174	1.498
∑PXDD (dw)	1.595	1.906	3.140	3.753	4.668	5.567	5.985	6.551
∑PXDF (dw)	3.752	6.045	6.688	10.445	8.313	11.188	9.021	20.849
∑PXDD/F (dw)	5.348	7.950	9.829	14.198	12.981	16.755	15.007	27.400

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of SDL derivation.

Table 3.10: Concentrations of target PXDD/Fs (pg g^{-1} OC, unless otherwise specified) in analysed sediment from S3 Halt Hall Lake.

	2015	2009	2004	1999	1985	1977	1969	1954	1935
Dioxins									
2-Br-7,8-CDD	1.149	2.784	2.577	3.365	1.114	<0.025	<0.024	<0.021	<0.021
Total Br-2CDD	1.757	4.141	3.967	5.273	2.137	11.145	7.134	2.259	<0.021
Total Br-2CDD (dw)	0.603	1.189	1.064	1.235	0.430	2.143	1.453	0.519	<0.005
2-Br-3,7,8-CDD	0.020	0.049	0.054	0.158	0.080	1.437	<0.035	<0.031	<0.03
Total Br-3CDD	0.770	2.114	2.437	2.662	2.247	18.245	<0.027	3.494	<0.023
Total Br-3CDD (dw)	0.264	0.607	0.653	0.624	0.453	3.509	<0.005	0.803	<0.005
2,3-Br-7,8-CDD	<0.013	0.095	0.062	<0.018	0.034	<0.022	<0.021	<0.019	<0.018
Total 2Br-2CDD	0.329	0.788	0.816	1.094	0.973	5.011	2.164	0.619	<0.017
Total 2Br-2CDD (dw)	0.113	0.226	0.219	0.256	0.196	0.964	0.441	0.142	<0.004
1-Br-2,3,7,8-CDD+2-Br-1,3,7,8-CDD*	<0.016	<0.019	<0.02	<0.023	<0.027	<0.028	<0.027	<0.024	<0.023
Total Br-4CDD	0.473	1.894	1.001	1.877	<0.021	<0.022	<0.021	0.710	<0.018
Total Br-4CDD (dw)	0.162	0.544	0.268	0.440	<0.004	<0.004	<0.004	0.163	<0.004
2-Br-3,6,7,8,9-CDD	<0.013	<0.015	<0.016	<0.018	0.595	<0.022	<0.021	<0.019	<0.018
Total Br-5CDD	<0.008	0.110	<0.01	<0.012	0.594	<0.014	<0.013	<0.012	<0.012
Total Br-5CDD (dw)	<0.003	0.032	<0.003	<0.003	0.120	<0.003	<0.003	<0.003	<0.003
Furans	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Br-7,8-CDF	<0.008	<0.01	<0.01	<0.012	0.527	<0.014	<0.013	<0.012	<0.012
Total Br-2CDF	4.721	7.850	7.745	11.701	9.569	88.235	88.739	14.639	9.506
Total Br-2CDF (dw)	1.620	2.254	2.077	2.741	1.927	16.969	18.067	3.362	2.226
2-Br-6,7,8-CDF+3-Br-2,7,8-CDF*	0.070	0.281	0.184	0.396	1.271	5.143	<0.017	0.633	<0.015
Total Br-3CDF	2.505	4.803	5.271	8.848	4.983	43.621	48.799	6.619	3.101
Total Br-3CDF (dw)	0.860	1.379	1.414	2.073	1.003	8.389	9.935	1.520	0.726
1-Br-2,3,7,8-CDF	<0.009	<0.011	<0.012	<0.014	<0.016	<0.017	<0.016	<0.014	<0.014
Total Br-4CDF	1.822	5.034	2.353	5.168	0.809	7.339	<0.016	3.493	4.427
Total Br-4CDF (dw)	0.625	1.445	0.631	1.211	0.163	1.411	<0.003	0.802	1.037

	2015	2009	2004	1999	1985	1977	1969	1954	1935
$\sum PXDD_{2/3,7,8}$	1.169	2.928	2.692	3.523	1.823	1.437	<0.021	<0.019	<0.018
$\sum PXDF_{2/3,7,8}$	0.070	0.281	0.184	0.396	1.798	5.143	<0.013	0.633	<0.012
$\sum PXDD/F_{2/3,7,8}$	1.239	3.209	2.877	3.919	3.622	6.580	<0.013	0.633	<0.018
∑PXDD	3.329	9.047	8.220	10.906	5.951	34.400	9.298	7.082	<0.012
∑PXDF	9.048	17.688	15.370	25.717	15.362	139.195	137.538	24.751	17.034
∑PXDD/F	12.377	26.735	23.590	36.622	21.313	173.596	146.836	31.832	17.034
$\sum PXDD_{2/3,7,8}$ (dw)	0.401	0.841	0.722	0.826	0.367	0.276	<0.004	<0.004	<0.004
$\sum PXDF_{2/3,7,8}$ (dw)	0.024	0.081	0.049	0.093	0.362	0.989	<0.003	<0.003	<0.003
$\sum PXDD/F_{2/3,7,8}$ (dw)	0.425	0.921	0.771	0.918	0.729	1.266	<0.003	0.145	<0.003
∑PXDD (dw)	1.143	2.597	2.204	2.555	1.198	6.616	1.893	1.626	<0.003
∑PXDF (dw)	3.106	5.077	4.122	6.025	3.093	26.769	28.003	5.684	3.989
∑PXDD/F (dw)	4.248	7.674	6.326	8.580	4.291	33.385	29.896	7.311	3.989

* Chromatographic co-elution.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of SDL derivation.

3.5.1 Concentrations, Temporal and Spatial Distribution of PXDD/Fs.

Unlike their exclusively brominated counterparts, PXDD/Fs were observed at concentrations >SDL across the entire time period covered by the sediment profiles analysed at both sites. S2 showed a maximum ∑PXDD/F concentration of 181.28 pg g^{-1} OC (27.40 pg g^{-1} dw) observed in sediment corresponding to deposition in the earliest recorded sample during 1954, with the lowest recorded value of 18.06 pg g^{-1} OC (5.35 pg g^{-1} dw) in benthic surface sediment dated to 2015. At S3 the lowest ∑PXDD/F recorded concentration was also observed in surficial sediment at a concentration of 12.37 pg g^{-1} OC (4.25 pg g^{-1} dw, 2015) and ranged to 173.60 pg g^{-1} OC (33.39 pg g^{-1} dw) in sediment dated to 1977.

These concentration ranges bear reasonable similarity to those observed in Japanese surficial marine sediments [104], were elevated with respect to 2 soil samples (1 industrial and 1 rural site) from the UK [115] and were lower than a single urban Japanese soil sample taken in 2000 [67]. Values for ∑PXDD/Fs in sediments observed here were also substantially lower than those observed at an unregulated e-waste recycling plant in China, as reported in Zennegg et al. 2009. Direct inter-data set comparisons are however difficult to interpret, for the most part because of the differing number and chemical composition of congener group concentrations reported, with respect to that of the total homologue concentrations as analysed here. However, some comparisons can be made.

Data from surficial coastal marine sediment from 6 different coastal locations across Osaka Bay, Japan was sampled in 1999 by Ohta et al (2002). The authors reported congener specific and specific congener sum concentrations of 5 mono –Br –xClDDs (x= 3-7), 2,3-Br-7,8-ClDD and 2 mono-Br-xClDFs (x= 3, 4) resulting in ∑PXDD/F concentrations of these congeners over a range of 2.9- 13.0 pg g^{-1} dw (Ohta et al., 2002, n= 6). These values are slightly reduced in comparison to those observed here (S2:

5.35- 27.40 pg g^{-1} dw; S3: 4.25- 33.39 pg g^{-1} dw). It is important to note, that other than concentration differences arising from the analysis of a differing target compound set, additional and significant deviations can be expected from dilution effects associated with the sampling of sediments derived from a much larger water body (Osaka Bay) as compared to that of the locations sampled here (as was the case for PBDF comparisons). Accordingly, direct concentration comparisons cannot be representative of actual differences in the quantities of environmental contamination of these compounds between these locations. In a study of atmospheric deposition contamination conducted by Hayakawa et al (2004) in 2000, a single surface soil sample from within the urban limits of Kyoto City, Japan was also analysed for PXDD/F concentrations. A ∑PXDD/F concentration of 52.0 pg g^{-1} dw derived entirely from mono-Br- (tri- penta) ClDFs was reported, with mono-Br- tri- heptaClDDs and mono-Br- hexa-heptaClDFs all reported at concentrations below detection limits. This value is substantially elevated even with respect to maximum ∑PXDF concentrations of 20.85 pg g^{-1} dw (S2, 1954) and 28.03 pg g^{-1} dw (S3, 1969) observed in our data set and factors of 4.9 and 8.6 higher than ∑PXDF concentrations observed at S2 in 1999 (10.45 pg g^{-1} dw) and S3 in 1999 (6.03 pg g^{-1} dw) respectively. Fernandes et al. (2011) included in a further analysis of PXDD/F contamination of UK food items, 2 soil samples to that analysis set. One sampled at an industrialised location and the other from a rural (unspecified) location and reported ∑PXDD/F concentrations for the identical set of congeners analysed here. That analysis yielded ∑PXDD/F concentrations of 3.49 pg g^{-1} (whole) and 0.56 pg g^{-1} (whole) for the industrial and rural sample respectively. Comparisons between the whole weight analysis reported for these samples adds an additional layer of uncertainty however, assuming a 10 % water content, values of ∑PXDD/F of 3.87 and 0.62 pg g^{-1} dw place the concentrations observed at these locations at levels below the lowest recorded values for ∑PXDD/F across our data set. In an investigation of soil samples at a highly contaminated, non- regulated e-waste recycling site in China, reported concentrations in excess of 5 µg g^{-1} dw for ∑PXDF (mono-Br-(tetra-octa) CDF) [61], values well above those observed here. The authors however, interestingly noted a distinct lack of PXDDs in samples taken, with concentration

ratios (furans: dioxins) on the order of 80. This was attributed to a preferential formation of mixed halogenated furans with respect to dioxins during formation involving PBDE precursor compounds, however it is worth noting that mass balance calculations were not performed and accordingly these values were assessed entirely from flue gas emissions alone [61].

Concentrations of ∑PXDD/Fs at S2 were detected as far back as 1954, representing the earliest sediment sample in the data set, at a concentration of 181.28 pg g^{-1} OC and showed a rapid decline to 56.62 pg g^{-1} OC as measured in the sediment deposited there in 1965. This decline was primarily attributed to decreasing furan concentrations (Figure 3.8). Between the period of 1965- 2015 PXDDs and PXDFs declined in concert producing a significant (Spearman's ρ= -0.943, p= 0.0167) linear reduction trend in ∑PXDD/F with respect to time, from 56.86- 18.62 pg g^{-1} OC, occurring at an average rate of -1.38 pg g^{-1} y^{-1} (OC basis, calculated slope value for linear polynomial regression, R^2= 0.69, p_{slope}= 0.01). Linear correlation across the entire temporal scope of the investigation yielded a highly significant (Spearman's ρ= -0.952, p< 1 x10^{-7}) negative association between ∑PXDD/F concentration with respect to time, for the most part due to the large reduction noted above, occurring between the 1954- 1965 samples.

The ∑PXDD/F concentration profile observed at S3 however, did not follow the same pattern as recorded at S2, and despite the lowest ∑PXDD/F concentration also being observed in sediment most recently deposited, large variation was observed between samples dated from 1985- 1954. During this period ∑PXDD/F levels increased from 31.83 pg g^{-1} OC (1954) to 146.84 pg g^{-1} OC (1969) rising slightly to 173.60 pg g^{-1} OC in 1977 before sharply reducing to 21.31 pg g^{-1} OC as observed in the 1985 sample. From the 1985 sediment to that dated from 2015, the appearance of a decline in ∑PXDD/F concentrations can be observed (Figure 3.7), however this was not found to be statistically

significant (Spearman's ρ= -0.313, p= 0.609) across this, nor the entire temporal scale of the investigation (Spearman's ρ= -0.201, p= 0.605; S3).

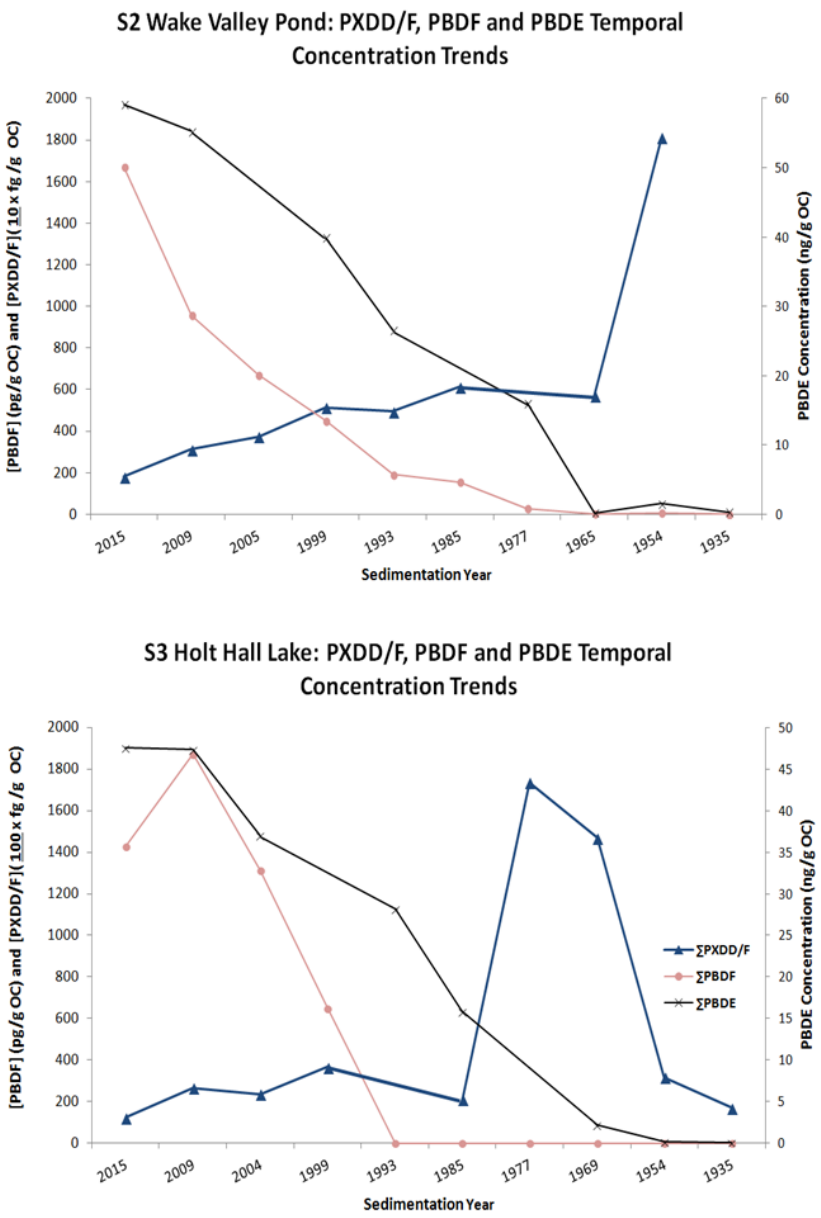


Figure 3.7 PXDD/F, PBDF and PBDE Concentration profiles in sediment with respect to sedimentation year, at S2 Wake Valley Pond and S3 Holt Hall Lake. Concentration scales for ∑PXDD/F at S2 correspond to x 10 fg/ g OC and x 100 fg/g OC at S3. PXDD/F concentrations showed a statistically significant negative correlation with respect to time at S2 over the period of 1965- 2015 (Spearman's ρ= -0.943, p= 0.0167). PXDD/Fs were not found to be statistically in decline at S3 over both the entire temporal scale nor between 1985- 2015.

3.5.2 Relationships between PXDD/Fs, PBDFs and PBDEs in English Freshwater Sediments.

Correlation analysis was performed to investigate the presence and extent of relationships between ∑PBDF and ∑PBDE concentration trends with respect to those of ∑PXDD/F at each of the 2 sites where ∑PXDD/F data was acquired. Spearman's pair-wise rank order correlation tests were used in this investigation for concentration pairs at discrete sedimentation years where data for each compound group was available. Results of the analysis yielded significant negative associations between ∑PXDD/F and both ∑PBDE and ∑PBDF at S2 with Spearman's $\rho = -0.943$ ($p = 0.0167$, $n = 6$) and $\rho = -0.929$ ($p < 1 \times 10^{-5}$, $n = 8$) for relationships between ∑PXDD/F and ∑PBDE and ∑PBDFs respectively. Correlations were also found to be significant (albeit less so) at S3. Despite statistical anticorrelation the presence of PXDD/Fs at substantial concentrations pre-dates the onset of PBDE and PBDF contamination, suggesting that the major drivers of PXDD/F contamination to these locations are in fact not substantively related to those of PBDEs or PBDD/Fs. This finding is in contrast to the prevailing scientific consensus, based on the relatively large body of evidence showing formation of PXDD/F in industrial (and other) processes from PBDE precursors [61,93] and accordingly warrants further investigation such as mass balance assessments of feedstock and emissions profiles at MWIs to aid in the identification of the major PXDD/F sources influencing sediment contamination at these sites.

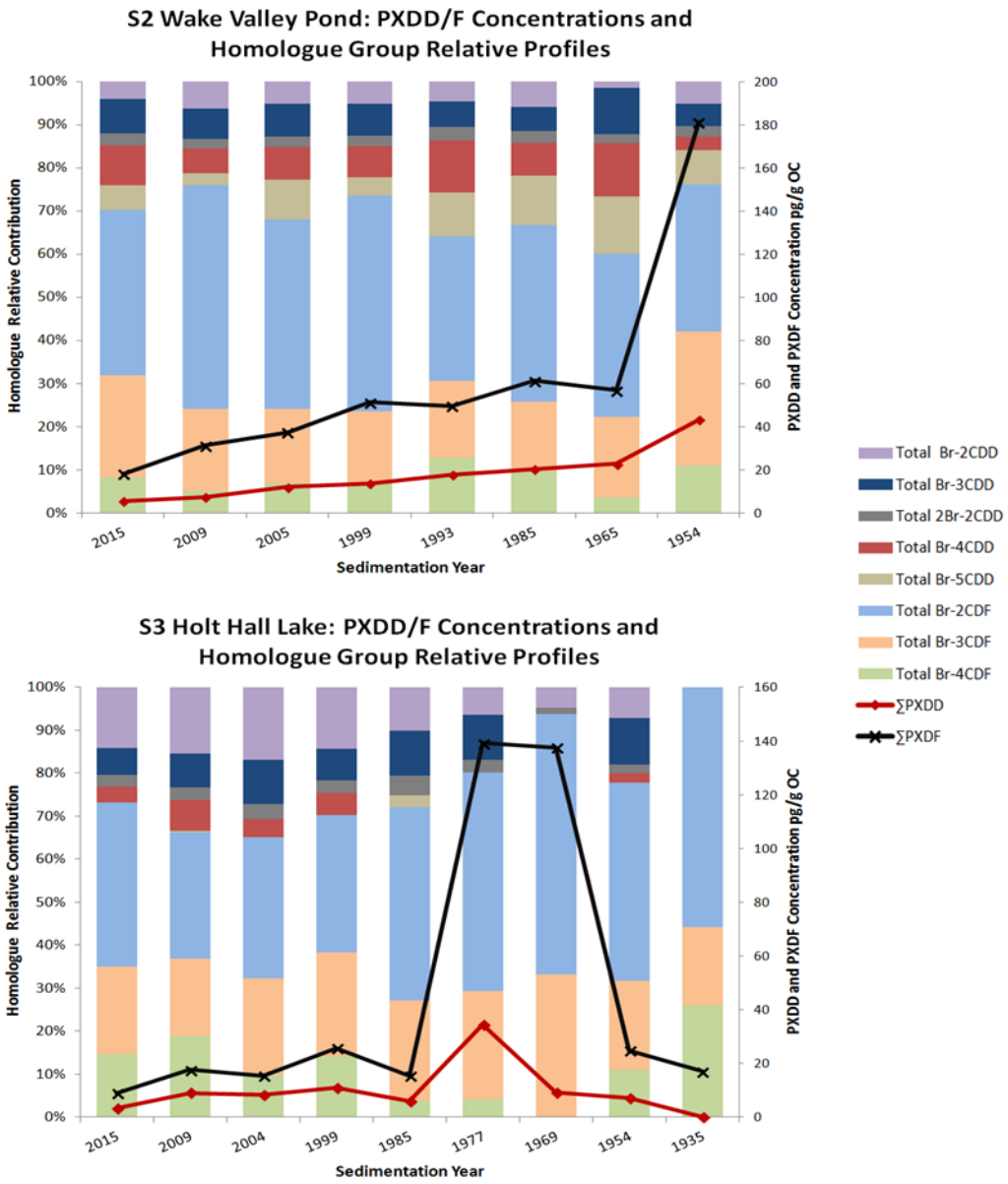


Figure 3.8: PXDD and PXDF concentrations and homologue group relative contributions at S2 Wake Valley Pond and S3 Halt Hall Lake, with respect to sedimentation year. The figure shows the presence of statistically significant correlation between these compound groups at S2 (Spearman's ρ= 0.881, $p < 1 \times 10^{-5}$) and S3 (Spearman's ρ= 0.817, p= 0.004).

3.5.3 Relationships between ∑PXDD and ∑PXDF in English Freshwater Sediments.

The ∑PXDD/F concentrations presented here are composed of single congeners representing of each of 5 homologue dioxin groups (excluding 1 chromatographic co-elution, Table 3.9, 3.10) of mono -bromo, -di to -penta –chlorinated dioxins (Br-xCDDs, where x= 2- 5) as well as a single congener representing the di -bromo, -di -chlorinated dioxin (2Br-2CDD) group. Target furans included in the analysis consist of single congeners (excluding 1 chromatographic co-elution, Tables 3.9, 3.10) representing homologue groups mono -bromo -di through –tetra chlorinated furans (BrxCDFs, where x= 2- 4).

Correlation analysis was performed between ∑PXDD and ∑PXDF concentrations and revealed strong associations between these data with a very high degree of statistical significance at both sites, with associations at S2 yielding a correlation coefficient of ρ= 0.881 (Spearman's, $p < 1 \times 10^{-5}$) and S3 yielding a coefficient ρ= 0.817 (Spearman's, p= 0.004). The results of these analyses confirm with a high degree of certainty that sources contributing to environmental contamination of PXDDs and PXDFs were related over the considerable temporal scope of this investigation (~80 y) at both sampling locations and accordingly suggests the presence of source commonality.

Positive and significant associations between these contaminant groups evaluated using the Spearman rank correlation test confirms the similarity between the directional magnitude of trends at each point in the time series, however does not provide a sufficiently rigorous indication as to the absolute magnitude of each data point considered. Accordingly, consistency of association over time was evaluated by calculating the relative contributions of ∑PXDD and ∑PXDF to the ∑PXDD/F total concentration at each time point. For the most part, % contributions of ∑PXDD and ∑PXDF remained relatively consistent across the temporal scale of investigation, yielding values of ∑PBDF relative contributions ranging from 60.1- 76.1 % at S2 (μ= 69.4, σ= 5.7) and 65.2- 93.6 % at S3 (μ= 77.6, σ= 12.0). Student's t-tests were performed to evaluate whether contributions of ∑PXDFs (and therefore

∑PBDDs) to total ∑PXDD/F concentrations were the same across the entire investigation period at each site. Results of the evaluation indicated that statistically significant differences in the contribution of ∑PXDF were present at S3, however that the contribution ratio at S2 in fact remained similar over the period of sampling within a statistical confidence of 95% (Student's t-test, 2-tailed, df= 10, p= 0.08 > α= 0.05). This lends strong evidence to indicate that sources of PXDDs and PXDFs at S2 are not only related but share commonality to an extent that has not resulted in a statistically significant change in contribution ratio over the period of this investigation. Sources of these compound groups at S3 however, show evidence indicating that they have changed significantly over time towards those that have significantly discriminated against contributions of PXDDs with respect to PXDFs over the contaminant chronology observed there.

3.5.4 ∑PXDD and ∑PXDF Homologue Contributions in English Freshwater Sediments.

Given the low chromatographic resolution employed in this analysis, as well as the exceedingly large number of possible mono- octa substituted congener combinations (1,550 PXDDs and 3,050 PXDFs) all present on extracted ion chromatograms, it is very probable that virtually all peaks reported in Tables 3.9 and 3.10 as individual congeners are composed of more than just these single congeners. All care was taken to include those congeners which were > 50% baseline separated in RT (See Chromatographic QA/QC section 2.6.1.6) however, given the vast numbers of PXDDs and PXDFs there is a high likelihood that multiple ('unseen') congeners contributed to these 'individual' ion intensities and therefore values reported cannot be assessed as individual congener concentrations alone. Accordingly, here we make use of homologue groups in the assessment of relative contributions alone. Figure 3.8 illustrates the PXDD/F homologue relative contributions and compound group concentrations observed at S2 and S3. Homologue contributions remained relatively consistent across the temporal scope of the investigation, as was observed for PBDFs at these locations, with no discernible trends identified in contribution with respect to sediment deposition year.

As described in Section 3.5.3, relative contributions of PXDFs were dominant across the temporal frame of analysis at both sites and showed mean contributions of 69.4 % and 77.6 % at S2 and S3 respectively. These contributions followed a consistent pattern at both sites with relative contributions increasing with respect to decreasing Cl substitution. This, as investigated for PBDF homologues, may reflect thermodynamic preference for formation of homologues providing the maximum number of binding site combinations possible, as was postulated for PBDF formation by Söderström and Marklund (1999). Dioxin homologue contributions were more varied than those of the furans in this investigation, with relative contributions in inter-site comparisons showing opposite trends with respect to contribution and Cl substitution extent. Homologue relative contributions at S2 followed a trend of: Br4/5CDD >BrC3CDD >Br2CDD >2Br2CDD. This is almost exactly inverse to that observed at S3, where the mono- brominated dioxins of: Br2CDD > Br3CDD Br4CDD >2Br2CDD with Br5CDD not observed above limits of detection across the sample set.

The preferential formation of PXDF with respect to PXDD was observed in Zennegg et al, 2009 for highly contaminated soils sampled at an e-waste recycling site in China, and was attributed to energetically preferable formation pathways for the formation of PXDF from PBDE precurcor compounds. Zennegg also observed a pattern for furan homologue relative contributions consistant with our observations with % contributions increacing with respect to decreacing Cl substution. Also observed were relative dioxin contributions increasing with respect to Cl substitution as reflected in our data at S2 [61]. PXDF congeners were also shown to be present in higher relative quantities in 2 soil samples taken from the UK [115] with furans contributing 60 % in soil sampled at a rural location and 53 % in soil derived from an industrially influenced site to the total ∑PXDD/F concentrations observed. Homologue trends observed in the above as well as those reported for our data, stand in contrast to those presented for sediments sampled from Osaka Bay in 1999. Here the authors report a substantive lack of furan congeners with only a single detection of Br3CDF at 2 pg g^{-1} dw in one of

the 6 cores analysed, with detections of 3 of the 6 dioxin congeners analysed for detected in 100 % of samples. Concentrations of PXDDs were observed at concentrations 5 fold higher in the sample in which Br3CDF was also observed [104].

3.5.5 Conclusions Concerning PXDD/F Contamination in English Fresh Water Sediments.

The presence and concentration of PXDD/Fs in UK freshwater sediments is established here for the first time. Concentration trends spanning ~80 y reveal a statistically significant trend of decline in both PXDD and PXDF concentrations at S2 Wake Valley Pond, with the appearance of a declining trend in the later years of the temporal range of investigation apparent (not statistically significant at 95 % confidence) at S3 Holt Hall Lake. Concentrations of PXDD/Fs present in the sediments at the locations investigated were found to be reasonably similar to those observed in Japanese marine sediments, higher than previously assessed UK soils, and far lower than soils from an e-waste site in China. Dioxin and Furan trends at both sites were observed to be statistically well correlated over the temporal scope of the investigation, and at S2 showed no compositional change over the entire data period. Statistically significant anticorrelation was observed between ∑PXDD/F trends and those of ∑PBDE and ∑PBDF at both sites, however with PXDD/F concentrations recorded at time periods preceding PBDE and PBDF contamination, indicating no relationship between the sources of these contaminants. Conclusions with respect to source attribution of PXDD/F at this point are purely speculative, however, given the trend data presented here it is possible to conclude that PXDD and PXDF contamination to these sites likely share common origins, which have remained consistent in time with respect to the relative contribution of each compound group. Presence of PXDD/Fs in sediments pre-dating those of PBDE and PBDFs indicate strongly that additional PXDD/F sources, as yet unidentified, exist external to formation by BFR and that the contribution of BFR precursor derived PXDD/F contamination to these sites is not a principal driver of these contamination trends.

Chapter 4 The use of a Novel HRMS Approach to Determine Infant Dietary Intake and Exposure to Legacy and Novel Flame Retardants, dl-PCBs, Chlorinated, Brominated and Mixed Halogenated Dioxins and Furans:

4.1 Synopsis.

This chapter describes the application of methodology (analytical and wet-chemical) outlined in Chapter 2, for the quantification of PBDEs, PBDD/Fs, PXDD/Fs and further expands target compound groups to include several novel BFRs, PCDD/Fs and dl-PCBs in human breast milk. Samples (whole) reported here were provided to the authors for quantification by The Health and Environment Department, Imperial College London and were sampled from primipara mothers residing in the Greater London Metropolitan Area. Concentrations of the above analytes were quantified, contrasted with similar data (where available) and converted to represent infant daily uptake values for comparison with appropriate chronic oral reference doses. Several guideline exceedances were observed throughout the data set, with concentration values reported all exceeding or meeting analytical QA/QC criteria. Accordingly, we find this method to have a high degree of suitability and utility for the quantification of trace- level environmental contaminants in further human breast milk studies.

4.2 Introduction.

Environmental organic contaminants, including BFRs, PCBs, Dioxins and Furans have been previously detected in human tissues originating from many countries. Human biomonitoring programs are important as they provide direct measurements of individual exposures and can be used to understand contaminant partitioning at many scales. Sampling of multiple tissues from single

individuals can provide insights into human physiology and metabolism and lends indications as to routes of exposure. Studies conducted at population scales provide baseline concentrations which can identify 'at-risk' individuals or groups. Recent advances in mass spectrometric technology as well as wet chemical techniques developed in the course of this study have made it possible to analyse a wider variety of environmental contaminants with relative ease with respect to traditional approaches. This chapter deals specifically with the application of these novel techniques to derive exposure data to infants and their respective primipara mothers by analysing concentrations of several classes of organic environmental contaminants present in breast milk samples. Breast milk was selected as a target matrix for this study to determine the method's robustness, selectivity and sensitivity in this complex biological matrix and as it provides a relatively non-invasive means to derive contaminant exposure to both nursing infants through direct transfer and, maternal body-burdens. The novelty of this method is inherent in its ability to detect a large set of 'ultra-trace' concentration target contaminants present in single sample extracts, thus reducing inter-sample variability and providing increased confidence in compound concentration comparisons. Classes of compounds analysed in this study include: brominated flame retardants (BFRs) including polybrominated diphenyl ethers (PBDEs) and 3 novel flame retardants (NBFRs): pentabromoethylbenzene (PBEB), hexabromobenzene (HBB) and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153). Also investigated are the non-ortho polychlorinated biphenyls (no-PCBs), poly-chlorinated,-brominated, and mixed halogenated dibenzo-dioxins and -furans (PCDD/Fs, PBDD/Fs and PXDD/Fs respectively).

4.3 PBDEs and Selected NBFRs in UK Breast Milk.

In the UK and elsewhere, BFRs have been investigated in multiple studies and infant dietary intakes calculated from breast milk concentrations using several infant intake scenarios. For the most part these studies only report Σtri-hexa BDEs (the principal components of the previously commercially

available pentabromodiphenyl ether product) and in some cases BDE-209 (reflective of the major component of the commercial decabromodiphenyl product). Abdallah and Harrad in 2014 used a simple one-compartment, first order pharmacokinetic (PK) model together with estimated values of UK adult exposure to successfully predict indicative maternal contaminant body burdens of several PBDEs. Data from this model was confirmed with body burden concentrations derived experimentally from the chemical analysis of breast milk sampled in the study. These data showed good agreement for the compounds targeted [27]. Importantly, this study was able to confirm previous assumptions regarding predominant maternal exposure pathways in the UK, showing that inhalation, dust ingestion as well as diet accounted for the vast majority of exposure observed. A recent investigation carried out by Tao *et. al.* in 2017 was successful in extending this model to evaluate exposure sources of 19 emerging FRs (EFRs) while also providing the first UK data on EFRs in human breast milk. Both studies also derived infant contaminant dietary intake following US EPA guidelines [116], with maternal milk concentrations showing no significant decreases over the sampling period of 2010 to 2014-15 for those congeners analysed. Mean values of Σtri-hexa BDEs of 5.9 ng/g lw (n=25) observed in the 2010 data set with 6.5 ng/g lw (n=10) found in data pertaining to the sampling period of 2014-15 respectively. The data also lends support for similar BDE-209 concentrations over this period with 0.31 ng/g lw observed in the Abdallah and Harrad data set with respect to values below detection limits of < 0.22 ng/g lw for those reported in 2014-15 [19]. These values were further supported by an additional study by Bramwell *et.al.* who observed mean Σtri-hexa BDEs concentrations of 7.47 ng/g lw (n=6) and mean BDE-209 concentrations of 0.52 ng/g lw (n=6), in UK primipara mothers' milk sampled in 2011- 2012 (Bramwell et al. 2017). Also previously reported in human breast milk samples were a number of 'novel' brominated analogues (NBFRs) including those analysed in this study: pentabromoethylbenzene (PBEB), hexabromobenzene (HBB) and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153). HBB was reported in Japanese mother's milk at mean concentrations of 0.53 ng/g lw (n=40) in 2005 [118] and in breast milk of New Zealand mothers at mean concentrations of 21.72 pg/g lw along with BB-153 and PBEB at 148.06 pg/g lw and

1.02 pg/g lw respectively (n=37 2007-2010) [119]. In the UK BB-156 was recorded at median concentrations of 80 pg/g lw (n=6) in milk sampled in 2011 (Bramwell et al. 2014).

4.3.1 PCBs, Chlorinated, Brominated and Mixed Halogenated Dioxins and Furans in UK Breast milk.

PCB contamination of UK human breast milk samples has been extensively studied with surveys conducted as far back as 1979 (Collins, *et al.,* 1982) with more recent sampling campaigns carried out in 1990-1991 [121] and again in 2001-2003 [122]. These studies have successfully confirmed a marked decline in human contamination since the advent of governmental restrictions. PCB congeners analysed in this study include the non-ortho PCBs-77, 81, 126 and 169 most relevant due to their dioxin-like toxicological effects [123]. Dioxins and furans unlike other compounds in this study were never deliberately synthesised in any great quantity, however are present in detectable concentrations in almost every environmental matrix. PCDD/Fs have been quantified in multiple UK breast milk studies dating back to at least the mid-1980s (Startin et al., 1989) and were therefore able to quantify the rapid reductions following the beginnings of legislative restrictions with ∑PCDD/F TEQs of 37 TEQ ng/kg lw observed in milk sampled over the period of 1987- 1988 in Birmingham to 21 TEQ ng/kg lw at the same location over 1993- 1994 [125]. Brominated and mixed halogenated dioxins and furans (PBDD/Fs and PXDD/Fs), unlike their comparatively well studied chlorinated analogues have received minimal scientific attention, especially with respect to human breast milk concentrations. This lack of available scientific data is due principally to the almost prohibitive expense and analytical difficulty of their analysis. Isobaric interferences with PBDEs, PCBs and PBBs (among others) require extensive clean-up procedures, analysis exclusively by high resolution mass spectrometry, judicious selection of quantification ions and meticulous data interpretation (Fernandes *et al.* 2011). PBDD/Fs and PXDD/Fs have previously been reported in only a very few studies of UK resident breast milk, as is the case worldwide [126].

Table 4.1: Concentrations of target PBDEs (ng g^{-1} lw) in analysed human milk samples.

	Milk 01	Milk 02	Milk 03	Milk 04	Milk 05	Milk 06	Milk 07	Milk 08	Milk 09	Milk 10	Milk 11
BDE-7	<0.005	<0.003	<0.004	<0.003	<0.004	0.217	<0.004	0.016	<0.005	<0.004	<0.004
BDE-10	<0.004	<0.002	<0.003	<0.002	0.078	0.306	<0.003	0.021	<0.004	0.051	<0.003
BDE-15	<0.001	<0.001	0.323	0.132	0.488	0.102	<0.001	0.277	<0.001	0.167	<0.001
BDE-17	<0.004	<0.002	<0.003	<0.002	<0.003	<0.003	<0.003	<0.002	<0.004	<0.003	<0.004
BDE-28	0.140	0.161	0.376	0.132	0.508	0.292	0.670	0.199	0.257	0.288	0.029
BDE-30	<0.003	<0.002	0.052	<0.002	0.029	0.020	<0.002	0.015	<0.003	0.007	<0.003
BDE-47	0.017	2.725	1.387	0.574	2.322	1.918	2.484	1.152	0.654	1.487	1.279
BDE-49	0.010	<0.005	0.299	0.237	0.482	0.151	0.308	0.133	<0.009	0.132	<0.008
BDE-66	0.892	<0.005	<0.006	<0.006	0.100	0.139	<0.006	<0.005	<0.009	<0.007	<0.008
BDE-71	<0.004	<0.002	0.074	0.014	0.590	0.074	0.056	0.043	0.108	0.033	<0.004
BDE-77	<0.004	<0.002	<0.003	<0.003	<0.004	0.008	0.020	0.012	<0.005	0.005	<0.004
BDE-85	0.016	<0.007	0.271	0.217	0.368	<0.008	<0.009	0.028	<0.013	0.009	<0.011
BDE-99	0.626	0.438	1.786	0.616	2.722	1.764	3.568	0.595	1.166	0.592	<0.007
BDE-100	0.508	0.416	1.012	0.396	1.228	1.193	2.268	1.105	1.140	0.564	<0.010
BDE-119	0.042	0.007*	0.149	0.016	0.123	0.043	0.098	0.024	<0.015	0.024	<0.013
BDE-126	0.023	<0.004	<0.006	<0.005	0.046	<0.005	<0.006	0.006*	<0.008	<0.006	<0.007
BDE-154+169[A]	0.340	0.960	1.560	0.490	1.950	0.590	0.450	0.990	1.230	0.450	0.780
BDE-153	0.650	0.580	1.230	0.670	3.700	0.770	1.320	0.445	0.340	1.620	1.100
BDE-139	<0.006	<0.003	<0.004	0.008	<0.005	0.004*	<0.004	0.006	<0.006	0.006	<0.005
BDE-140	<0.006	0.005	0.091	0.021	0.106	0.117	0.137	0.029	<0.006	0.037	<0.005
BDE-138	0.553	<0.003	0.063	0.020	0.052	0.048	0.080	0.024	<0.007	0.027	<0.006
BDE-156	0.169	<0.004	<0.006	<0.005	0.024	<0.005	<0.006	<0.004	<0.008	<0.006	<0.007
BDE-171	0.008	0.006	0.005	0.003	0.018	0.003	0.017	0.005	0.006	0.003	<0.008
BDE-180	<0.008	0.002	0.006*	0.008	0.006	0.004	0.021	0.005	0.011	0.003	<0.007
BDE-183	0.017	<0.006	0.045	0.014	0.050	0.036	0.106	0.025	0.030	0.019	0.073
BDE-184	0.005	<0.002	0.005	<0.002	0.003	<0.002	0.018	<0.002	0.006	<0.003	<0.003
BDE-191	0.010	<0.001	<0.001	0.007	<0.001	0.005	0.024	0.004	0.015	0.005	<0.001

	Milk 01	Milk 02	Milk 03	Milk 04	Milk 05	Milk 06	Milk 07	Milk 08	Milk 09	Milk 10	Milk 11
BDE-196	0.788	0.133	0.024	0.044	0.023	0.026	0.276	0.093	0.132	0.025	<0.007
BDE-203	<0.010	0.030	0.086	0.055	0.140	0.028	0.186	0.044	0.035	0.055	<0.009
BDE-204	<0.009	0.016	0.037	0.012	0.071	0.025	0.117	0.040	<0.009	0.028	<0.008
BDE-205	<0.016	<0.008	0.081	0.027	0.028	<0.010	<0.012	<0.008	<0.016	<0.012	<0.014
BDE-206	0.043	0.042	0.097	0.048	0.122	0.086	0.279	0.149	0.057	0.075	0.734
BDE-207	0.766	0.353	0.194	0.087	0.230	0.142	0.617	0.306	0.137	0.170	1.929
BDE-208	0.576	0.303	0.087	0.035	0.112	0.059	0.234	0.119	0.062	0.078	0.576
BDE-209	1.538	0.931	0.157	0.405	0.177	0.096	0.357	0.259	0.070*	0.095	0.164
∑PBDE (n)	7.73 (22)	7.11 (18)	9.49 (26)	4.29 (28)	15.89 (30)	8.27 (31)	13.71 (24)	6.16 (31)	5.46 (18)	6.05 (28)	6.66 (9)
$\sum PBDE_{tri\text{-}hexa}$ (n)	3.99 (13)	5.29 (8)	8.35 (13)	3.41 (14)	14.35 (16)	7.13 (15)	11.46 (12)	4.80 (16)	4.90 (7)	5.28 (15)	3.19 (4)
$\sum PBDE_{(b)}$	2.17	5.12	7.54	3.20	12.77	6.39	10.40	4.45	4.53	4.85	3.16
$\sum PBDE_{(c)}$	2.16	5.12	7.02	2.76	11.97	6.27	10.20	4.31	4.56	4.73	3.23
$\sum PBDE_{(d)}$	1.29	3.74	4.40	1.86	8.74	4.45	7.37	2.19	2.16	3.70	2.38

[a] Chromatographic co-elution.

[b] Lb Sum of BDE-47, -49, -85, -99, -100, -153, -154 and -169.

[c] Lb Sum of BDE-47, -99, -100, -153, -154, -169 and -183.

[d] Lb Sum of BDE-47, -99 and -153.

[*] Value equal to sample method detection limit (MDL).

< *i* indicates quantification below method detection limits (MDL, *i*)- See Chapter 2 Section 2.6.3.1 for detailed description of MDL derivation.

Table 4.2: Summary statistics of PBDEs breast milk samples analysed here and comparative studies (ng g^{-1} lw).

	Comparative Study (Location, Collection Year, Sample *n*)	Occurrence %(n)	Mean	σ	Median	Min	Max
BDE-7		18.2	0.116	0.142	0.116	0.016	0.217
BDE-10		36.4	0.114	0.130	0.065	0.021	0.306
BDE-15		54.5	0.248	0.145	0.222	0.102	0.488
BDE-17		0.0	0.000	0.000	0.000	0.000	0.000
BDE-28		100.0	0.277	0.184	0.257	0.029	0.670
BDE-30		45.5	0.025	0.017	0.020	0.007	0.052
BDE-47		100.0	1.454	0.852	1.387	0.017	2.725
BDE-47	Birmingham, UK (2010- 11; *n*= 12)[1]				2.30		
BDE-47	Birmingham, UK (2010; *n*= 34)[2]				2.80		
BDE-47	North East England, UK (2011- 12; *n*= 6)[3]				2.05		
BDE-47	Central North Carolina, USA (2004– 06; *n*= 303)[4]				28		
BDE-47	Norway (2001- 2009; *n*= 393)[5]				0.99		
BDE-47	Ireland (2010; *n*= 11)[6]				1.11		
BDE-47	New Zealand (2010; n= 33)[7]				2.14		
BDE-47	France (2004- 2006; *n*= 77)[8]				1.152		
BDE-49		72.7	0.219	0.145	0.194	0.010	0.482
BDE-66		27.3	0.377	0.446	0.139	0.100	0.892
BDE-71		72.7	0.124	0.191	0.065	0.014	0.590
BDE-77		36.4	0.011	0.007	0.010	0.005	0.020
BDE-85		54.5	0.151	0.154	0.123	0.009	0.368
BDE-99		90.9	1.387	1.066	0.896	0.438	3.568
BDE-99	Birmingham, UK (2010- 11; *n*= 12)[1]				1.04		
BDE-99	Birmingham, UK (2010; *n*= 34)[2]				0.69		
BDE-99	North East England, UK (2011- 12; *n*= 6)[3]				0.97		
BDE-99	Central North Carolina, USA (2004– 06; *n*= 303)[4]				5		
BDE-99	Norway (2001- 2009; *n*= 393)[5]				0.27		
BDE-99	Ireland (2010; *n*= 11)[6]				0.27		

BDE-99	New Zealand (2010; n= 33)[7]				0.56		
BDE-99	France (2004- 2006; *n*= 77)[8]				0.527		
BDE-100		90.9	0.983	0.564	1.058	0.396	2.268
BDE-119		81.8	0.058	0.052	0.042	0.007	0.149
BDE-126		27.3	0.023	0.022	0.023	0.001	0.046
BDE-154+169[a]		100.0	0.890	0.515	0.780	0.340	1.950
BDE-153		100.0	1.130	0.941	0.770	0.340	3.700
BDE-153	Birmingham, UK (2010- 11; *n*= 12)[1]				0.48		
BDE-153	Birmingham, UK (2010; *n*= 34)[2]				0.91		
BDE-153	North East England, UK (2011- 12; *n*= 6)[3]				0.93		
BDE-153	Central North Carolina, USA (2004– 06; *n*= 303)[4]				6		
BDE-153	Norway (2001- 2009; *n*= 393)[5]				0.45		
BDE-153	Ireland (2010; *n*= 11)[6]				1.00		
BDE-153	New Zealand (2010; n= 33)[7]				0.52		
BDE-153	France (2004- 2006; *n*= 77)[8]				0.781		
BDE-139		36.4	0.006	0.002	0.006	0.004	0.008
BDE-140		72.7	0.068	0.050	0.064	0.005	0.137
BDE-138		72.7	0.108	0.181	0.050	0.020	0.553
BDE-156		27.3	0.065	0.091	0.024	0.001	0.169
BDE-171		90.9	0.007	0.006	0.005	0.002	0.018
BDE-180		81.8	0.007	0.006	0.006	0.002	0.021
BDE-183		100.0	0.038	0.030	0.030	0.005	0.106
BDE-184		72.7	0.005	0.006	0.004	0.001	0.018
BDE-191		63.6	0.010	0.007	0.007	0.004	0.024
BDE-196		90.9	0.156	0.236	0.069	0.023	0.788
BDE-203		81.8	0.073	0.055	0.055	0.028	0.186
BDE-204		72.7	0.043	0.035	0.032	0.012	0.117
BDE-205		36.4	0.034	0.034	0.027	0.001	0.081
BDE-206		100.0	0.157	0.203	0.086	0.042	0.734
BDE-207		100.0	0.448	0.535	0.230	0.087	1.929

BDE-208		100.0	0.204	0.201	0.112	0.035	0.576
BDE-209		100.0	0.39	0.45	0.18	0.07	1.54
BDE-209	Birmingham, UK (2010- 11; *n*= 12)[1]				0.08		
BDE-209	Birmingham, UK (2010; *n*= 34)[2]				0.25		
BDE-209	North East England, UK (2011- 12; *n*= 6)[3]				0.70		
BDE-209	Norway (2001- 2009; *n*= 46)[5]				0.32		
BDE-209	Ireland (2010; *n*= 10)[6]				0.77		
BDE-209	New Zealand (2010; n= 33)[7]				0.19		
BDE-209	France (2004- 2006; *n*= 62)[8]				1.615		
∑PBDE		--	8.26	3.56	7.11	4.29	15.89
$\sum PBDE_{tri\text{-}hexa}$		--	6.56	3.54	5.28	3.19	14.35
$\sum PBDE_{(b)}$		54.5	5.87	3.24	4.85	2.17	12.77
$\sum PBDE_{(c)}$		90.9	5.67	3.06	4.73	2.16	11.97
$\sum PBDE_{(d)}$		90.9	3.85	2.35	3.70	1.29	8.74
$\sum PBDE_{(d)}$	Central North Carolina, USA (2004– 06; *n*= 303)[4]				39		
$\sum PBDE_{(e)}$		90.9	4.36	3.31	3.23	0.87	11.53
$\sum PBDE_{(e)}$	Birmingham, UK (2010- 11; *n*= 12)[1]				3.9		
$\sum PBDE_{(e)}$	Birmingham, UK (2010; *n*= 34)[2]				4.65		
$\sum PBDE_{(e)}$	North East England, UK (2011- 12; *n*= 6)[3]				4.65		
$\sum PBDE_{(e)}$	Norway (2001- 2009; *n*= 46)[5]				2.03		
$\sum PBDE_{(e)}$	Ireland (2010; *n*= 10)[6]				3.15		
$\sum PBDE_{(e)}$	New Zealand (2010; n= 33)[7]				3.64		
$\sum PBDE_{(e)}$	France (2004- 2006; *n*= 62)[8]				3.625		

Values listed in the absence of a corresponding comparative study pertain to samples analysed by the authors.

[a] Chromatographic co-elution. **σ** Denotes 1 standard deviation of the mean value.

[b] Lb Sum of BDE-47, -49, -85, -99, -100, -153, -154 and -169.

[c] Lb Sum of BDE-47, -99, -100, -153, -154, -169 and -183.

[d] Lb Sum of BDE-47, -99 and -153.

[e] Lb Sum of BDE-47, -99, -153 and -209.

[1- 8] References: **1**, Harrad and Abdallah, 2015 (Harrad and Abdallah 2015); **2**, Abdallah and Harrad, 2014 [27]; **3**, Bramwell et al., 2014 [26]; **4**, Daniels et al., 2010 [128]; **5**, Thomsen et al., 2010 [129]; **6**, Pratt et al., 2013 [66]; **7**, Coakley et al., 2013 [130]; **8**, Antignac et al., 2009 [131].

Table 4.3: Concentrations of target NBFRs (ng g^{-1} lw) in analysed human milk samples.

	Milk 01	Milk 02	Milk 03	Milk 04	Milk 05	Milk 06	Milk 07	Milk 08	Milk 09	Milk 10	Milk 11
PBEB	0.001*	<0.001	0.024	0.005	0.015	0.017	0.022	0.009	0.006	0.007	0.001
HBB	0.048	<0.001	<0.001	<0.001	0.070	0.006	<0.001	0.023	<0.001	<0.001	0.048
BB-153	0.014	0.042	0.035	0.017	0.062	0.090	0.056	0.033	0.098	0.050	0.014

*Value equal to sample method detection limit (MDL)

< *i* indicates quantification below method detection limits (MDL, *i*)- See Chapter 2 Section 2.6.3.1 for detailed description of MDL derivation

Table 4.4: Summary Statistics of NBFRs detected in breast milk samples (ng g^{-1} lw).

	Occurrence (%)	Mean	σ	Median	Min	Max
PBEB	81.8	0.01	0.01	0.01	<0.005	0.02
HBB	36.4	0.04	0.03	0.04	0.01	0.07
BB-153	90.9	0.05	0.03	0.05	0.01	0.10

σ Denotes 1 standard deviation of the mean value

< *i* indicates quantification below method detection limits (MDL, *i*)- See Chapter 2.6.3.1 for detailed description of MDL derivation.

4.4 Concentrations of BFRs in human milk samples.

4.4.1 PBDEs.

In total 46 individual PBDE congeners were analysed. All congeners were chromatographically baseline separated accept for a single pair (BDE-154 and BDE-169) which occurred across all samples. Concentrations of sum PBDEs ranged from 15.89 ng g^{-1} lw consisting of 30 individual congeners to 4.29 ng g^{-1} lw derived from a total of 28 congeners (lower bound data). A mean total PBDE concentration of 8.26± 3.56 ng g^{-1} lw was obtained for all samples (n= 11), indicating significant inter-sample variation across the data set. These values are somewhat elevated from those previously reported for UK human breast milk samples with sum-PBDE concentrations ranging from 0.2-27.02 ng g^{-1} lw (mean= 6.26± 5.65 ng g^{-1} lw, n= 35) for breast milk sampled in 2010 [27]; 1.28-22.02 ng g^{-1} lw (median= 5.67 ng g^{-1} lw, n=6) for samples taken in 2011-12 (Bramwell et al., 2014) and 1.7- 14 ng g^{-1} lw (mean= 6.5 ng g^{-1} lw, n=10) for samples obtained in 2014-15 [19]. These values remain at levels approximately 10-50 times lower than those mean values observed in US samples taken over the last 15 years (66.8 ng g^{-1} lw) [132].

Although this may be suggestive of an increasing UK overall trend, it is important to note that sum-PBDE concentrations calculated in this study are derived from analyses targeting several additional analyte peaks (46 with respect to 17 in Bramwell et al., 2014 and 8 in Abdallah & Harrad, 2014 as well as Tao et al., 2017). A more representative comparison can be made by comparing congener groups present in each study. Bramwell et al., 2014 reported a median concentration of 4.59 ng g^{-1} lw for sum BDE-47, -99, -100, -153, -154 and -183. These concentrations compare well with our value of 4.73 ng g^{-1} lw for the same congeners with the addition of BDE- 169 which was unable to be excluded due to its co-elution with BDE- 154. Mean $\sum PBDE_{tri\text{-}hexa}$ values of 5.95 ng g^{-1} lw and 6.5 ng g^{-1} lw were reported in Abdallah & Harrad, 2014 and Tao et al., 2017 respectively and consisted of sum total mean concentrations of BDE- 47, -49, -85, -99, -100, -153, -154 present in samples. This was also found to agree well with our value of 5.87 ng g^{-1} lw for the identical congener set, with however,

the additional concentration contribution of the co-eluted BDE- 169. In this study a mean (Lb) $\sum PBDE_{tri\text{-}hexa}$ concentration of 6.56 ng g^{-1} lw was calculated from 19 individual PBDE congeners across the 11 samples in the data set. This value when compared to those of the previous study does not differ significantly, confirming that accurate $\sum PBDE_{tri\text{-}hexa}$ values may be reliably estimated by analysing the lesser number of more biologically relevant contributing congeners. Significant differences were however, observed between median concentrations of BDE- 183 in breast milk samples analysed by Bramwell et al., 2014 where a value of 0.05 ng g^{-1} lw was reported. This study observed a median value of 0.25 ng g^{-1} lw, approximately equal to the maximum concentration value of 0.23 ng g^{-1} lw reported in Bramwell et al., 2014. Interestingly, an analysis of congener profiles from samples taken in Birmingham (Abdallah and Harrad 2014; Tao et al. 2017) shows increasing dominance of the BDE- 153 congener with respect to BDE-47 over time, with ratios of mean BDE-153/BDE-47 concentrations increasing from 0.35 in 2010 to 0.61 over 2014-15 to the value of 0.77 observed in the current study. This trend was also present in data sets analysed in Swedish mothers milk over a period of 1980 to 2004 with ratios of 0.30 and 0.99 observed respectively [133]. A similar trend is observed in US mothers milk (Marchitti et al. 2017) where relative levels of BDE-153 are increacing with respect to a corresponding temporal decrease in BDE-47 (resulting in a BDE-153/BDE-47 ratio of 0.15 in 2004). An explanation of this trend was offered by Fängström et al. 2008 where they propose that the increased metabolic degradation of the lower brominated congeners with respect to that of BDE-153 in combination with legislation that has banned Penta-BDE (prior to bans on Octa-BDE) is likely to have contributed to the overall observed trend.

Unlike their lower brominated counterparts, hepta-nona BDEs have, outside of this study not been previously quantified in UK human breast milk samples. A comparison with breast milk from 2008 collected and analysed in New Zealand [135] showed a mean $\sum PBDE_{hepta\text{-}nona}$ concentration of 0.415± 0.072 ng g^{-1} lw (mean ± 1σ, n= 37), less than half the value of 1.12± 0.95 ng g^{-1} lw (mean ± 1σ) observed in this data set. Increased variability in the case of samples analysed in this study can be attributed principally to elevated concentrations of the dominant $PBDE_{hepta\text{-}nona}$ congener, BDE- 207

which in unexplained elevated concentrations was observed in 3 of the 11 samples analysed at: 0.766, 0.617 and 1.929 ng g^{-1} lw (milk samples 1, 7 and 11 respectively). The increased concentrations of $PBDE_{hepta\text{-}nona}$ may be possibly attributable to exposure to de-brominated BDE- 209 degraded either abiotically (La Guardia et al. 2006) or through metabolic de-bromination of BDE- 209 *in vivo* [9] and may also be a contributing driver of the increasing BDE-153/BDE-47 concentration ratio trend observed.

BDE- 209 was observed above detection limits in all samples in the data set at a mean (Lb) concentration of 0.39± 0.45 ng g^{-1} lw, almost identical to the mean concentration of 0.31± 0.30 ng g^{-1} lw previously reported by Abdallah & Harrad, 2014, but slightly lower than that reported in Bramwell et al., 2014 (median = 0.53 ng g^{-1} lw) as compared to the median (Lb) value of 0.18 ng g^{-1} lw reported here. This may indicate that despite regulatory phase out and decreasing BDE- 209 concentrations observed in food as well as office dust in the UK [19] concentrations, likely from legacy sources remain a continuing route of human exposure.

4.4.2 NBFRs.

BB-153, HBB and PBEB were observed at occurrences of 90.9% (n= 10), 36.4% (n= 4) and 81% (n= 9) across the data set respectively. BB- 153 was observed as the largest contributor to the NBFRs measured with a lower bound mean concentration of 0.05± 0.03 ng g^{-1} lw, followed by HBB at 0.04± 0.03 ng g^{-1} lw and PBEB at 0.01± 0.01 ng g^{-1} lw. We report a slightly lower median value of 0.05 ng g^{-1} lw for BB- 153 with respect to that observed in Bramwell et al., 2014 (0.08 ng g^{-1} lw) and approximately one third of the mean values reported for New Zealand breast milk samples (0.148 ng g^{-1} lw; Mannetje et al. 2013a), as well as 20 fold reduction with respect to those observed in the US (median= 1.0 ng g^{-1} lw; Marchitti et al. 2017). HBB was detected here in UK breast milk samples for the first time despite previous attempts [19] at a mean concentration of 0.04 ng g^{-1} lw over a range of 0.01- 0.07 ng g^{-1} lw, concentrations of approximately double that observed in the New Zealand

study by Mannetje et al. (0.0217 ng g^{-1} lw). HBB was manufactured and utilised in relatively low quantities (~350 t/ year) [118] in Japan where breast milk contamination appears most prevalent. Mean concentrations of 0.86 ng g^{-1} lw with some samples as high as 2.5 ng g^{-1} lw were observed in a 2012 study by Fujii et al, far above the concentrations observed in the current study. HBB has also been confirmed as a pyrolysis product of BDE -209 [135] which may contribute to HBB exposure in the UK given its previous wide-spread use [137]. PBEB was also previously analysed for in Tao et al. 2017 however was not detected in human milk or food samples. Here we report a mean concentration of 0.01 ng g^{-1} lw approximately one order of magnitude higher than that observed in Mannetje et al. 2013 for New Zealand breast milk. Quantification of HBB and PBEB in this study despite the previous attempt in Tao et al. 2017 is at least in part attributable to increased analytical sensitivity employed in this study where either 5.4 g or 8 g dw breast milk was extracted for analysis with respect to 500 mg as extracted in Tao et al. This as well as analysis conducted using HRGC-HRMS on the GC-Q Exactive platform resulted in MDLs in the sub pg range (see chapter 2.7.2.3 for details).

Table 4.5: Concentrations of target PCDD/Fs (pg g^{-1} lw) in analysed human milk samples.

	Milk 01	Milk 02	Milk 03	Milk 05	Milk 06	Milk 07	Milk 08	Milk 09	Milk 10	Milk 11
Dioxins										
2,3,7,8-TCDD	0.42	<0.04	0.12	0.12	0.39	<0.05	0.40	<0.08	0.10	0.10
1,2,3,7,8-PeCDD	2.47	1.98	1.71	0.96	1.60	0.28	1.61	0.89	0.53	0.89
1,2,3,4,7,8+1,2,3,6,7,8-HxCDD	0.56	2.09	1.37	1.00	4.12	1.69	3.75	<0.54	<0.42	<0.46
1,2,3,7,8,9-HxCDD	<0.29	<0.15	<0.20	<0.24	<0.18	0.81	<0.14	<0.29	<0.22	<0.25
1,2,3,4,6,7,8-HpCDD	8.01	0.81	2.39	8.87	1.44	9.23	6.30	5.59	1.11	3.25
OCDD	40.27	15.98	20.93	34.79	18.12	47.38	29.07	22.48	17.46	25.64
Furans										
2,3,7,8-TCDF	0.15	<0.05	<0.06	0.20	<0.06	<0.06	0.10	0.15	0.08	0.06*
1,2,3,7,8-PeCDF	<0.11	<0.05	<0.07	<0.09	<0.06	<0.07	<0.05	<0.10	<0.08	<0.09
2,3,4,7,8-PeCDF	6.97	11.79	5.29	2.26	4.40	5.00	8.11	2.37	1.81	2.55
1,2,3,4,7,8+1,2,3,6,7,8-HxCDF [a-]	0.86	<0.13	<0.18	0.64	0.14*	<0.17	3.32	<0.25	<0.19	<0.21
2,3,4,6,7,8-HxCDF	<0.16	<0.08	<0.11	<0.13	<0.10	<0.11	<0.08	<0.15	<0.12	<0.13
1,2,3,7,8,9-HxCDF	<0.13	<0.07	<0.09	<0.11	<0.08	<0.09	<0.06	<0.13	<0.10	<0.11
1,2,3,4,6,7,8-HpCDF	<0.07	<0.03	<0.05	0.87	<0.04	<0.05	<0.03	<0.07	<0.05	<0.06
1,2,3,4,7,8,9-HpCDF	<0.10	<0.05	<0.07	<0.08	<0.06	<0.07	<0.05	<0.09	<0.07	<0.08
OCDF	<0.02	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.02	<0.02	<0.02
Non-ortho PCBs										
PCB-77	0.82	0.68	0.77	<0.12	0.32	1.16	1.43	0.48	0.35	0.26
PCB-81	2.45	3.45	12.14	<0.13	2.71	6.31	29.97	2.78	1.76	2.80
PCB-126	30.87	47.42	35.05	10.84	8.36	19.61	49.25	11.91	6.09	7.80
PCB-169	26.75	59.69	27.23	7.38	11.08	11.00	27.72	8.48	7.89	5.46
$\sum PCDD_{2,3,7,8}$	51.73	20.86	26.52	45.74	25.67	59.39	41.13	28.96	19.2	29.88
$\sum PCDF_{2,3,7,8}$	7.98	11.79	5.29	3.97	4.54	5.00	11.53	2.52	1.89	2.61
$\sum PCDD/F_{2,3,7,8}$	59.71	32.65	31.81	49.71	30.21	64.39	52.66	31.48	21.09	32.49
$\sum PCBs_{non\text{-}ortho}$	60.89	111.24	75.19	18.22	22.47	38.08	108.37	23.65	16.09	16.32
WHO98-TEQ PCDD/F (Lb)	6.62	8.09	4.64	6.62	4.62	3.13	6.85	2.15	1.56	2.31
WHO98-TEQ PCDD/F (Ub)	6.68	8.18	4.71	6.68	2.55	4.68	3.23	6.88	2.37	1.67

WHO05-TEQ PCDD/F (Lb)	5.23	5.74	3.58	5.23	2.05	3.74	2.14	5.23	1.68	1.2
WHO05-TEQ PCDD/F(Ub)	5.29	5.83	3.65	5.29	2.10	3.80	2.24	5.26	1.89	1.31
WHO98-TEQ PCB (Lb)	3.35	5.34	3.78	3.35	1.16	0.95	2.07	5.21	1.28	0.69
WHO98-TEQ PCB (Ub)	3.35	5.34	3.78	3.35	1.16	0.95	2.07	5.21	1.28	0.69
WHO05-TEQ PCB (Lb)	3.89	6.53	4.33	3.89	1.31	1.17	2.29	5.77	1.45	0.85
WHO05-TEQ PCB (Ub)	3.89	6.53	4.33	3.89	1.31	1.17	2.29	5.77	1.45	0.85
∑WHO98-TEQ (Lb)	9.97	13.43	8.42	9.97	3.65	5.57	5.2	12.05	3.42	2.24
∑WHO98-TEQ (Ub)	10.04	13.52	8.49	10.04	3.71	5.62	5.30	12.09	3.64	2.35
∑WHO05-TEQ (Lb)	9.12	12.27	7.91	9.12	3.36	4.91	4.43	11	3.12	2.04
∑WHO05-TEQ (Ub)	9.18	12.36	7.98	9.18	3.41	4.97	4.53	11.03	3.34	2.16

[a] Chromatographic co-elution.

All reported TEQ values correspond to lower bound values.

All Sum values refer to lower bound totals unless otherwise indicated.

[*]Value equal to sample method detection limit (MDL)

< i indicates quantification below method detection limits (MDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of MDL derivation.

Table 4.6: Summary Statistics of PCDD/Fs and *non-Ortho PCBs* analysed in breast milk samples (pg g^{-1} lw).

	Occurrence (%,(n))	Mean	σ	Median	Min	Max
Dioxins						
2,3,7,8-TCDD	70.0 (7)	0.24	0.16	0.12	0.10	0.42
1,2,3,7,8-PeCDD	100.0 (10)	1.29	0.69	1.28	0.28	2.47
1,2,3,4,7,8+1,2,3,6,7,8-HxCDD[a-]	70.0 (7)	2.08	1.36	1.69	0.56	4.12
1,2,3,7,8,9-HxCDD	10.0 (1)	0.81	--	0.81	0.81	0.81
1,2,3,4,6,7,8-HpCDD	100.0 (10)	4.70	3.30	4.42	0.81	9.23
OCDD	100.0 (10)	27.21	10.57	24.06	15.98	47.38
Furans						
2,3,7,8-TCDF	60.0 (6)	0.12	0.05	0.13	0.06	0.20
1,2,3,7,8-PeCDF	0.0	--	--	--	0.00	0.00
2,3,4,7,8-PeCDF	100.0 (10)	5.06	3.17	4.70	1.81	11.79
1,2,3,4,7,8+1,2,3,6,7,8-HxCDF[a]	40.0 (4)	1.24	1.42	0.75	0.14	3.32
2,3,4,6,7,8-HxCDF	0.0	--	--	--	0.00	0.00
1,2,3,7,8,9-HxCDF	0.0	--	--	--	0.00	0.00
1,2,3,4,6,7,8-HpCDF	10.0 (1)	0.87	--	0.87	0.87	0.87
1,2,3,4,7,8,9-HpCDF	0.0	--	--	--	--	--
OCDF	0.0	--	--	--	--	--
Non-ortho PCBs						
PCB-77	90.0 (9)	7.15	9.14	2.80	1.76	29.97
PCB-81	90.0 (9)	0.70	0.40	0.68	0.26	1.43
PCB-126	100.0 (10)	22.72	16.68	15.76	6.09	49.25
PCB-169	100.0 (10)	19.27	16.79	11.04	5.46	59.69
$\sum PCDD_{2,3,7,8}$		34.91	13.74	29.42	19.20	59.39
$\sum PCDF_{2,3,7,8}$		5.71	3.58	4.77	1.89	11.79
$\sum PCDD/F_{2,3,7,8}$		40.62	14.67	32.57	21.09	64.39
$\sum PCBs_{non\text{-}ortho}$		49.05	37.70	30.87	16.09	111.24
WHO98-TEQ PCDD/F (Lb)		4.24	2.29	3.87	1.56	8.09
WHO98-TEQ PCDD/F (Ub)		4.34	2.26	3.95	1.67	8.18
WHO05-TEQ PCDD/F (Lb)		3.24	1.69	2.86	1.20	5.74
WHO05-TEQ PCDD/F(Ub)		3.33	1.67	2.94	1.31	5.83
WHO98-TEQ PCB (Lb)		2.47	1.82	1.67	0.69	5.34
WHO98-TEQ PCB (Ub)		2.47	1.82	1.67	0.69	5.34
WHO05-TEQ PCB (Lb)		2.85	2.12	1.87	0.85	6.53
WHO05-TEQ PCB (Ub)		2.85	2.12	1.87	0.85	6.53
∑WHO98-TEQ (Lb)		6.71	4.00	5.38	2.24	13.43
∑WHO98-TEQ (Ub)		6.80	3.97	5.46	2.35	13.52
∑WHO05-TEQ (Lb)		6.09	3.69	4.67	2.04	12.27
∑WHO05-TEQ (Ub)		6.18	3.67	4.75	2.16	12.36

[a] Chromatographic co-elution.
All reported mean and sum values correspond to lower bound values unless otherwise indicated.
< i indicates quantification below method detection limits (MDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of MDL derivation.

4.5 Concentrations of PCDD/Fs and non-*Ortho* PCBs in UK human milk samples.

Chlorinated Dioxins and Furans were detected in all samples analysed with the exception of milk sample 04 which suffered from analytical errors and showed a complete absence of PCDD/Fs (all congeners below detection limits). This sample was subsequently removed and is not referred to further in this section.

4.5.1 PCDD/Fs.

In the absence of milk sample 04, mean WHO2005 TEQ values for detected PCDD/Fs ranged from 0.12± 0.05 pg g^{-1} lw for 2,3,7,8-TCDF (n=6) to 27.21± 10.57 pg g^{-1} lw observed for OCDD across all 10 samples. Mean sum lower bound WHO2005 and WHO1998 TEQ values for PCDD/F of 3.24± 1.69 pg TEQ_{05} g^{-1} lw and 4.24± 2.29 pg TEQ_{98} g^{-1} lw were calculated from the samples analysed respectively, the latter for comparison purposes. 2,3,7,8 substituted PCDD/Fs have been quantified in UK breast milk samples on two previous occasions over 1987- 1988 and 1993- 1994. These showed a marked decline from 37 pg TEQ_{98} g^{-1} lw to 21 pg TEQ_{98} g^{-1} lw for samples originating in Birmingham, UK [125] over this period, with our value of 4.24± 2.29 pg TEQ_{98} g^{-1} lw (Lb TEQ) confirming the continuation of decreasing temporal PCDD/F breast milk contamination trends. Since 1987 the WHO has coordinated a number of comprehensive global assessments of PCDD/Fs in breast milk, and in 2016 published the latest data set aimed at establishing baseline concentration values for 52 countries. Samples for analysis were derived from pooled samples taken over the periods of 2000-2003 and 2005-2010. PCDD/Fs in UK breast milk were not included, however data generated in this study, despite the difference in sampling date is shown in Figure 4.1 for comparison [10]. Our values for PCDD/F TEQ_{05} when compared with those observed over 2005-2010 in other locations, place the UK at levels generally lower than those of other European countries, this does not however take into consideration reductions that have likely occurred in those locations since the time of sampling, and there for are presented here only indicatively.

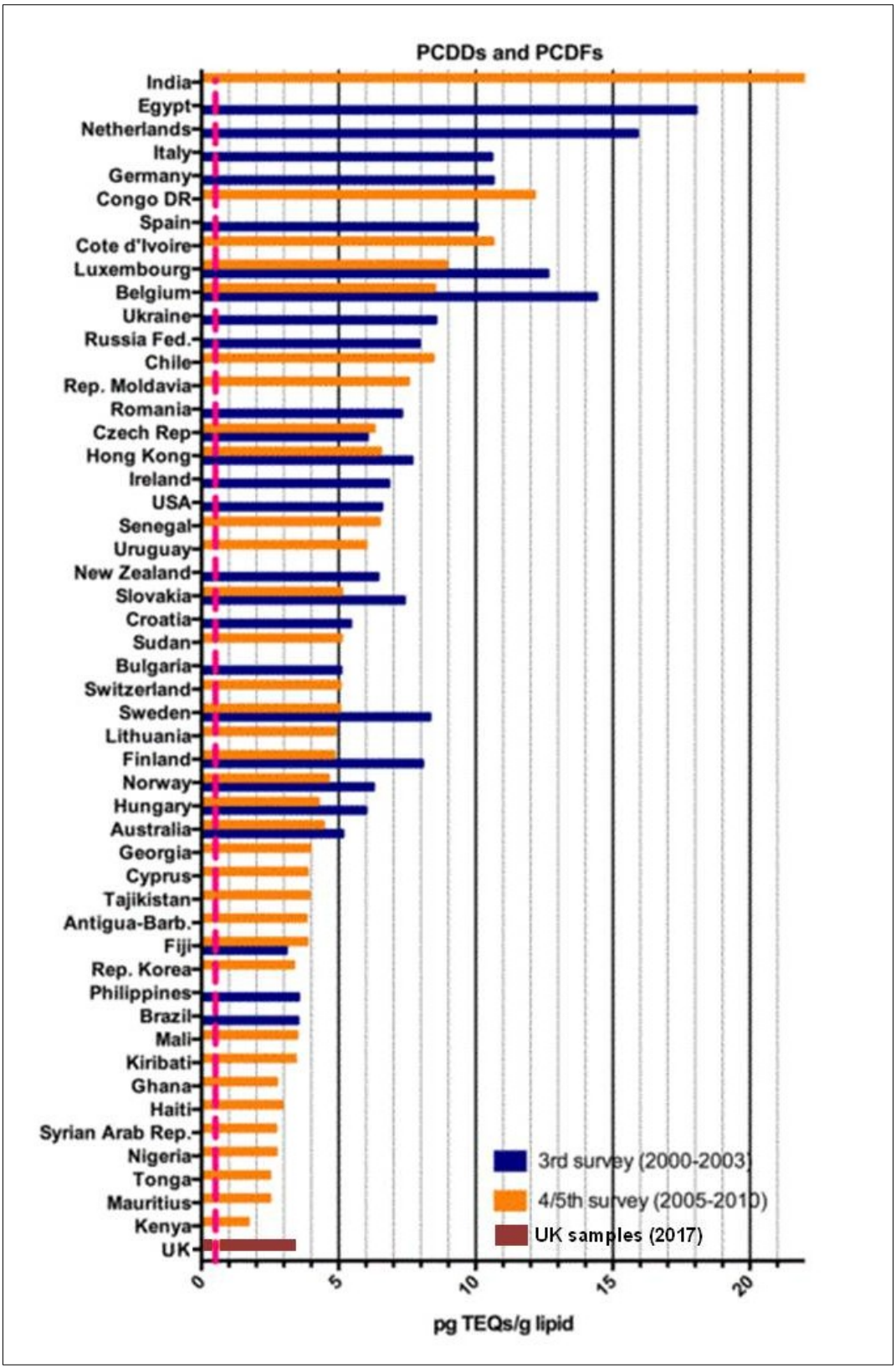


Figure 4.1: Results of the WHO/UNEP surveys for PCDD/Fs in human breast milk and UK 2017 PCDD/F breast milk data (this study). Results are in pg TEQ_{05} g^{-1}lw. The red broken line represents calculated safe levels for breast fed infants. –Figure adapted and modified from van den Berg et al. 2016 [10].

PCDD/F congener profiles generated in this study were consistent with those observed previously in the UK [121] and follow a characteristic profile for breast milk contamination reported in studies from New Zealand, Australia, France, Belgium, Sweden and Japan(Mannetje et al. 2013; Harden et al. 2007; Focant et al. 2013; Focant et al. 2002; Fång et al. 2013; Guan et al. 2006). These profiles reflect local exposure trends as well as bio-accumulation and metabolic processes which combined, tend to reveal a propensity for accumulation of dioxins rather than furans, especially the higher chlorinated congeners (OCDD > 1,2,3,4,6,7,8- HeptaCDD > 1,2,3,6,7,8- and 1,2,3,4,7,8-HexaCDD). This pattern as well as the dominant presence of the 2,3,4,7,8-PeCDF congener was observed in our samples and is also typically observed globally. 2,3,4,7,8-PeCDF was present in all samples analysed in our data set at a mean (Lb) concentration of 5.06± 3.17 pg g^{-1} lw, making this the second highest contributing congener behind OCDD (Lb mean= 27.21 pg g^{-1} lw; Figure 4.2). 2,3,7,8-dioxins analysed were observed above MDL concentrations in 7 of the 10 samples with the exception of 1,2,3,7,8,9-HxCDD which was observed above MDL in only one sample.

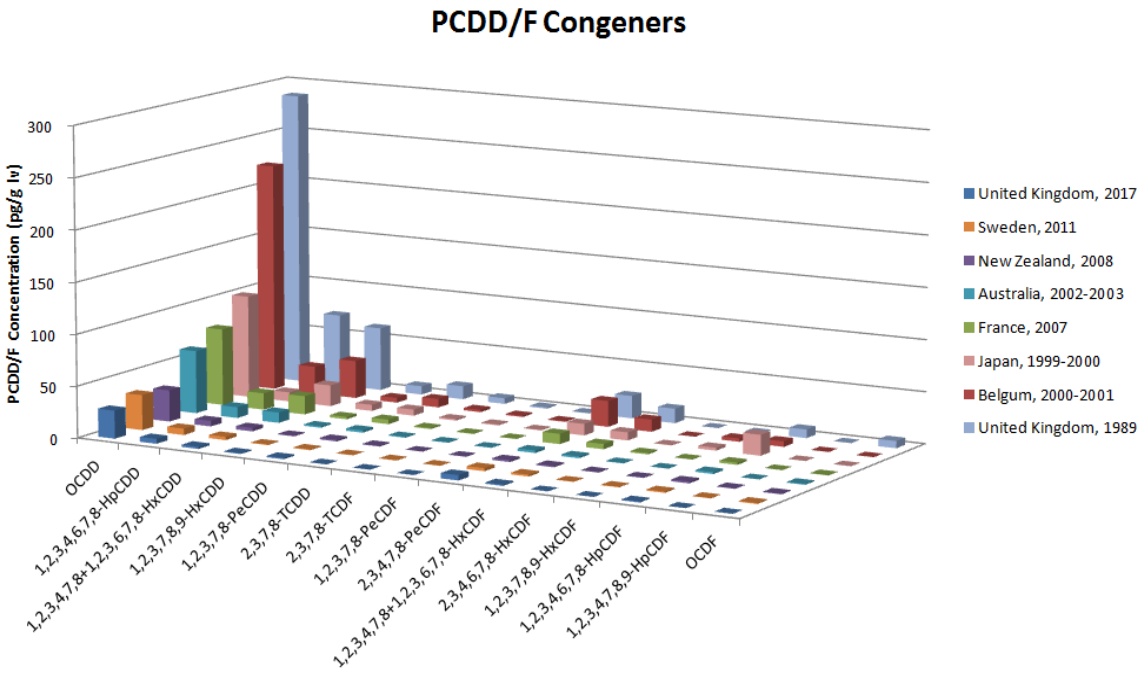


Figure 4.2: Global breast milk PCDD/F congener profile data of Primipara and non-Primipara mothers. Data was adapted from: Duarte-Davidson et al. 1992 (UK, 1989), Focant et al. 2002 (Belgum, 2001), Guan et al. 2006 (Japan, 1999-2000), Focant et al.2013 (France, 2007), Harden et al. 2007 (Australia, 2002-2003), Mannetje et al. 2013 (New Zealand, 2008) and Fång et al. 2013 (Sweden, 2011). Duarte-Davidson et al. 1992 (UK, 1989) did not include values for 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9, HxCDF or 1,2,3,4,7,8,9-HpCDF and are subsequently represented as 0 pg g-1 lw on the graph. Values taken from Harden et al. 2007 (Australia, 2002-3) are weighted means and Focant 2002 (Belgum, 2000-2001) samples originate from a potentially highly exposed population sub-set.

4.5.2 Non-*Ortho* PCBs

The non-*ortho* PCBs -77, -81, -126 and -169 were analysed in this study and detected at least once above MDLs in all samples. The penta-CB congener, PCB -126 was quantified at the highest mean concentration of 22.72 pg g^{-1} lw with PCB -81 detected at concentrations ranging from below MDL to 1.43 pg g^{-1} lw (Lb mean = 0.70 pg g^{-1} lw) representing the lowest concentrations observed in the data set. PCBs analysed in samples showed a reasonable degree of inter-sample variability with relative standard deviations ranging from 60- 128% of their respective mean values, similar to the variability seen in the PCDD/F analyses. The 4 non-*ortho* PCBs contributed 46.8% (2.85 pg TEQ_{05} g^{-1} lw) to the total 6.09 pg TEQ_{05} g^{-1} lw observed for both PCDD/Fs and PCBs combined. This value is elevated when compared to studies from New Zealand, Australia, France, Belgium, Sweden and Japan (Mannetje et al. 2013; Harden et al. 2007; Focant et al. 2013; Focant et al. 2002; Fång et al. 2013; Guan et al. 2006), not due to elevated concentrations of PCBs but rather due to the relatively lower PCDD/F concentrations observed in UK breast milk.

PCBs followed a concentration trend of PCB-126 > PCB-169 > PCB-77 > PCB-81 not dissimilar to those previously observed in the studies listed above and displayed in Figures 4.2 and 4.3. As was observed for PCDD/Fs, the PCB profile reflects a combination of both exposure as well as congener specific metabolic degradation tendencies.

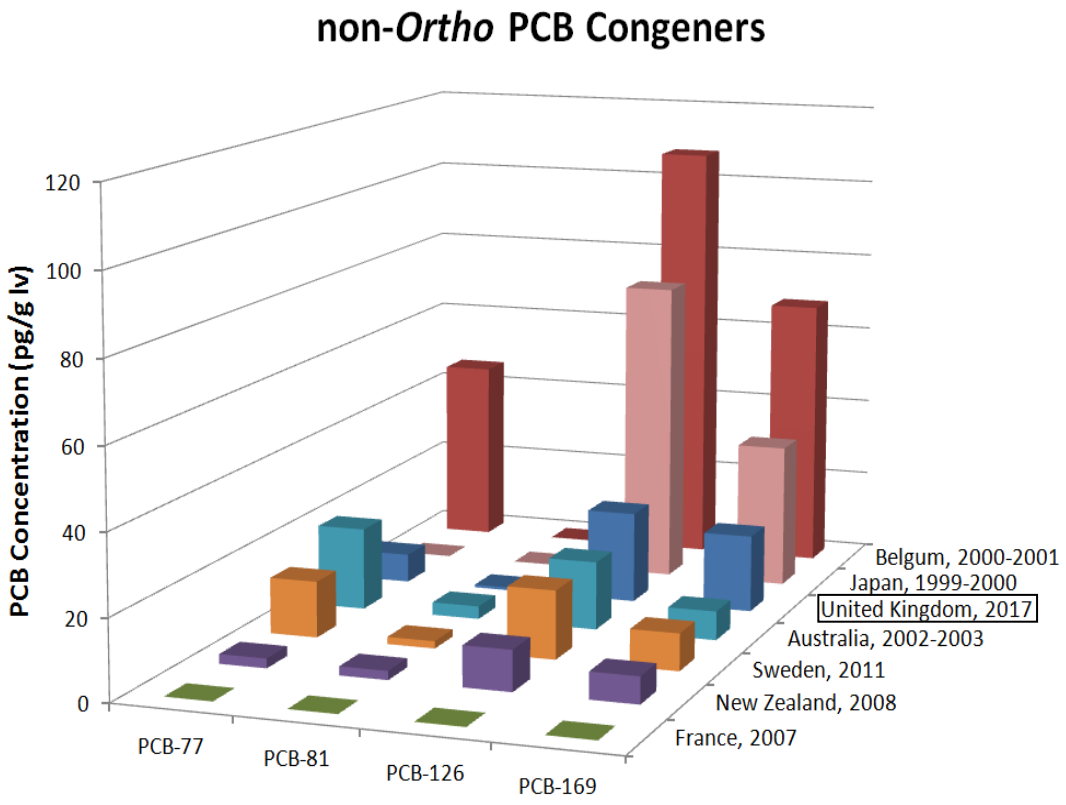


Figure 4.3: Global breast milk non-Ortho PCB congener profile data of Primipara and non-Primipara mothers. Data was adapted from: Focant et al. 2002 (Belgum, 2001), Guan et al. 2006 (Japan, 1999-2000), Focant et al.2013 (France, 2007), Harden et al. 2007 (Australia, 2002-2003), Mannetje et al. 2013 (New Zealand, 2008) and Fång et al. 2013 (Sweden, 2011). Values taken from Harden et al. 2007 (Australia, 2002-3) are weighted means and Focant 2002 (Belgum, 2000-2001) samples originate from a potentially highly exposed population sub-set.

Table 4.7: Concentrations of target PBDD/Fs (pg g^{-1} lw) in analysed human milk samples.

	Milk 01	Milk 02	Milk 03	Milk 05	Milk 06	Milk 07	Milk 08	Milk 09	Milk 10	Milk 11
Dioxins										
2,3,7,8-TBDD	<0.46	<0.23	<0.32	<0.38	<0.28	<0.31	<0.23	<0.45	<0.35	<0.39
1,2,3,7,8-PeBDD	<0.25	<0.13	<0.17	**0.69**	<0.16	**0.79**	<0.12	<0.25	<0.19	<0.21
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD [a]	<0.88	<0.44	<0.61	<0.72	<0.54	<0.60	<0.43	<0.86	<0.66	<0.73
1,2,3,7,8,9-HxBDD	<0.93	<0.47	<0.639	<0.76	<0.57	<0.63	<0.45	<0.91	<0.70	<0.77
1,2,3,4,6,7,8-HpBDD	<1.44	<0.72	<0.987	**9.53**	<0.88	<0.88	<0.97	<0.70	<1.40	<1.08
OBDD	<6.41	<3.20	**15.74***	**43.06***	<3.93	<3.93	<4.34	<3.13	<6.25	<4.81
Furans										
2,4,6,8-TBDF	<0.19	<0.09	**2.1**	**0.45**	**0.91**	**2.36**	**0.31**	**1.57**	**0.69**	<0.16
2,3,7,8-TBDF	**1.11**	<0.07	**0.9**	**0.65**	<0.09	<0.10	**0.49**	<0.14	<0.11	**1.69**
1,2,3,7,8-PeBDF	**8.88**	<0.34	<0.46	**1.13**	**4.29**	<0.46	<0.33	<0.66	<0.51	<0.56
2,3,4,7,8-PeBDF	**3.43**	<0.32	**3.61**	**2.86**	<0.39	<0.43	**1.63**	**2.37**	**1.99**	**1.89**
1,2,3,4,7,8-HxBDF	<1.27	<0.63	<0.87	<1.03	<0.78	<0.86	<0.62	<1.24	<0.95	<1.06
1,2,3,4,6,7,8-HpBDF	<0.83	<0.42	<0.57	**3.82**	<0.51	<0.56	<0.41	<0.81	<0.62	<0.69
OBDF	<7.55	<3.78	<5.19	**8.89***	<4.63	<5.12	<3.69	<7.36	<5.66	<6.28
$\sum PBDD_{2,3,7,8}$	<MDL	<MDL	15.74	53.28	<MDL	0.79	<MDL	<MDL	<MDL	<MDL
$\sum PBDF_{2,3,7,8}$	13.42	<MDL	4.51	17.35	4.29	<MDL	2.12	2.37	1.99	3.58
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$	13.42	<MDL	6.61	17.80	5.2	2.36	2.43	3.94	2.68	3.58
$\sum PBDD/F_{2,3,7,8}$	13.42	<MDL	20.25	71.08	4.29	0.79	2.12	2.37	1.99	3.58
WHO98-TEQ PBDD/F (Lb)	2.27	--	1.90	2.38	0.21	0.79	0.86	1.19	1.00	1.11
WHO98-TEQ PBDD/F (Ub)	3.32	0.71	2.64	3.01	1.06	1.57	1.39	2.25	1.82	2.01
WHO05-TEQ PBDD/F (Lb)	1.41	--	1.18	1.80	0.13	0.79	0.54	0.71	0.60	0.74
WHO05-TEQ PBDD/F (Ub)	2.46	0.64	1.91	2.42	0.90	1.48	1.06	1.77	1.41	1.63

[a] Chromatographic co-elution.

All reported mean and sum values correspond to lower bound values unless otherwise indicated.

< i indicates quantification below method detection limits (MDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of MDL derivation

Table 4.8: Summary Statistics of PBDD/Fs analysed in breast milk samples (pg g^{-1} lw).

	Occurrence (%,(n))	Mean	σ	Median	Min	Max
Dioxins						
2,3,7,8-TBDD	n.d	--	--	--	--	--
1,2,3,7,8-PeBDD	20 (2)	0.74	0.07	0.74	0.69	0.79
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD[a-]	n.d	--	--	--	--	--
1,2,3,7,8,9-HxBDD	n.d	--	--	--	--	--
1,2,3,4,6,7,8-HpBDD	10 (1)	9.53	--	--	--	--
OBDD	20 (2)	29.40	19.32	29.40	15.74	43.06
Furans						
2,4,6,8-TBDF[b]	70 (7)	1.20	0.82	0.91	0.31	2.36
2,3,7,8-TBDF	50 (5)	0.97	0.47	0.90	0.49	1.69
1,2,3,7,8-PeBDF	30 (3)	4.77	3.90	4.29	1.13	8.88
2,3,4,7,8-PeBDF	70 (7)	2.54	0.78	2.37	1.63	3.61
1,2,3,4,7,8-HxBDF	n.d	--	--	--	--	--
1,2,3,4,6,7,8-HpBDF	10 (1)	3.82*	--	--	--	--
OBDF	10 (1)	8.89*	--	--	--	--
$\sum PBDD_{2,3,7,8}$	30 (3)	23.27	27.04	15.74	0.79	53.28
$\sum PBDF_{2,3,7,8}$	80 (8)	6.20	5.84	3.94	1.99	17.35
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$	90 (9)	6.45	5.48	3.94	2.36	17.80
$\sum PBDD/F_{2,3,7,8}$	90 (9)	13.32	22.61	3.58	0.79	71.08
WHO98-TEQ PBDD/F (Lb)		1.30	0.73	1.11	0.21	2.38
WHO98-TEQ PBDD/F (Ub)		1.98	0.84	1.91	0.71	3.32
WHO05-TEQ PBDD/F (Lb)		0.88	0.50	0.74	0.13	1.80
WHO05-TEQ PBDD/F (Ub)		1.57	0.60	1.55	0.64	2.46

[a] Chromatographic co-elution.

*Values represent single occurrence in the data set.

n.d represents congeners not detected in the data set.

All reported mean and sum values correspond to lower bound values unless otherwise indicated.

< i indicates quantification below method detection limits (MDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of MDL derivation

4.6 PBDD/Fs in UK human milk samples.

4.6.1 Analytical Considerations.

The analysis of PBDD/Fs is notoriously difficult [53,73]. Extensive wet chemical clean up and purification is necessary to remove interfering matrix constituents, standards and extracts must be protected from light as much as is feasible due to photolytic instability while high thermal lability during chromatographic separation requires the use of short, thin film chromatographic columns and finely tuned injection and elution temperatures. The principal challenge however, is to ensure the removal and or control of isobaric interferences which arise from the use of EI+ ionisation, principally from M+ PBDE ions present containing one or two additional bromines than the PBDF congener monitored for. These interfering PBDE ions are not as yet mass resolvable on current commercially available MS platforms and therefore their presence in samples injected for PBDD/F analysis must be limited or removed by wet-chemical separation prior to MS injection (See Section 2.4.6). Low analyte concentrations, lack of available reference and analytical standards further complicate analysis efforts, especially in cases involving complex matrices, such as biological materials and sediments. In order to control for such interferences Hagberg in 2009 proposed a criteria for PBDD/F mass spectrometric conformation based on work from Donnelly et al., 1987 (See section 2.6.2 for further detail). In short, confirmation of PBDD/Fs requires 5 prerequisites, 3 of which are a general requirement of MS confirmation: (1) correct native analyte retention time (within ± 1 sec of internal standard), (2) recovery of internally labelled compounds to within 50-120% and (3) isotopic ratio between the selected quantification and qualification ion to be within ± 15% of theoretical values. Additional requirements for PBDD/F confirmation proposed by Donnelly et al. include: (a) all m/z monitored for a given analyte including quantification and qualification native PBDD/F peaks must elute within ± 1 sec and (b) when monitoring for PBDFs one must demonstrate the presence of at least one additional qualification ion: either $[PBDF\text{-}COBr^{\bullet}]^{+}$ or $[PBDF\text{-}2Br]^{+\bullet}$. For the purposes of this investigation we propose two additional criteria: (c) for HxBDF

and higher brominated congeners the $[PBDF^{+}- 4Br]^{+\bullet}$ should also be present at 15- 20% abundance of the M+ ion and (d) that the base peak of PBDF congeners to be confirmed must be baseline separated from any interfering $[PBDE-2Br]^{-}$ ions analysed under identical chromatographic conditions. For comparison (d) the Wellington Labs analytical calibration standard BFR-CS3, containing 41 native PBDE congeners of differing environmental relevance was used.

4.6.2 Concentrations of PBDD/Fs in UK human milk samples.

In total 11 milk samples were analysed for 2,3,7,8-PBDD/Fs. Recoveries of $^{13}C_{12}$ labelled standards were observed in all cases at between 40-120 %, with the exception of sample Milk 04 which suffered from analytical errors and showed a complete absence of labelled PBDD/Fs. This sample was subsequently removed and is not referred to further in this section

Only PBDD/F concentration data that has passed the selection criteria outlined in 2.6.2 are reported in this section and are displayed in Tables 4.7 and 4.8. This is with the exception of OBDD and OBDF observed in 2 samples, where recoveries were 40 % for each compound, below the stated requisite 50% value and are therefore indicated as such.

2,3,7,8-PBDD/F congeners were observed in 8 of the 10 samples analysed at concentrations exceeding the MDL. Furans dominated congener profiles with quantifiable concentrations in 8 of the 10 samples analysed with a mean sum concentration of 6.20± 5.84 pg g^{-1} lw (Lb mean ± 1SD). Dioxin congeners were identified in only 3 samples yet yielded a mean (Lb) sum concentration of 23.27± 27.04 pg g^{-1} lw, attributed almost entirely to the elevated concentrations of higher brominated species present in only 2 samples ([OBDD] Milk 03 = 15.74 pg g^{-1} lw; [OBDD] Milk 05 = 43.06 pg g^{-1} lw; [1,2,3,4,6,7,8-HpBDD] Milk 05 = 9.53 pg g^{-1} lw). 2,3,7,8-PBDD/F lower bound sum mean concentrations and standard deviations for those congeners detected in more than one sample in order of detection frequency observed are as follows: 2,3,4,7,8-PeBDF (n=7; 2.54± 0.78 pg g^{-1} lw) >

2,3,7,8-TBDF (n=5; 0.97± 0.47 pg g^{-1} lw) > 1,2,3,7,8-PeBDF (n=3; 4.77± 3.90 pg g^{-1} lw) > OBDD (n=2; 29.40± 19.32 pg g^{-1} lw). Interestingly, 2,4,6,8-TBDF was detected in 7 of the 10 samples analysed at a mean concentration of 1.20± 0.82 pg g^{-1} lw despite this compound's reduced tendency to bioaccumulate relative to its 2,3,7,8 conjugated counterparts [51]. A sum mean concentration order of: OBDD > 1,2,3,4,6,7,8-HpBDD > OBDF > 1,2,3,7,8-PeBDF > 1,2,3,4,6,7,8-HpBDF > 2,3,4,7,8-PeBDF > 2,3,7,8-TBDF > 1,2,3,7,8-PeBDD was observed for those 2,3,7,8 congeners quantified. 2,3,7,8-TBDD, HxBDD, and 1,2,3,4,7,8-HxBDF were not observed in any sample analysed above MDL. OBDD, and OBDF to the best of the author's knowledge has not previously been quantified in human biological matrices and despite recoveries below the 50% recovery condition were presented here. WHO 1998 and WHO 2005 PCDD/F TEF values were used to convert sum mean PBDD/F concentrations to TEQ as has become somewhat standard practice (Pratt et al. 2013, Bramwell et al. 2017) and yielded 1.30± 0.73 pg TEQ g^{-1} lw and 0.88± 0.50 pg TEQ g^{-1} lw (lower bound) respectively across the entire data set.

4.6.3 PBDD/F exposure source attribution and previously reported levels in human samples.

Due to the complications inherent in their analysis, very few studies have been successful in quantifying PBDD/Fs in human and other biological matrices. They were first investigated in human breast milk in a 1992 study by Wiberg et al, which was unsuccessful in quantifying PBDD/Fs from a single sample taken from Sweden, despite a high level of analytical sensitivity (LOQ ~1 ppt) and acceptable recoveries of internal standards [144]. A recent attempt to quantify PBDD/Fs in Taiwanese mother's milk (n= 25) [126] also yielded values below limits of detection and speculated that this may be due to a low environmental levels as reported in a related study of classroom and other dusts [145]. Few studies were however successful in quantifying PBDD/Fs in breast milk and in general, data reported are comparable to those observed in this study. A 2005 survey by Kotz et al. analysed pooled human breast milk from 17 countries obtained under the 3rd round of WHO-coordinated exposure studies in 2002 [146]. In that study they reported a sum mean concentration value of 0.7 pg g^{-1} lw for 2,3,7,8-TBDF over a range of <0.1- 2.7 pg g^{-1} lw. This compound was detected above LOQ in almost every sample analysed (n=17). 2,3,4,7,8-PeBDF was detected at a higher sum mean concentration of 0.23 pg g^{-1} lw (< 0.1-1.1 pg g^{-1} lw) and at lower occurrence to 2,3,7,8-TBDF. 2,3,7,8-TBDD was also reported over a range of 0.06- 0.28 pg g^{-1} lw along with 1,2,3,7,8-PeBDD from 0.14- 1.0 pg g^{-1} lw. 1,2,3,7,8-PeBDF and 1,2,3,4,7,8-HxBDF were found to be present in only 'some' of the 17 samples analysed. Hepta- and Octa- congeners were not observed above limits of detection in any sample [147]. Interestingly, Kotz et al. found no significant difference in PBDD/F contamination in participants from the USA, despite approximately 500-fold elevations PBDEs with respect to European samples, strongly suggesting that increased exposure to PBDEs does not necessarily facilitate increased PBDD/F body burdens. Pratt *et al.* 2013, in the most comprehensive survey conducted to date, analysed PBDD/Fs in Irish primipara mothers and observed similar congener profiles to those in Kotz et al. 2005 as well as to those observed in our data set, with congeners following a concentration trend of (sum mean, range in pg g^{-1} lw):

1,2,3,4,6,7,8-HpBDF (1.36, <0.22–2.12), 2,3,7,8-TBDF (0.89, 0.72–1.46), 2,3,4,7,8-PeBDF (0.77, 0.50–1.41), 1,2,3,7,8-PeBDF (0.36, 0.24–0.69), 1,2,3,4,7,8-HxBDF (0.21 <0.09–0.37) and a distinct lack of 2,3,7,8-dioxins with only 2,3,7,8-TBDD detected, at the lowest mean 2,3,7,8-PBDD/F concentration in the sample set (mean =0.09; range= 0.07- 0.17 pg g^{-1} lw) [66]. The greater occurrence of PBDFs, specifically 2,3,7,8-TBDF and 2,3,4,7,8-PeBDF, with respect to PBDDs as well as a congener profile consistent with the data generated in this study, were also previously established in Swedish human adipose tissue [99], Japanese mother's milk [148], food stuffs originating from the UK (Bramwell et al. 2017; Fernandes et al. 2018) and Ireland [150,151] further indicating that ingestion of contaminated foods may be a substantial driver of human PBDD/F contamination.

Studies where higher brominated furans were included in analyses have confirmed elevated concentrations of HpBDF in almost all cases, and across a range of different matrices [151]. This pattern is most notable in Bramwell et al. (2017) where 1,2,3,4,6,7,8-HpBDF was observed at lower bound mean concentrations approximately 35 fold higher than 2,3,4,7,8-PeBDF, the second most abundant PBDD/F congener recorded in a UK total diet study data set (Bramwell et al. 2017). This apparent positive correlation between bromination extent and concentration emphasises the importance of the inclusion of these congeners to any analysis data set for a more accurate determination of human contaminant loadings and likely indicates an underestimation of previously reported body burdens.

The contribution of PBDD/Fs to the total (chlorinated and brominated) dioxin and furan TEQ can serve as an indicator of potential health effects attributable to PBDD/F contamination and was calculated from those studies considered in this section. Kotz et al. (2005) found that when averaging lower bound TEQ_{05} values for PCDD/Fs and PBDD/Fs across pooled breast milk lipids from 17 locations, a contribution of 12% could be attributed to PBDD/F contamination. Similarly, Pratt et al. (2013) analysing Irish breast milk found that approximately 10% TEQ_{05} (Lb) could be attributed to PBDD/Fs. Both studies compare well with the mean value of 13% TEQ_{05} calculated from samples

analysed in this studay as well as those reported from Swedish adipose tissues and plasma (15% PBDD/F TEQ_{05} contribution; Ericson Jogsten et al. 2010). Interestingly, these contributions whilst being derived from a varying number of PBDD/F congeners analysed in their respective data sets, remain remarkably similar, indicating that the relevant health impact may in fact be due to only a small number of highly contributing furan congeners, in this case mostly 2,3,4,7,8- PeBDF.

Unfortunately the lack of available data prevents the assessment of meaningful temporal PBDD/F contamination trends.

4.7 PXDD/Fs in UK human milk samples.

Mixed halogenated dioxins and furans were analysed in breast milk samples and in all cases yielded values below MDLs. In all, 10 PXDD/F compounds were targeted including 6 dioxin congeners: 2-Br-7,8-CDD, 2-Br-3,7,8-CDD, 2,3-Br-7,8-CDD, 1-Br-2,3,7,8-CDD, 2-Br-2,3,7,8-CDD and 2-Br-2,6,7,8,9-CDD, and 4 furans: 2-Br-7,8-CDF, 2-Br-6,7,8-CDF, 3-Br-2,7,8-CDF and 1-Br-2,3,7,8-CDF. This set of target compounds was selected based on their detection in previous studies [66] and the toxicological relevance of the 2,3,7,8-PXDD/F substituted congeners. Of the target compounds analysed for 2-Br-7,8-CDD, 2-Br-3,7,8-CDD and 2-Br-6,7,8-CDF were detected sporadically in several samples (∑n= 5) at levels above instrument detection levels (ILDs, 0.05- 0.08 pg g^{-1} lw) along with comparatively high concentrations of unknown non- 2,3,7,8-Tetra and Penta substituted homologues. Accordingly the presence and ubiquity of PXDD/Fs in human breast milk samples is expected and has been confirmed previously in breast milk from Japan [148] and Ireland [66]. Our observation of the presence of non-2,3,7,8 substituted PXDD/Fs, however was not supported by the data presented in Ohta et al. 2004, where the absence of these species was specifically noted. We believe this is likely to be attributed to limitations in the mass spectrometric platform selected by Ohta et al. for quantification (specifically the use of Selected Ion Monitoring RT windows with respect to the high sensitivity Full-Scan approach utilised in this study).

In addition to the difficulties associated with PBDD/F analysis (outlined in section 1.6.1), which also hamper efforts to successfully quantify PXDD/Fs (isobaric interferences, lack of available analytical standards, Etc); PXDD/Fs have been confirmed to occur at levels approximately one order of magnitude lower than their corresponding PBDD/Fs. This is the predominant reason for the observed sparseness of data available on the prevalence of PXDD/F contamination of human and environmental matrices.

Despite these challenges, Pratt et al. in 2013 was successful in identifying and quantifying: 2-B-7,8-CDD, 2-B-3,7,8-CDD, 2,3-B-7,8-CDF and 4-B-2,3,7,8-CDF at 0.02, 0.04, 0.02 and 0.08 pg g^{-1} lw respectively in breast milk from Irish mothers. These data currently stand as the most comprehensive data set available in the literature. In a 2005 study Kotz et al. were unable to detect tetra- or penta- substituted congeners from a set of pooled samples originating from 17 different countries [147] although only these 2 congeners were analysed for. Reported limits of detection in the Pratt et al. study for those congeners quantified ranged from 0.01– 0.04 pg g^{-1} lw, approximately 1 order of magnitude below those MDLs observed in our data set for the same target congeners (MDLs 0.1 – 0.28 pg g^{-1} lw). The increased limits of quantification observed in our analysis are attributable to the decreased sensitivity of the GC-Q Exactive analysis platform with respect to the magnetic sector instrument employed in the Pratt et al. study, as well as the limited availability of breast milk sample for extraction in our study. Limits of detection were further elevated in our case as analysis on the GC-Q Exactive was exclusively performed in Full-Scan Mode, as opposed to the use of Selective Ion Monitoring. The former provided for the simultaneous detection and analysis of those other compound groups reported throughout this chapter with a consequential reduction in sensitivity A more targeted MS analysis approach and further optimisation of the wet-chemical clean up procedure would have most likely yielded quantifiable PXDD/F data for the samples analysed here.

4.8 Estimation of infant daily contaminant intake.

Breast milk has long been regarded as a direct transfer medium for contaminant exposure to infants. Tao et al. in 2017 calculated the dietary intake (DI) of contaminants present in UK mothers' breast milk utilising USEPA (2002) guidelines and estimations of daily lipid consumption for a 1 month old infant weighing 4.14 kg [19]. Estimated dietary intake was calculated here as a function of the concentration of contaminant present and estimated lipid intake on an infant per kg body weight basis following Eq. 4.1:

Eq. 4.1: $$\boldsymbol{DI} \cong \frac{\boldsymbol{C_i \times F_{Lipid}}}{\boldsymbol{BW_{Infant}}}$$

Where: DI is the approximate Dietary Contaminant Intake (ng or pg kg^{-1} BW day^{-1}); C_i is the concentration of the target contaminant present (ng or pg g^{-1} liquid weight); F_{Lipid} refers to the infant daily lipid intake derived from the USEPA, 2002 guideline value of 702 mL of milk for a 1 month old infant weighing 4.14 kg (BW_{Infant}). Calculations were performed based on individual measured sample % lipid concentrations and not mean values thereof.

Infant contaminant dietary intake estimations (DI) for target PBDEs, NBFRs, PCDD/Fs with PCBs and PBDD/Fs are displayed in tables 4.9- 4.12 respectively. Mean, Median, Minimum and Maximum values presented in tables refer to DIs corresponding to target compound concentrations quantified above individual MDLs as well as those not detected above MDL. Compounds not detected above MDL, were assumed to be present at 50% of their respective MDL concentrations and are hereafter referred to as Middle bound (Mb). Ub and Lb Mean values refer to DI estimations calculated on quantified target compound data where concentrations below MDLs were assumed at MDL and 0 respectively.

4.8.1 Estimation of UK infant daily PBDE intake.

PBDE DIs were estimated for all 37 target PBDE congeners with Middle, Upper and Lower bound Mean congener values displayed in Table 4.9. A PBDE ∑Mean (Mb) PBDE uptake of 35.88 (3.59-108.04) ng kg^{-1} BW day^{-1} was calculated from the sum of mean DIs derived from each of the 11 individual breast milk samples analysed. This value appears consistent with previous reported estimations of 36.70 and 38.65 ng kg^{-1} BW day^{-1} from UK breast milk sampled in Birmingham in 2010 and 2014-2015 respectively [19,27], however only accounts for 6 of the 37 PBDE congeners reported here.

To account for the contribution of additional congeners analysed in this study, composite congener group Means were also calculated (Table 4.9). A Mb $\sum_{Tri\text{-}Hexa}$BDE value of 28.77 ng kg^{-1} BW day^{-1} was observed in our data set which represents 80% of the total PBDE contamination uptake estimated, a comparative reduction of 18% from measurements taken in 2010 (34.9 ng kg^{-1} BW day^{-1} ;Abdallah and Harrad 2014) and 25% from estimations reported in the Tao et al. data set of 2014-2015 (38.0 ng kg^{-1} BW day^{-1} ;Tao et al. 2017). Bramwell in 2014 reported composite PBDE DIs for BDEs -47, -99 and -153 sampled in 2012 and estimated a sum uptake value of 27 ng kg^{-1} BW day^{-1} for those congeners, a value that is also significantly elevated with respect to our value of 16.8 ng kg^{-1} BW day^{-1} for the same congeners.

Despite the apparent reduction in $\sum_{Tri\text{-}Hexa}$BDE DIs, UK infants nevertheless remain more exposed to these compounds than do infants from other European nations. Median$\sum_{Tri\text{-}Hexa}$BDE DIs based on breast milk PBDE concentrations from Belgium [20], France (Antignac et al. 2009 in Roosens et al. 2010), Spain (Gómara et al. 2007 in Roosens et al. 2010) and Sweden (Lignell et al. 2009 in Roosens et al. 2010) all show median DI values below 15 ng kg^{-1} BW day^{-1}, approximately 1/3 of the DIs estimated from our data set (22.33 ng kg^{-1} BW day^{-1}), with US infants being exposed at levels approximately 10-fold higher than those observed here (mean $\sum_{Tri\text{-}Hexa}$BDE DI= 225± 27.4 ng kg^{-1} BW day^{-1}; Guo et al. 2016).

The BDE-209 mean (Mb) DI estimate of 1.549 ng kg^{-1} BW day^{-1} from our data set agreed reasonably well with the previously established UK intakes of 1.8 ng kg^{-1} BW day^{-1} from 2010 [27], 3 ng kg^{-1} BW day^{-1} from 2012 (Bramwell et al. 2014) and 0.65 ng kg^{-1} BW day^{-1} from milk sampled in 2014 [19] with the 3-fold increase observed in our data with respect to those in Tao expected to be contributed to analytical and statistical uncertainty, namely instrument insensitivity and low sample numbers.

DIs derived from BDE -47, -99, -100, -153 and -209 in this study were compared against USEPA corresponding chronic oral reference doses (RfDs) of 100, 100, 2000, 200 and 7000 ng kg^{-1} BW day^{-1} respectively. In all cases data obtained by analysis were observed to be well below reference doses, with the maximum recorded DI estimate in our data set observed at 16.89 ng kg^{-1} BW day^{-1} for BDE-99 [29]. Uptake levels, particularly those observed here for $\sum_{Tri\text{-}Hexa}$BDE (Mb Median= 28.77 ng kg^{-1} BW day^{-1}) are approximately equal to those associated with congenital cryptorchidism in Danish-Finnish newborn males [155], irregular menstruation cycles in the Taiwanese population (Chao et al. 2010) as well as other associated birth irregularities (Chao et al. 2007) despite being below reported reference doses.

4.8.2 Estimation of UK infant daily NBFR intake.

Sum (Mb) mean intake estimates of 0.044, 0.055 and 0.197 ng kg^{-1} BW day^{-1} were calculated for PBEB, HBB and BB-153 respectively, representing the 3 target NBFR compounds quantified in this study. These values compare well with previous UK breast milk concentration data obtained in 2011-2012 (Bramwell et al. 2014). To the best of our knowledge, no other further data on UK infant exposure to these compounds has been reported to date. Trends and international comparisons therefore need to be conducted on established lipid weight concentrations and will reflect those outlined in section 4.4.

Table 4.9: Breast-fed Infant PBDE dietary intake estimations of target compounds (ng kg^{-1} BW day^{-1}).

	Mean	Median	Min	Max	Ub Mean	Lb Mean
BDE-7	0.120	0.009	0.006	1.175	0.125	0.113
BDE-10	0.212	0.006	0.004	1.657	0.216	0.209
BDE-15	0.601	0.484	0.002	2.046	0.602	0.600
BDE-17	0.006	0.007	0.005	0.007	0.012	0.000
BDE-28	1.225	0.869	0.111	3.159	1.225	1.225
BDE-30	0.055	0.005	0.003	0.254	0.058	0.053
BDE-47	6.480	6.493	0.059	11.898	6.480	6.480
BDE-49	0.714	0.581	0.010	2.020	0.717	0.710
BDE-66	0.400	0.015	0.010	3.116	0.409	0.390
BDE-71	0.387	0.188	0.005	2.473	0.389	0.386
BDE-77	0.024	0.007	0.005	0.094	0.028	0.019
BDE-85	0.362	0.039	0.015	1.543	0.372	0.353
BDE-99	5.631	2.598	0.013	16.825	5.632	5.630
BDE-100	3.944	3.783	0.019	10.695	3.946	3.942
BDE-119	0.221	0.105	0.025	0.729	0.226	0.217
BDE-126	0.035	0.014	0.004	0.193	0.044	0.025
BDE-154+169[a]	3.787	3.194	1.188	8.174	3.787	3.787
BDE-153	4.868	4.169	1.128	15.509	4.868	4.868
BDE-139	0.015	0.010	0.006	0.029	0.021	0.009
BDE-140	0.235	0.127	0.010	0.646	0.238	0.232
BDE-138	0.311	0.118	0.007	1.932	0.314	0.308
BDE-156	0.074	0.014	0.009	0.590	0.083	0.063
BDE-171	0.028	0.020	0.007	0.080	0.029	0.027
BDE-180	0.028	0.022	0.009	0.099	0.031	0.026
BDE-183	0.167	0.109	0.026	0.500	0.167	0.166
BDE-184	0.019	0.013	0.005	0.085	0.021	0.016
BDE-191	0.027	0.022	0.001	0.113	0.028	0.026
BDE-196	0.556	0.161	0.013	2.753	0.557	0.555
BDE-203	0.268	0.192	0.018	0.877	0.272	0.265
BDE-204	0.148	0.122	0.015	0.552	0.152	0.143
BDE-205	0.076	0.027	0.018	0.396	0.092	0.056
BDE-206	0.660	0.466	0.150	2.820	0.660	0.660
BDE-207	1.825	0.964	0.319	7.412	1.825	1.825
BDE-208	0.824	0.469	0.128	2.213	0.824	0.824
BDE-209	1.549	0.768	0.232	5.372	1.549	1.549
∑PBDE	35.88	26.19	3.59	108.04	36.00	35.76
$\sum PBDE_{tri\text{-}hexa}$	28.77	22.33	2.63	79.89	28.85	28.70
$\sum PBDE_{(b)}$	25.79	20.86	2.43	66.66	25.80	25.77
$\sum PBDE_{(c)}$	24.88	20.35	2.43	63.60	24.88	24.87
$\sum PBDE_{(d)}$	16.98	13.26	1.20	44.23	16.98	16.98

[a] Chromatographic co-elution.[b] Sum of BDE-47, -49, -85, -99, -100, -153, -154 and -169.[c] Sum of BDE-47, -99, -100, -153, -154, -169 and -183.[d] Sum of BDE-47, -99 and -153.

Mean, Median, Min and Max values and composites refer DI estimations where target concentrations <MDL are assumed to be present at 50% MDL.

Table 4.10: Breast-fed Infant NBFR dietary intake estimations of target compounds (ng kg^{-1} BW day^{-1}).

	Mean	Median	Min	Max	Ub Mean	Lb Mean
PBEB	0.044	0.030	0.002	0.116	0.045	0.044
HBB	0.055	0.002	0.001	0.293	0.056	0.054
BB-153	0.197	0.183	0.000	0.488	0.197	0.197

Table 4.11: Breast-fed Infant PCDD/F and PCB dietary intake estimations of target compounds (pg kg^{-1} BW day^{-1}).

	Mean	Median	Min	Max	Ub Mean	Lb Mean
Dioxins						
2,3,7,8-TCDD	0.76	0.47	0.08	2.11	0.79	0.72
1,2,3,7,8-PeCDD	5.54	5.53	1.32	8.66	5.54	5.54
1,2,3,4,7,8+1,2,3,6,7,8-HxCDD[a-]	7.13	5.45	0.89	22.31	7.40	6.86
1,2,3,7,8,9-HxCDD	0.79	0.49	0.31	3.82	1.20	0.38
1,2,3,4,6,7,8-HpCDD	19.51	15.52	3.54	43.53	19.51	19.51
OCDD	115.64	100.44	69.77	223.43	115.64	115.64
Furans						
2,3,7,8-TCDF	0.34	0.29	0.10	0.84	0.40	0.29
1,2,3,7,8-PeCDF	0.16	0.17	0.11	0.18	0.33	0.00
2,3,4,7,8-PeCDF	21.95	23.70	7.86	51.48	21.95	21.95
1,2,3,4,7,8+1,2,3,6,7,8-HxCDF[a]	2.33	0.43	0.28	14.50	2.57	2.09
2,3,4,6,7,8-HxCDF	0.24	0.26	0.17	0.28	0.49	0.00
1,2,3,7,8,9-HxCDF	0.20	0.21	0.14	0.23	0.40	0.00
1,2,3,4,6,7,8-HpCDF	0.46	0.11	0.07	3.65	0.55	0.36
1,2,3,4,7,8,9-HpCDF	0.15	0.16	0.10	0.17	0.30	0.00
OCDF	0.03	0.04	0.02	0.04	0.07	0.00
Non-ortho PCBs						
PCB-77	28.62	12.72	0.27	130.86	28.65	28.59
PCB-81	2.74	2.30	0.25	6.24	2.77	2.72
PCB-126	98.06	68.96	26.59	215.04	98.06	98.06
PCB-169	83.46	55.93	20.98	260.62	83.46	83.46
$\sum PCDD_{2,3,7,8}$	149.37	127.88	75.92	303.85	150.08	148.66
$\sum PCDF_{2,3,7,8}$	25.87	25.36	8.86	71.35	27.04	24.70
$\sum PCDD/F_{2,3,7,8}$	175.24	153.24	84.78	375.20	177.12	173.36
$\sum PCBs_{non\text{-}ortho}$	212.88	139.90	48.09	612.77	212.94	212.83
WHO05-TEQ PCDD/F	14.22	14.00	5.46	25.25	14.41	14.03
WHO05-TEQ PCB	12.32	8.57	3.63	28.53	12.32	12.32
∑WHO05-TEQ	26.54	23.95	9.16	53.78	26.73	26.35

[a] Chromatographic co-elution.

Table 4.12: Infant PBDD/F dietary intake estimations of target compounds (pg kg^{-1} BW day^{-1}) and Sum TEQ Values (pg TEQ kg^{-1} BW day^{-1}).

	Mean	Median	Min	Max	Ub Mean	Lb Mean
Dioxins						
2,3,7,8-TBDD	0.71	0.75	0.49	0.81	1.42	0.00
1,2,3,7,8-PeBDD	0.78	0.42	0.27	2.89	1.27	0.66
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD[a-]	1.36	1.44	0.94	1.54	2.72	0.00
1,2,3,7,8,9-HxBDD	1.43	1.51	0.99	1.62	2.86	0.00
1,2,3,4,6,7,8-HpBDD*	5.96	2.34	1.53	39.95	7.93	3.99
OBDD	33.44	10.43	6.83	180.49	41.14	25.75
Furans						
2,4,6,8-TBDF[b]	3.86	2.45	0.21	11.13	3.95	3.78
2,3,7,8-TBDF	2.07	1.19	0.16	6.49	2.18	1.96
1,2,3,7,8-PeBDF	6.70	1.10	0.72	31.02	7.28	5.90
2,3,4,7,8-PeBDF	7.53	7.56	0.69	17.65	7.80	7.26
1,2,3,4,7,8-HxBDF	1.95	2.06	1.35	2.22	3.91	0.00
1,2,3,4,6,7,8-HpBDF*	2.74	1.35	0.89	16.01	3.88	1.60
OBDF*	14.07	12.29	8.05	37.26	24.41	3.73
$\sum PBDD_{2,3,7,8}$	43.69	16.88	11.05	227.30	57.34	30.40
$\sum PBDF_{2,3,7,8}$	35.07	25.56	11.85	110.66	49.46	20.44
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$	38.93	28.01	12.05	121.79	53.41	24.22
$\sum PBDD/F_{2,3,7,8}$	78.75	42.44	22.90	337.96	106.80	50.85
WHO05-TEQ PBDD/F	4.74	4.25	1.39	8.84	6.56	3.28
WHO05-TEQ DFs[c]	18.96	20.38	9.85	26.64	20.97	17.32
WHO05-TEQ[d]	31.28	27.09	13.54	55.17	33.29	29.64
PBDD/F (% -TEQ)	15.15	15.68	10.27	16.02	19.71	11.07

[a] Chromatographic co-elution.
[b] Value not included in TEQ calculations.
[c] DFs refers to all target 2,3,7,8-dioxin and furans quantified in the data set (Cl and Br- analogues).
[d] Value refers to sum TEQ from all 2,3,7,8-dioxins, furans and PCBs quantified in the data set.
*Values represent single positive quantification in the data set.

4.8.3 Estimation of UK infant daily Dioxin, Furan and PCB intake from human milk

The use of toxic equivalence factors (TEF_{05}) relative to the toxicity of 2,3,7,8-TCDD have been derived for 'Dioxin-Like' compounds including PCDD/Fs and certain PCBs. This has provided for the aggregation and direct comparison of negative health effects associated with the exposure of the multiple congeners across these differing compound groups through their common toxic mode of action on the Ah receptor [44]. While PBDD/Fs and PXDD/Fs have not as yet been officially included in the TEQ system, their health effects, modes of action and biological half-lives in humans has been hypothesised to be at least similar to their relevant chlorinated counterparts (Birnbaum et al. 2003). This has led to their inclusion in TEQ calculations made in the comparatively few studies focused on their occurrence in human and biological matrices [66,147,148], and accordingly have been treated as such here.

DI values were estimated for the 17 2,3,7,8-PCDD/Fs quantified in this study with a ∑PCDD/F Mb mean value of 175.24 pg kg^{-1} BW day^{-1} calculated. Over 85% of the PCDD/F DI was attributable to dioxin contamination (∑PCDD Mb Mean= 149.37 pg kg^{-1} BW day^{-1}) (Table 4.11) with OCDD contributing 66% to the ∑PCDD/F DI and accounting for 77% of the ∑PCDD DI calculated. The US Agency for Toxic Substances and Disease Registry (ATSDR) has set a revised (2018) Minimal Risk Level (MRL) for chronic oral exposure, exclusively for 2,3,7,8-TCDD at 1 pg kg^{-1} BW day^{-1} for a negative developmental endpoint [158]. Data generated in this study shows a medium bound mean DI value of 0.76 pg kg^{-1} BW day^{-1} just below the MRL value. However, this value was exceeded in 3 of the 10 individual breast milk samples analysed, in one case by over 100%. Upper, middle and lower bound mean uptake TEQ_{05} values for ∑PCDD/F were calculated at 14.41, 14.22 and 14.03 TEQ pg kg^{-1} BW day^{-1} respectively. The WHO has listed a tolerable daily intake (TDI) range of 1- 4 TEQ pg kg^{-1} BW day^{-1} for dioxins and dioxin-like compounds which our (Mb) mean value of 14.22 TEQ pg kg^{-1} BW day^{-1} substantially exceeds [44].

Four non-*Ortho* PCB DIs were calculated in this study with a (Mb) ∑PCB mean value of 212.88 pg kg^{-1} BW day^{-1} obtained. PCB-169 was identified as the highest contributor to ∑PCB contamination with a maximum mean (Mb) value of 260.62 pg kg^{-1} BW day^{-1}. The current ATSDR revised MRL for Aroclor 1254 (2018) is 0.02 µg kg^{-1} BW day^{-1} for chronic oral exposure at an immunological endpoint [158], well above all PCB DIs calculated in this study (Table 4.11). As with PCDD/Fs the WHO TDI value for dioxins and dioxin-like compounds (1- 4 TEQ pg kg^{-1} BW day^{-1}) is substantially exceeded by the (Mb) mean ∑PCB TEQ_{05} values obtained in our study (12.32 TEQ pg kg^{-1} BW day^{-1}) and more closely represents the minimum (Mb ∑PCB TEQ_{05}) value of 3.63 TEQ pg kg^{-1} BW day^{-1} estimated from our data set [44].

PBDD/F uptake values for those compounds targeted in this study were also estimated (Table 4.12). Upper, middle and lower bound mean ∑PBDD/F uptakes of 106.8, 78.75 and 50.85 pg kg^{-1} BW day^{-1} were calculated. Of note is the large difference between the upper and lower bound ∑PBDD/F values reported. This is of course, entirely attributed to elevated MDL values, for the most part derived from OBDD (MDL: 3.1- 6.4 pg g^{-1}lw) and OBDF (MDL: 3.7- 7.5 pg g^{-1}lw) which represent between 13 and 22 pg kg^{-1} BW day^{-1} additional uptake for those higher brominated congeners mentioned. In this case lower bound mean DI values may be more relevant for use in comparisons against TDI values. A Lb mean ∑PBDD/F TEQ of 3.23 TEQ pg kg^{-1} BW day^{-1} was calculated from our data and still compares with the upper range of the WHO TDI reported, with the middle bound mean ∑PBDD/F TEQ (4.74 TEQ pg kg^{-1} BW day^{-1}) and upper bound mean ∑PBDD/F TEQ (6.56 TEQ pg kg^{-1} BW day^{-1}) exceeding the WHO TDI range [44].

Sum DIs in TEQ_{05} equivalent values for Dioxins and Furans, Dioxins, Furans and PCBs (Total TEQ) were also estimated following Eq. 4.1. A total TEQ (Mb mean) of 31.28 TEQ pg kg^{-1} BW day^{-1} was estimated across the entire data set. Dioxins and Furans (both Chlorinated and Brominated congeners) were found to contribute 18.96 TEQ pg kg^{-1} BW day^{-1} (60.0%; Mb mean) with 15.2% derived from PBDD/Fs (mb mean) to a nursing infants total TEQ DI. Analytical uncertainty, as

mentioned, necessitates the use of Lb and Ub mean values for PBDD/F DI comparisons. In this case PBDD/Fs can be observed to contribute to between 11.07 and 19.71% (Lb and Ub means respectively) of the overall TEQ observed and further highlights the need to include such congeners in future studies aiming to accurately define human contamination of dioxin and dioxin like compounds.

4.9 Conclusions.

Here we report and contrast concentrations of PBDEs, PCDD/Fs, dl-PCBs, PBDD/Fs and PXDD/Fs derived of a set of 11 human breast milk samples. These samples were extracted, purified and successfully quantified using the novel, multi-residue analytical methodology reported in Chapter 2. Concentrations of PBDEs, PCDD/Fs, dl-PCBs and PBDD/Fs observed in the data set were converted to infant daily intake values and compared against ATSDR MRLs and WHO TDIs. PBDEs showed no exceedances in these values, yet were observed at levels shown to elicit a variety of negative health outcomes. PCDD/Fs, dl-PCB and PBDD/Fs were all observed in individual samples at levels in excess of WHO TDI guidelines. Planar compound concentrations in the data set (PCDD/Fs, dl-PCBs, PBDD/Fs and PXDD/Fs) were all derived from single sample injections, significantly reducing analysis time and complexity with respect to traditional MS approaches and were shown here to provide meaningful and relevant environmental data. Accordingly, we find this method fit-for-purpose and capable of overcoming the analytical challenges impeding the analysis of trace- level contaminants in human breast milk studies.

Chapter 5 A Semi- Quantitative Analysis Method for the Determination of PBDD/Fs in Archived Samples.

Application to PM_{10} for the elucidation of PBDE and PBDD/F relationships in air sampled at Santiago City during the Santa Marta municipal waste facility fire, Chile, 2016.

5.1 Synopsis.

This chapter utilises the full scan analysis methodology for archived samples as outlined in Chapter 2, for the semi- quantification of PBDD/Fs present in samples previously analysed for a range of environmental contaminants. Pre- extracted and purified samples of atmospheric particulate matter were provided to the authors for analysis along with corresponding PBDE concentration data. These samples were collected from 4 locations Santiago City, Chile during, pre- and post- fire event at the Santa Marta municipal waste facility located approximately 20 km SW of metropolitan boundaries. PBDD/F formation from PBDE precursors is known to occur under such conditions and is of concern due to their higher relative toxicity as well as potentially increased environmental stability. Factors enhancing formation have been reported to occur during the insufficient combustion of waste items treated with PBDEs, typical of municipal fire conditions. Here we report concurrent measurements of atmospheric PBDD/Fs and PBDEs (PBDE data provided to the authors) in individual samples collected and contrast their short-term temporal trends. Air mass trajectory modelling was additionally performed and provided a reasonable explanation of the observed inter- site spatial and temporal variation.

The analytical methodology demonstrated here was found to perform well, was capable of generating both homologue group and congener specific PBDD/F concentrations. All measurements taken were observed to conform to the QA/QC guidelines stipulated in Chapter 2. Accordingly, we find this method appropriate for the analysis of 'archived' atmospheric PM_{10} sample extracts for

PBDD/Fs. Further, we provide a baseline procedure which can be retrospectively applied to a wider variety of environmental matrices and target compound groups present in previously quantified sample extracts, providing supplementary scientific insight and reducing the need for additional environmental sampling.

5.2 Introduction.

Formation pathways of PBDFs have, since 1987 been shown to occur from PBDE precursors [159]. Many formation pathways have been proposed and experimentally investigated including: *de novo* synthesis, Br_2/HBr abstraction and many others [160]. While formation is thermodynamically favoured, kinetic limitations prevent formation at STP and therefore, formation has only been observed to occur in conjunction with sufficiently energetic thermal inputs such as heat from fires, incinerators and other industrial activities [60]. Observations of these activities have yielded positive identification of PBDD/F formation from PBDEs in several cases. Notably, Du et al. 2010 found elevated concentrations of PBDD/Fs in air stack measurements from various metal smelting processes, crematoriums, and municipal and hazardous waste incinerations, each with distinguishingly different congener profiles [59]. Most alarming, however are concentrations observed in residential and municipal fire events, where concentrations at milligram levels were quantified on protective clothing worn by firefighters [62,63]. These data, coupled with the fact that PBDD/Fs were in all instances investigated not present in appreciably elevated concentrations in fire feedstock/fuel, leaves little doubt as to the de novo source of PBDD/Fs observed. Despite those findings, very little is currently known as to the extent of ambient PBDD/F contamination. Several studies have focused on quantifying members of this contaminant group in environmental and human matrices; however progress has been seriously hampered due to the complex nature of analysis, with issues arising at almost every stage of extraction, cleanup and chemical analysis (see

2.2.3). A handful of studies however, have been successful in quantifying PBDD/Fs at ambient levels and even fewer have concentrated on quantifying concomitant PBDE concentrations for comparison.

On the 18th January 2016, a fire event at a municipal landfill located just outside the metropolitan boundaries of Santiago, Chile lasted for approximately 96 hours and allowed for the opportunity for measurements of PBDD/Fs and PBDEs to be conducted in PM_{10} samples taken which were additionally analysed as part of routine air monitoring conducted by the Chilean Ministry for the Environment. This chapter is dedicated to investigating the concentrations of these compounds with the intent to not only quantify their absolute concentrations, but to investigate the effect of this fire on the congener patterns of each compound group. In addition, we examine potential correlations between these groups of compounds in particulate matter sampled within Santiago's metropolitan boundaries in an effort to assist source apportionment of PBDD/Fs in ambient matrices and enhance understanding of the relationship between these chemical groups.

5.2.1 Sample Custody.

Samples analysed in this chapter were provided by Dr. Karla Pozo, Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Czech Republic. All sampling, extraction and clean-up procedures were conducted under the auspices of Dr. Pozo and the RECETOX Trace Analytical Laboratories group. PBDE data discussed in this section was also provided by Dr. Karla Pozo and was analysed in accordance with established methodologies and appropriate QA/QC procedures under ISO/IEC 17025 laboratory accreditation. Details of these procedures as well as site selection, sampling particulars and the PBDD/F analysis performed by the author are summarised in the following sections.

5.3 Sampling Strategy.

A total of 10 individual PM_{10} samples were collected over 24 hour periods on quartz fibre filters using high-volume air sampling equipment stationed at each site. Sampling was conducted intermittently from the 12th January 2016 to the 31st January 2016. In all 2 samples each were collected on the 12th and 18th January from site (S1) Cerrillos and (S2) Ñuñoa on the 15th and 31st January 2016, with 3 samples each collected from sites (S3) La Pintana on the 12th, 18th and 30th January and (S4) San Bernardo on the 15th 21st and 27th of the same month (Table 5.1). The fire event took place entirely during the period of sampling within sufficient proximity as to potentially affect air quality at the sampling locations. Visual observations of air quality at the San Bernardo sampling site indicated heavy atmospheric particulate loadings as seen photographs of the vicinity taken during fire (Figure 5.2).

All samples were previously extracted and analysed for PCDD/Fs, PAHs and PBDEs by the Trace Analytical Laboratories, RECETOX, Masaryk University and were provided to the authors by Dr. Karla Pozo for PBDD/F analysis. Analysis was performed by external calibration against a calibration series of known native PBDD/F concentrations on a Thermo Scientific GC Q Exactive MS (Section 2.6.3 for details).

5.3.1 Air Mass Forward Trajectory Modelling.

Modelling of air masses originating from the site of the fire - forward in time - were calculated by the author using the NOAA Hysplit Lagrangian Model from the Reanalysis data set. This was conducted to provide an indication as to whether locations where sampling was conducted were likely to be impacted as a result of the particulate plume generated by the fire event. Figure 5.2 shows the forward trajectory results of the model as well as the location of sampling sites overlaid on the map of Santiago City. Results are for air masses leaving the site of the fire for its entire duration (96

hours), calculated hourly and displayed as 6 hour averages (a total of 16 trajectories composed of 96 hours model simulation time).

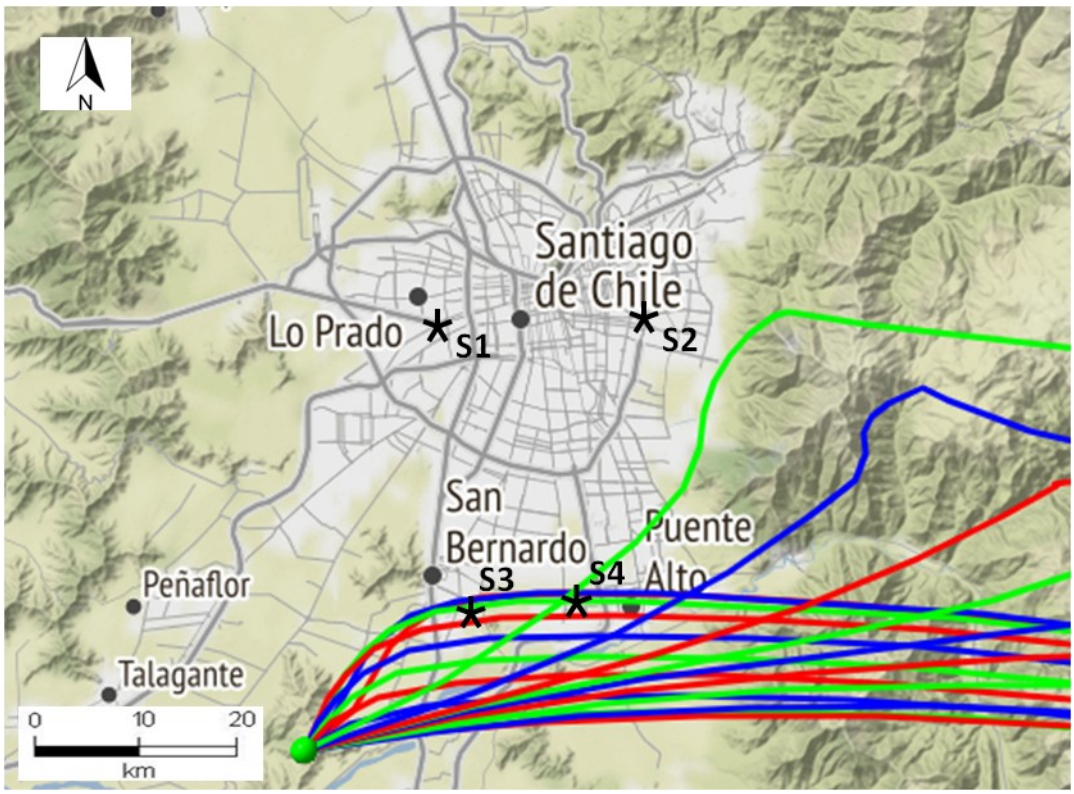


Figure 5.2: NOAA Hysplit Forward Air Mass Trajectory Model results for air masses leaving the location of the Santa Marta municipal landfill and fire site (located at trajectory convergence). Model simulation runtime encompasses the entire period of the fire event (96 hours at 6 hourly composite traces). Calculated trajectories indicate a high probability for contaminated air masses to arrive at sampling sites S3 and S4, San Bernardo and La Pintana respectively during the period of forecast. Trajectories over the same period indicate far less potential for negative air quality impacts as a result of the fire event to be present at sampling sites S1, Cerrillos and S2 Ñuñoa.

Results of the air mass trajectory simulations indicate the presence of strongly prevalent westerly winds over the entire fire event period. Wind vector quantities were not calculated in the model and therefore no information as to the wind speed or effectiveness of particulate matter entrainment was provided. However, given the high consistency of air mass trajectory, air quality is highly expected to be impacted at sampling site (S3) San Bernardo and (S4) La Pintana as a direct result of the fire event. No single simulation was calculated by which air masses moved towards the central districts of Santiago, and therefore it is expected that air quality at sampling sites (S1) Cerrillos and (S2) Ñuñoa would remain largely unaffected. It is worth noting however, that the model employed for the production of these simulations is purely advective and does not include a diffusive component for trajectory simulations. Accordingly it is expected that dispersive effects of the plume predominantly due to diffusion may exert negative air quality impacts over a larger area than indicated by the calculated trajectories displayed.

5.4 Concentrations of PBDD/Fs in PM_{10} Air Samples from Santiago, Chile.

Sample extracts post PCDD/F, PCB, and PBDE analysis, were provided to the authors by Dr. Karla Pozo, Masaryk University, Czech Republic. PBDD/Fs were semi-quantified in air sample extracts using an external calibration series on a Thermo Scientific GC Q Exactive MS. QA/QC procedures employed utilised a 1 in 3 standard to sample injection of a quality assurance standard (CIL-CS-3) mid-point calibration standard. Method accuracy determination was performed by the calculation of relative error observed between QC injections and known concentrations and yielded values within ± 10% for the majority of congeners. Details of method performance, accuracy and Limits of quantification can be found in Section 2.6.3.

Concentrations of individual 2,3,7,8-PBDD/Fs as well as homologue group, totals and TEQ concentrations observed over the period of the 12th to the 31st January 2016 across the 4 sampling sites are displayed in Table 5.1. PBDD, PBDF as well as PBDE (PBDE data provided by Karla Pozo) concentrations and congener contributions observed across the data set are shown in Figure 5.3.

5.4.1 Concentrations of ∑PBDD/Fs in PM_{10} Air Samples from Santiago, Chile.

PBDD/Fs were present in all samples with sum total concentrations ranging from 1,250 to 24 fg Nm^{-3} observed at (S3) La Pintana (18 Jan) and (S4) San Bernardo (27 Jan) respectively. Of this, 2,3,7,8-PBDD/Fs contributed 63 fg Nm^{-3} (5.0 %) equivalent to 2.0 fg TEQ_{05} Nm^{-3} (Lb) in the La Pintana sample and 0.4 fg Nm^{-3} (1.8 %; 0.004 fg TEQ_{05} Nm^{-3} (Lb)) to the sample taken at San Bernardo.

Statistically significant increases in total congener concentrations (Students' t-test, 2 sided; $p< 0.05$), specifically attributed to total PBDFs were observed during the period of the fire event at the (S3) San Bernardo and (S4) La Pintana sites. These locations showed similar concentration trends with lower levels observed before the fire event (∑PBDD/F= 120 fg Nm^{-3} San Bernardo, 15 Jan; ∑PBDD/F= 195 fg Nm^{-3} La Pintana, 12 Jan) with significant increases seen during the period of burning (∑PBDD/F= 665 fg Nm^{-3} San Bernardo, 21 Jan; ∑PBDD/F= 1,250 fg Nm^{-3} La Pintana, 18 Jan) followed by subsequent concentration reduction to values similar or lower than those observed under pre-fire atmospheric conditions (∑PBDD/F= 24 fg Nm^{-3} San Bernardo, 27 Jan; ∑PBDD/F= 177 fg Nm^{-3} La Pintana, 30 Jan). These trends represent 6.4 and 5.6 fold increases in ∑PBDD/F concentrations during the fire event with respect to those observed pre-fire for San Bernardo and La Pintana respectively and are consistent with the atmospheric air mass trajectory results presented in section 5.3.1. Also consistent with trajectory results are the ∑PBDD/F concentration trends observed at (S1) Cerrillos and (S2) Ñuñoa. Here concentrations remained relatively consistent throughout the sampling campaign. (S1) Cerrillos was sampled on the 12th and 18th of January with ∑PBDD/F concentrations of 43 and 52 fg Nm^{-3} observed respectively. This period coincided with sampling carried out at (S4) La

Pintana where significant increases were observed and therefore in the context of this study (S1) concentrations are considered at background levels. (S2) Ñuñoa on both sampling occasions (15th and 31st Jan) showed elevated ∑PBDD/F concentrations with respect to other sites sampled over this period with concentrations of 780 and 1010 fg Nm^{-3} observed respectively. Fire effects on PBDD/F concentrations were expected to be minimal at this site as air mass trajectories showed a very low probability of fire influence to air quality at this site over the sampling time frame. Further, a ∑PBDD/F concentration of 780 fg Nm^{-3} was observed prior to the fire event and suggests the influence of contamination sources other than the landfill fire.

∑PBDD/F concentrations observed in the fire affected samples, as well as background values recorded all remain well within those previously reported for samples taken in urban settings as compared with the relatively few data sets available in the literature. These are presented for comparison in Table 5.3.

Table 5.1: Concentrations of target PBDD/Fs (fg Nm^{-3}) in analysed air samples by location and date, Santa Marta fire event from: 18th to 22nd Jan 2016.

	Cerrillos (S1)		Ñuñoa (S2)		San Bernardo (S3)			La Pintana (S4)		
	12/01/16	18/01/16	15/01/16	31/01/16	15/01/16	21/01/16	27/01/16	12/01/16	18/01/16	30/01/16
Dioxins										
2,3,7,8-TBDD	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Total TBDD	<0.3	<0.3	**2.3**	**2.6**	<0.3	<0.3	<0.3	<0.3	**4.8**	**0.5**
1,2,3,7,8-PeBDD	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.1	<0.1	<0.1
Total PeBDD	<0.1	<0.1	<0.2	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD [a]	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	**0.9**	<0.3
1,2,3,7,8,9-HxBDD	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	**0.2**	**0.2**
Total HxBDD	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	**0.336***
1,2,3,4,6,7,8-HpBDD	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	**1.7**	**0.8**
Total HpBDD	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	**1.7**	**0.8**
OBDD	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	**0.8**
Furans										
2,4,6,8-TBDF	**3.2**	**4.9**	**46.1**	**78.1**	**10.1**	**12.1**	**3.7**	**12.8**	**83.1**	**10.514**
2,3,7,8-TBDF	<0.05	<0.05	<0.05	<0.05	<0.05	**4.8**	<0.05	<0.05	<0.05	<0.05
Total TBDF	**18.4**	**16.9**	**153.9**	**267.4**	**30.5**	**57.2**	**9.0**	**34.0**	**300.5**	**31.8**
1,2,3,7,8-PeBDF	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
2,3,4,7,8-PeBDF	<0.4	<0.4	**3.2**	**3.5**	**0.4**	<0.4	<0.4	**0.5**	**4.8**	**1.0**
Total PeBDF	**14.6**	**26.9**	**351.7**	**502.2**	**60.6**	**435.1**	**14.9**	**84.0**	**523.4**	**85.1**
1,2,3,4,7,8-HxBDF	<0.5	<0.5	<0.5	<0.5	<0.5	**9.7**	<0.5	<0.5	<0.5	<0.5
Total HxBDF	**8.8**	**13.5**	**215.4**	**200.7**	**25.4**	**159.7**	<0.5	**60.9**	**344.6**	**47.8**
1,2,3,4,6,7,8-HpBDF	**1.1**	**1.7**	**33.9**	**21.9**	**2.3**	**11.3**	**0.4**	**10.0**	**38.7**	**6.6**
Total HpBDF	**1.3**	**1.9**	**41.2**	**30.9**	**2.7**	**12.9**	**0.4**	**15.8**	**54.9**	**10.0**
OBDF	<5	<5	**16.6**	**7.6**	<5	<5	<5	<5	**16.2**	<5
$\sum PBDD_{2,3,7,8}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8	1.8
$\sum PBDF_{2,3,7,8}$	1.3	1.9	53.6	33.0	2.7	25.8	0.4	10.5	59.7	7.6
$\sum PBDF_{2,3,7,8 + 2,4,6,8}$	4.5	6.8	99.7	111.1	12.8	37.9	4.2	23.4	142.8	18.1

∑PBDD/F$_{2,3,7,8}$	1.3	1.9	53.6	33.0	2.7	25.8	0.4	10.5	62.5	9.4
∑PBDD	0.0	0.0	2.3	2.6	0.0	0.0	0.0	0.0	6.5	2.5
∑PBDF	42.9	58.9	778.6	1008.9	119.2	664.9	23.8	194.6	1239.5	174.6
∑PBDD/F	42.9	58.9	780.9	1011.5	119.2	664.9	23.8	194.6	1246.0	177.0
WHO05-TEQ PBDD/F (Lb)	0.0	0.0	1.3	1.3	0.1	1.6	0.0	0.3	2.0	0.4
WHO05-TEQ PBDD/F (Ub)	0.6	0.7	1.8	1.8	0.7	2.1	0.6	0.8	2.4	0.9

[a] Chromatographic co-elution.

All reported mean and sum values correspond to lower bound values unless otherwise indicated.

< i indicates quantification below sample detection limits (SDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of SDL derivation

*****Indicates quantification at the SDL

Table 5.2: Concentrations of target PBDEs (pg Nm^{-3}) in analysed air samples by location and date.

	Cerrillos (S1)		**Ñuñoa (S2)**		**San Bernardo (S3)**			**La Pintana (S4)**		
	12/01/16	18/01/16	15/01/16	31/01/16	15/01/16	21/01/16	27/01/16	12/01/16	18/01/16	30/01/16
BDE-28	0.011	0.019	0.013	0.014	0.010	0.017	0.008	0.003	0.013	0.007
BDE-47	0.560	1.173	0.249	0.286	0.198	0.240	0.154	0.079	0.223	0.126
BDE-66	0.018	0.067	0.021	0.027	0.018	0.056	0.023	0.008	0.039	0.015
BDE-85	0.010	0.015	0.009	0.014	0.008	0.023	0.014	0.004	0.010	0.009
BDE-99	0.484	0.924	0.314	0.423	0.308	1.242	0.263	0.088	0.324	0.152
BDE-100	0.094	0.191	0.061	0.078	0.047	0.142	0.039	0.022	0.069	0.044
BDE-153	0.037	0.149	0.077	0.093	0.073	2.033	0.067	0.028	0.103	0.152
BDE-154	0.039	0.100	0.060	0.085	0.073	2.105	0.073	0.023	0.075	0.061
BDE-183	0.054	0.180	0.249	0.218	0.174	3.196	0.147	0.088	0.217	0.400
BDE-209	1.446	1.900	4.357	4.487	2.605	3.954	2.719	1.435	3.551	1.866
∑PBDE$_{Tri\text{-}Hexa}$	1.253	2.638	0.804	1.019	0.735	5.858	0.640	0.255	0.855	0.568
∑PBDE$_{Tri\text{-}Hepta}$	1.307	2.818	1.052	1.238	0.908	9.054	0.788	0.343	1.072	0.968
∑PBDE	2.753	4.718	5.409	5.725	3.513	13.008	3.507	1.778	4.624	2.834

All reported mean and sum values correspond to lower bound values unless otherwise indicated.

< i indicates quantification below method detection limits (MDL, i)- See Chapter 2 Section 2.6.3.1 for detailed description of MDL derivation

Table 5.3: Levels of ∑PBDD/Fs and ∑PBDEs in air from various rural, urban and industrial environments. Both total levels and toxic equivalents (TEQ_{05}) are given for PBDD/Fs. Table adapted and expanded from [65].

	ΣPBDD/F (fg Nm^{-3})	**ΣPBDD/F (fg TEQ Nm^{-3})**	**ΣPBDE (pg Nm^{-3})**	**Reference**
Rural/Remote				
Various, China	3.4-20			Wang et al. (2008)
Råö, Sweden	7.2-690		0.49-9.8	Remberger et al. (2014)
Pallas, Finland	14-30		0.94-1.4	Remberger et al. (2014)
Guangzhou, China	57-390		110	Chen et al. (2006); Li et al. (2011)
Urban/Industrial				
Gothenburg, Sweden	2.5-86		2.9-9.2	Remberger et al. (2014)
Varoius, China	15-30			Wang et al. (2008)
Cerrillos (S1)	**43-59**	**0.63-0.65**	**2.8-4.7**	**This Study**
Sci.park, China	58-130			Wang et al. (2008)
San Bernardo (S3)**	**24-119**	**0.63-0.67**	**3.5-3.5**	**This Study**
La Pintana (S4)**	**177-195**	**0.77-0.90**	**1.8-2.8**	**This Study**
Ñuñoa (S2)	**781-1012**	**1.81-1.83**	**5.4-5.7**	**This Study**
Shanghai, China	700-1400			Li et al. (2008)
Guangzhou, China	140-1700		88	Chen et al. (2006); Li et al. (2011)
Kyoto, Japan	1800-12000		4400-80000	Hayakawa et al. (2004)
Taizhou, China	3500-81000	13-310	41-160	Zhang et al. (2012)
Guiyu, China (e-waste site)	8100-61000			Li et al. (2007)
Taizhou, China (e-waste site)	37000-155000	96-690	160-540	Zhang et al. (2012)
Guangzhou, China (industrial site)	420-4200		230-3700	Chen et al. (2006); Li et al. (2011)
San Bernardo (S3)*	**665**	**2.14**	**13.0**	**This Study**
Close to MSWI, Taiwan	420		52	M-S Wang et al. (2010)
La Pintana (S4)*	**1246**	**2.44**	**4.6**	**This Study**
Close to BFR- fac. Japan	10000-1000000			Tadami et al. (2008)
Air, e-waste dismantling hall	2400000		510 000	Takigami et al. (2006)

* Refers to samples affected by the fire event, ** Refers to samples taken at fire affected sites pre-or post the fire event.

5.4.2 Concentrations and Homologue Profiles of PBDDs in PM_{10} Air Samples from Santiago, Chile.

PBDDs contributed very little to total concentrations observed across all sites and were detected in only 4 of the 10 samples analysed. ∑PBDD concentrations quantified above SDLs ranged from 6.5 fg Nm^{-3} observed in the fire affected sample collected on the 18 Jan at (S4) La Pintana to 2.3 fg Nm^{-3} at the non fire affected site (S2) Ñuñoa on the 15 Jan. Sampling at Ñuñoa showed consistent ∑PBDD concentrations with 2.6 fg Nm^{-3} observed in the 31 Jan sample. Similarly, ∑PBDD concentrations <SDLs were observed in samples taken at (S1) Cerrillos under pre-fire conditions as well as during the landfill fire.

∑PBDDs were not observed in sampling conducted at (S4) La Pintana pre-fire. However, they did rise in concert with the arrival of the combustion plume from <SDLs on the 12 Jan to the highest recorded ∑PBDD concentration of 6.5 fg Nm^{-3} (18 Jan) before reducing to 2.5 fg Nm^{-3} over the 30 Jan collection period. This pattern was not however, reflected in samples taken at (S3) San Bernardo, where despite significant increases in ∑PBDFs over the fire period, ∑PBDDs remained below SLDs in all samples. Conclusions pertaining to the causation of ∑PBDD concentrations at sampling sites in this study are not feasible due to the low number of samples taken and the variance of concentrations observed. The reduced concentrations of PBDDs in air samples with respect to PBDFs is consistent with virtually all data sets reported in the literature [161–163], has been estimated from *in-silico* and other theoretical studies of formation of PBDD/Fs from PBDEs [60] and has also been established from studies investigating PBDD/F contamination in stack flue gases from MSWIs [100] and controlled fire simulations (Zhang et al. 2016).

Of the samples in which dioxins were detected, the contribution of 2,3,7,8-substituted congeners was varied (Figure 5.5, 5.6). 2,3,7,8-PBDDs at (S4) La Pintana contributed 42 % during the fire event (sample collected over 18 Jan) and 73 % (30 Jan, post-fire) to the ∑PBDD concentrations equivalent to 0.2 and 1.0 % of ∑PBDD/Fs respectively. The 18 Jan sample was composed principally of

1,2,3,4,7,8-, 1,2,3,6,7,8- and 1,2,3,7,8,9- HxBDDs at 0.6 fg Nm^{-3} (co-eluted 1,2,3,4,7,8- + 1,2,3,6,7,8-HxBDD), 0.2 fg Nm^{-3} 1,2,3,7,8,9- HxBDD and 1.7 fg Nm^{-3} 1,2,3,4,6,7,8- HpBDD. The sample collected on 30 Jan also revealed the presence of exclusively higher brominated 2,3,7,8- species and was composed of 0.2 fg Nm^{-3} 1,2,3,7,8,9- HxBDD, 0.8 fg Nm^{-3} 1,2,3,4,6,7,8- HpBDD with an additional contribution of 0.843 fg Nm^{-3} OBDD, consistent with congener patterns observed in other studies, where homologue patterns of 2,3,7,8- PBDDs tended, when present, to consist of higher brominated congeners - specifically hexa, hepta and octa congeners (Gullett et al. 2010). Non 2,3,7,8-substituted congener contributions in the (S4) La Pintana samples were exclusively derived from TBDDs with 4.8 and 0.490 fg Nm^{-3} observed on the 18^{th} and 30^{th} Jan respectively. 2,3,7,8- PBDD profiles were vastly different from those observed at (S2) Ñuñoa where 2,3,7,8- substituted PBDDs were not observed >SDLs in both samples. Non-2,3,7,8- TBDD isomers however contributed to the entirety of the PBDD congener profile, with 2.3 and 2.6 fg Nm^{-3} observed on 15 and 31 Jan at this site respectively (Figures: 5.3 and 5.4).

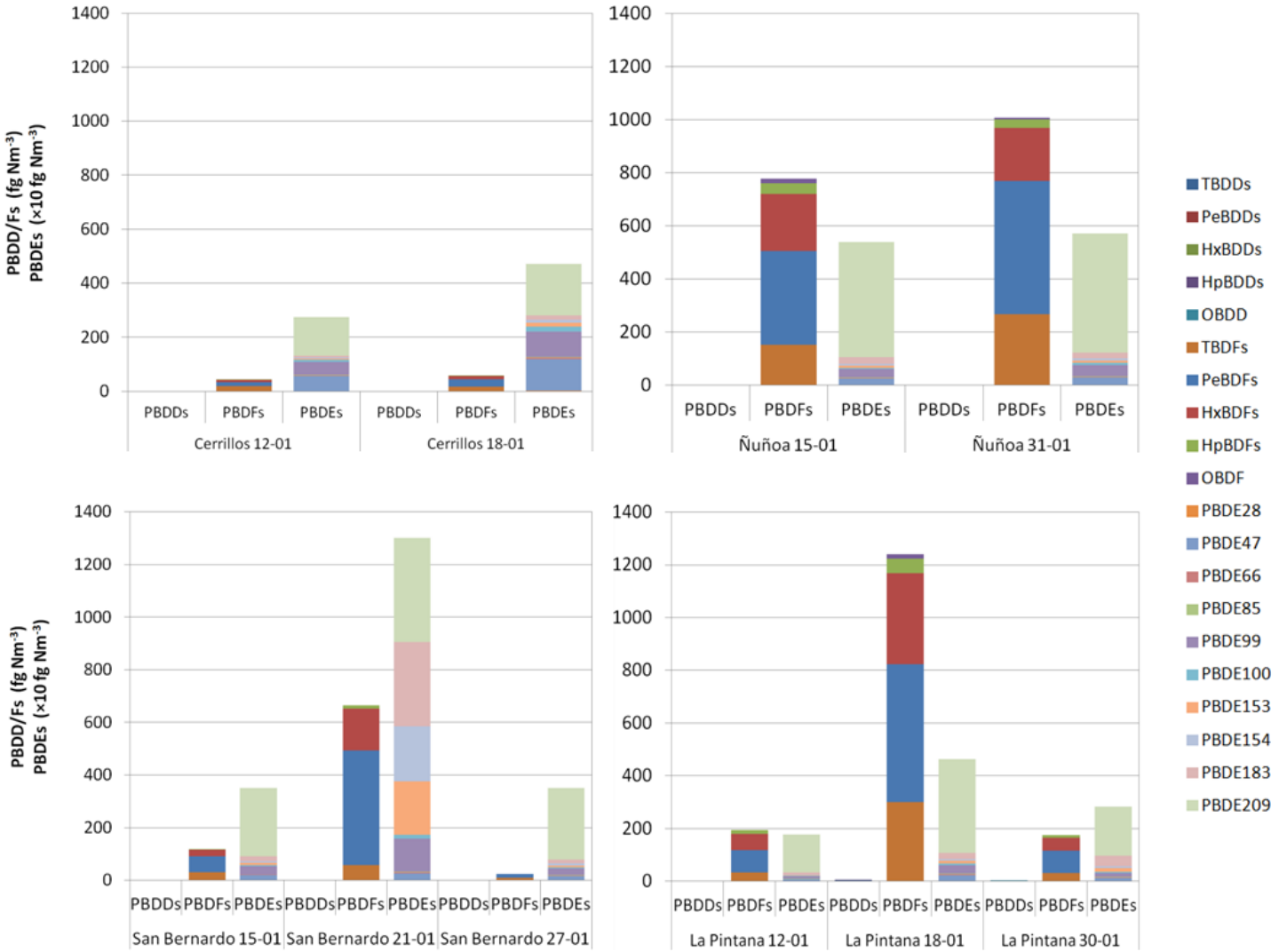


Figure 5.3: Concentrations of PBDD/F homologue groups and individual PBDE congeners in air samples taken over Santiago, Chile by site and sampling period in January 2016. PBDD/Fs on y-axis are in fg Nm^{-3} and PBDEs at ×10 fg Nm^{-3}.

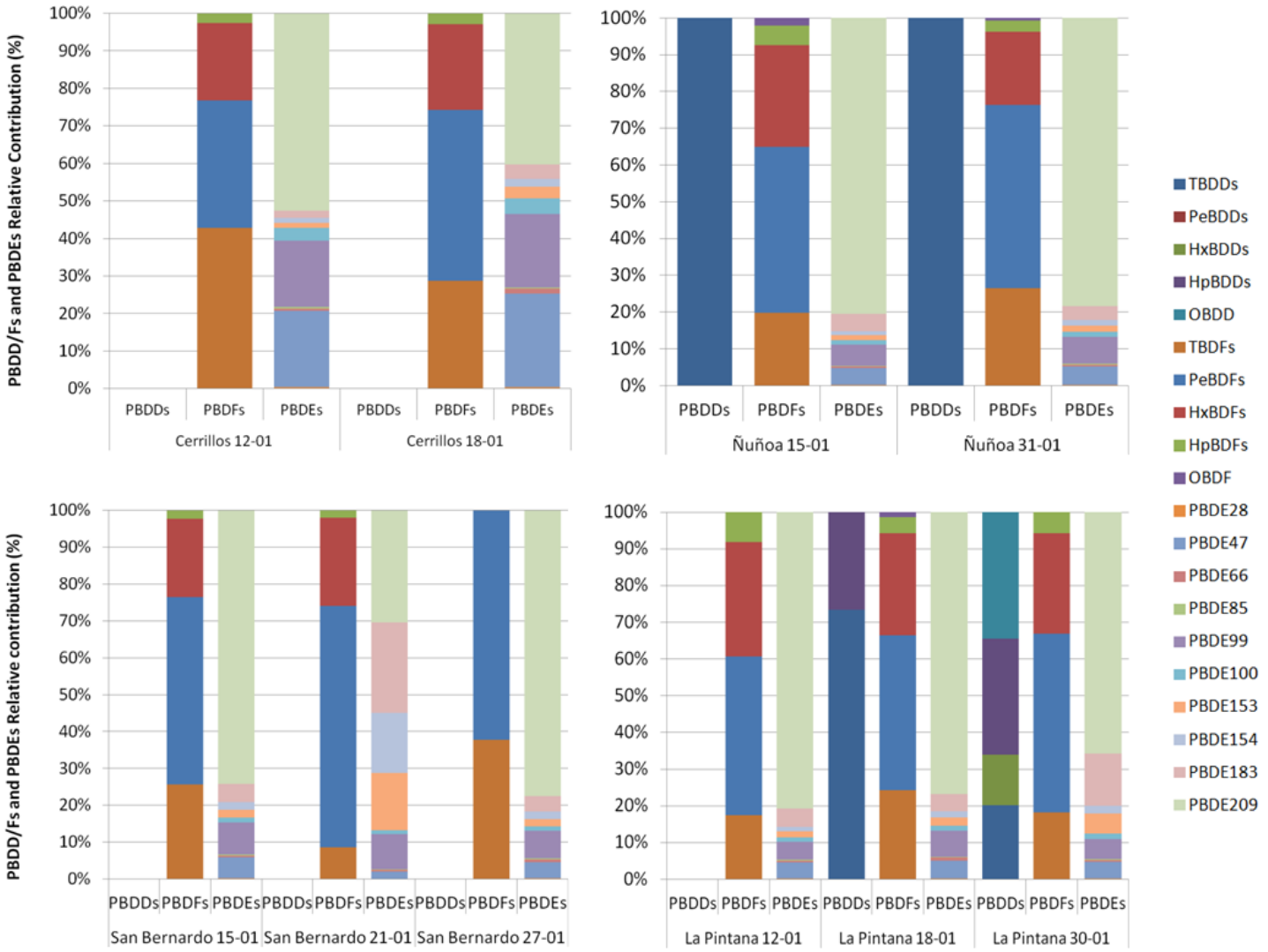


Figure 5.4: Relative total homologue contributions to ΣPBDD/Fs and ΣPBDEs in air samples taken over Santiago, Chile by site and sampling period in January 2016.

5.4.3 Concentrations of PBDFs in PM_{10} Air Samples from Santiago, Chile.

PBDF congeners dominated concentration profiles at all sites sampled. ∑PBDF concentrations were highest in samples affected by the fire with the exception of consistently elevated concentrations at (S2) Ñuñoa (Fig. 5.2, 5.3). ∑PBDF concentrations at (S3) San Bernardo increased from 119.2 fg Nm^{-3} in the sample taken on the 15th Jan to 664.9 fg Nm^{-3} during the fire event as sampled over the 21st before reducing to 23.8 fg Nm^{-3} in samples taken on the 27th Jan. A similar trend was observed at (S4) La Pintana with ∑PBDF concentrations recorded at 194.6 fg Nm^{-3} pre-fire (12 Jan) with an increase to 1239.5 fg Nm^{-3} during the fire event (18 Jan). A reduction in concentrations was also observed post-fire at this site to a ∑PBDF concentration of 174.6 fg Nm^{-3} in the 30th January sample.

∑PBDF concentrations at Site (S1) Cerrillos remained relatively consistent over the sampling period with concentrations of 42.9 and 58.9 fg Nm^{-3} observed over the 12th and 18th Jan respectively, the latter within the temporal frame of the fire event. This suggests, as mentioned in section 5.4.1 that air sampled at this location was essentially unaffected by the fire event and concentrations at this location are assumed to be reflective of background conditions. Concentrations of ∑PBDF at site (S2) Ñuñoa also remained relatively consistent across the sampling period, with respect to those sites directly impacted by the fire event, with ∑PBDF concentrations of 778.6 and 1008.9 fg Nm^{-3} recorded over the sampling periods of the 15th and 31st Jan respectively. These concentrations appear as indicated in section 5.4.1 to be influenced by sources other than the landfill fire.

PBDF concentrations present in samples taken at (S1) Cerrillos as well as those unaffected by the fire at (S3) San Bernardo and (S4) La Pintana all remain well within concentrations previously observed in the small number of studies published to date and are comparative with concentrations observed in Swedish background air samples (∑PBDF= 100 – 500 fg Nm^{-3}; Råö, Sweden; Remberger et al. 2014) as well as those sampled at some urban sites including a science park in Hsinchu, China (∑PBDF= 24.9-85.3 fg Nm^{-3}; Wang et al. 2008). Sites affected by the fire as well as ∑PBDF concentrations observed at (S2) Ñuñoa are more reflective of higher urban concentrations such as those observed in

Guangzhou (∑PBDF= ~555- 896 fg Nm^{-3}, Li et al. 2008) and Shanghai, China (∑PBDF= ~652- 1235 fg Nm^{-3}, Li et al. 2011).

5.4.4 Homologue Profiles of PBDFs in PM_{10} Air Samples from Santiago, Chile.

PeBDFs in all cases were the highest contributing homologue group quantified with the exception of the sample taken at (S1) Cerrillos on the 12th Jan in which the dominate homologue group were the TBDFs observed at 42.6 % (18.4 fg Nm^{-3}) with respect to PeBDFs at 33.9 % (14.6 fg Nm^{-3}). PeBDFs ranged from 49.0- 49.7%, 50.1- 65.4% and 42.0- 48.1% at sites S2, S3, S4 respectively showing remarkable consistency across the sampling period and with respect to changes in ∑PBDD/F concentrations. The highest ∑PeBDF concentration recorded was at (S4) La Pintana in the fire affected sample of the 18th Jan at 523.4 fg Nm^{-3} representing a homologue contribution of 42.0%, the lowest contribution observed across the sampling period at this site. PeBDF homologue trends at (S3) San Bernardo, conversely were highest during the fire event with 435.1 fg Nm^{-3} observed at a 65.4 % contribution to total PBDD/Fs. HxBDF congeners were observed to be the second most dominant homologue group in fire affected samples contributing 24.0 % (159.7 fg Nm^{-3}) to the (S3) San Bernardo 21 Jan sample and 27.7 % (344.8 fg Nm^{-3}) at (S4) La Pintana on the 18 Jan. HxBDFs were also the second most prevalent homologue group in the pre-fire sample taken at (S4) La Pintana 12 Jan contributing 31.3 % (60.89 fg Nm^{-3}) and at (S2) Ñuñoa on the 15 Jan with 27.6% (215.4 fg Nm^{-3}). In all other samples TBDFs were second most prominent homologue present, with the exception of the background concentration observed at (S1) Cerrillos on the 12 Jan where TBDFs were the dominant congener group contributing 42.6 % at a concentration of just 18.374 fg Nm^{-3} to the total PBDD/Fs quantified. HpBDFs were represented in homologue profiles across sampling sites and times ranging from 8.1- 1.7 % contributions and were also not observed to be correlated with the temporal time frame of the fire event in those samples affected. Trends and relative contributions of homologue groups with comparison to those of PBDEs are displayed in Figure 5.4.

Our observations of PeBDF homologue dominance in the majority of samples taken in this study is in contrast to the majority of the limited number of data sets in literature where homologue profiles of PBDD/F have been reported. Studies of homologue profiles in urban or background ambient air from various countries (Taizhou, China; Zhang et al. 2012), (Sweden; Remberger et al. 2014), at sites affected by industrial activities [59] including electronic waste handling (Li et al. 2007) as well as in controlled residential burning scenarios [62] almost always observe TBDF homologue dominance, in some cases contributing up to 80 % total homologue fraction [59]. An explanation of TBDF formation propensity was postulated by Söderström and Marklund in 1999 in which they propose a statistical preference towards lower brominated congener formation based on the number of possible isomers [109]. Accordingly, it is possible that Mono- and Di- substituted congener groups are substantially represented in our data set; however, they were not analysed here. Also conceivable, is that the MS analysis procedure utilised in this study was capable of quantifying a larger number of non- 2,3,7,8 congeners as was previously possible with traditional HRMS approaches. This is primarily due to the advantage of the full m/z range scanning capability of the GC Q Exactive HRMS, not previously employed for PBDD/F quantification in previous studies. This capability allows for all congeners targeted to be quantified at all retention times in the sample and is not limited by the use of specified m/z RT windows as is required with traditional HRMS approaches, and may have provided a more realistic representation of actual homologue profiles than those previously reported from 2,3,7,8- targeted analysis alone.

There are however, some recorded exceptions to TBDF homologue dominance observed in the literature that have also observed elevated PeBDF and HxBDF homologue contributions. Du et al. 2010 studied PBDD/Fs concentrations in flue gas emissions from a variety of industrial processes, including metal smelters, municipal and hazardous waste incinerators, crematoria as well as ambient air from a single background location. In all cases TBDF homologue dominance was reported, with a mean contribution of 72 % from the 10 sites investigated, with the notable exception of emissions from hazardous waste incinerators, where PeBDFs were the dominant homologue sampled. Further,

in all cases in that study HxBDFs were shown to be highly represented, accounting for up to 60 % of the total tetra- to Hexa- PBDFs observed at sites involved with sintering and the use of electronic arc furnaces for metal refinement [59]. This exception was also reflected in the only study to date of PBDD/F emissions factors for the uncontrolled burning of municipal waste, conducted by Gullett et al. across 2 sites in Mexico. Here 1,2,3,4,6,7,8-HpBDF was the dominant congener observed over TBDF in 5 of the 10 samples taken, in one case showing concentrations 4.5 fold higher than 2,3,7,8-TBDF. Represented also were the HxBDFs at appreciable concentrations (Gullett et al. 2010).

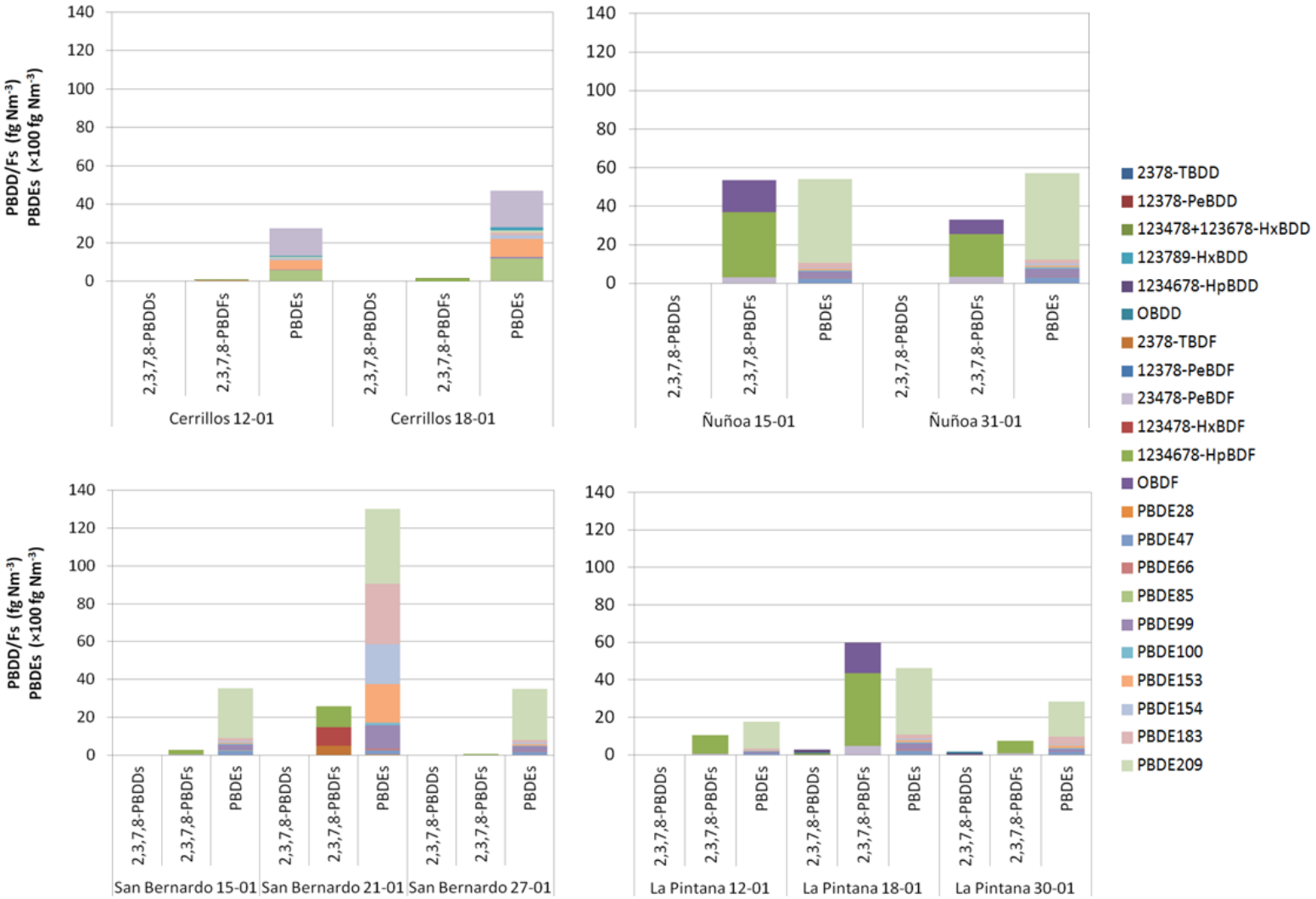


Figure 5.5: Concentration profiles of composite 2,3,7,8- PBDD/Fs and PBDEs in air samples taken over Santiago, Chile by site and sampling period in January 2016. PBDD/Fs on y-axis are in fg Nm^{-3} and PBDEs at ×100 fg Nm^{-3}.

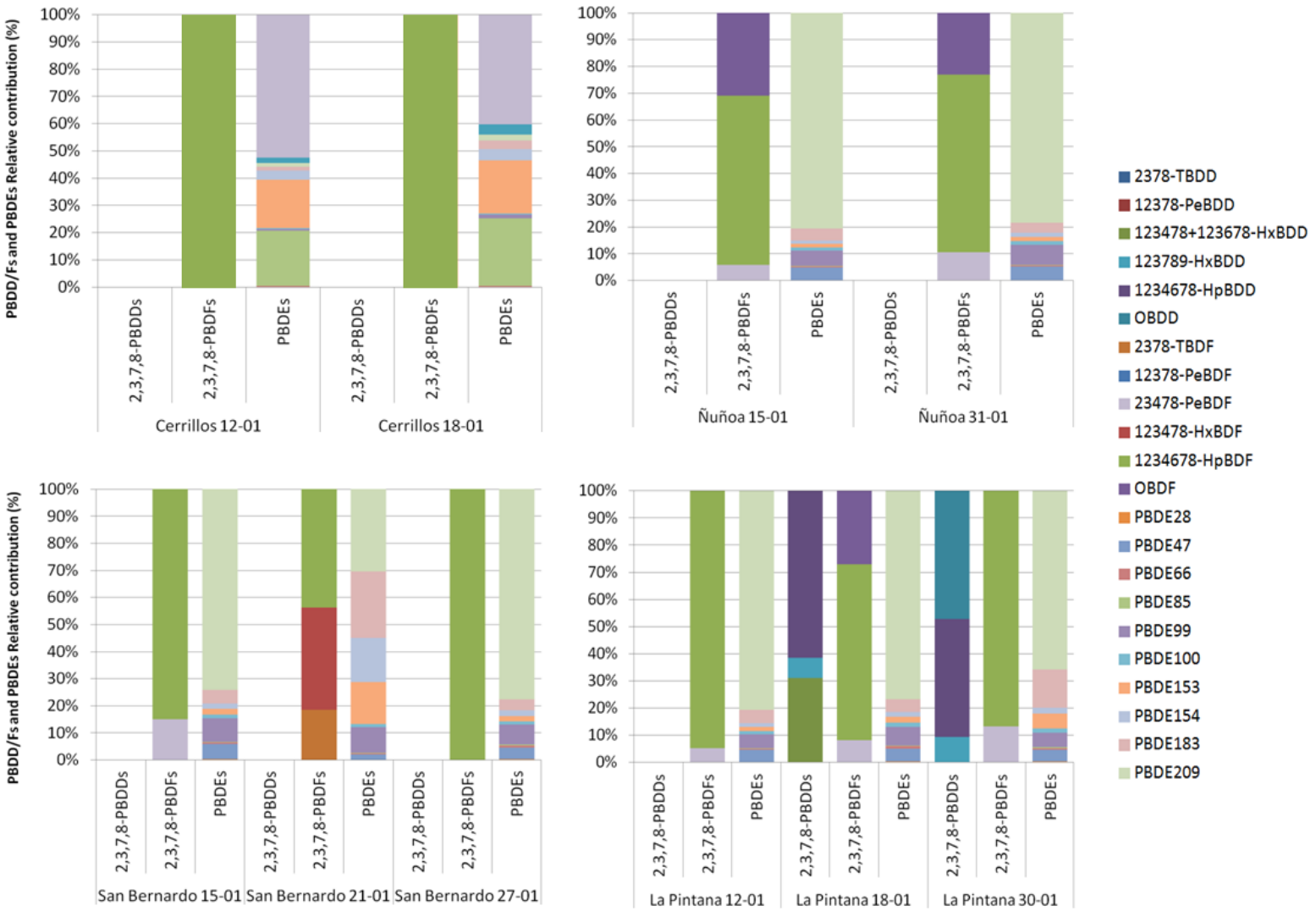


Figure 5.6: Relative contributions of individual 2,3,7,8- PBDD/Fs to Σ2,3,7,8-PBDD/F concentrations and PBDE congener profiles in air samples taken over Santiago, Chile by site and sampling period in January 2016.

5.4.5 Concentrations and Homologue Profiles of 2,3,7,8- PBDFs and 2,4,6,8- PBDF in PM_{10} Air Samples from Santiago, Chile.

Relative and total and 2,3,7,8- PBDF specific congener profiles with respect to ∑2,3,7,8- PBDD/Fs for each site are displayed in Figures 5.5 and 5.6. When compared to total homologue concentrations and profiles, contributions of 2,3,7,8- substituted congeners were low throughout the sample set. Highest contributions of 2,3,7,8- PBDFs were observed in the fire affected sample taken over the 18th Jan at (S4) La Pintana with a concentration of 59.7 fg Nm^{-3} (4.8 % of ∑PBDD/F, 95.6 % of ∑2,3,7,8- PBDD/F) representing a 5 fold increase in concentrations observed pre-fire (10.5 fg Nm^{-3}; 5.4 % of ∑PBDD/F, 100 % of ∑2,3,7,8- PBDD/F) with a subsequent reduction observed in the post-fire sample taken over the 30 Jan (7.6 fg Nm^{-3}; 4.3 % of ∑PBDD/F, 80.9 % of ∑2,3,7,8- PBDD/F). This concentration trend was also observed at (S3) San Bernardo, where maximum concentrations peaked during the fire to 25.8 fg Nm^{-3} with pre- and post- fire concentrations of 2.7 and 0.4 fg Nm^{-3} respectively. In all cases at this location 2,3,7,8- PBDDs were not present above SDLs and therefore 100 % of the ∑2,3,7,8- PBDD/F concentrations observed, were derived from 2,3,7,8- PBDFs with the maximum value of 25.8 fg Nm^{-3} representing 3.9 % of the total PBDD/Fs. The 15 Jan pre-fire sample was found to contribute 2.3 % to ∑PBDD/F concentrations with the post- fire (27 Jan) sample contributing only 1.9 %. As was reflected in the concentrations of other congeners and homologue sets, consistently elevated concentrations of ∑2,3,7,8-PBDFs with respect to other background samples were observed on both sampling occasions at (S2) Ñuñoa with a ∑2,3,7,8- PBDF concentration of 53.6 fg Nm^{-3} recorded over the 15 Jan and 33.0 fg Nm^{-3} observed over the 31 Jan. These concentrations, as were observed at (S3) San Bernardo contributed the entirety of the ∑2,3,7,8- PBDD/F concentrations and 6.8 and 3.3 % to the total PBDD/F concentrations at this site respectively. As was expected from ∑PBDD/F values, 2,3,7,8- substituted congener concentrations were lowest in samples taken at (S1) Cerrillos. Here, 2,3,7,8- PBDFs also contributed 100 % to the ∑2,3,7,8- PBDD/F concentrations observed, with ∑2,3,7,8- PBDF concentrations of 1.1 fg Nm^{-3} representing 2.6 % of the ∑PBDD/F concentration recorded on the 12 Jan and 1.7 fg Nm^{-3}

representing 2.8 % of the ∑PBDD/F concentration over the 18 Jan sampling period. Despite the reduced concentrations observed here, these % contributions to ∑PBDD/Fs were comparable with other sites where ∑2,3,7,8- PBDF contributed between 6.8 % (S2, Ñuñoa, 15 Jan) and 1.8 % (S3, San Bernardo, 27 Jan).

The highest recorded concentrations consistently observed in the data set were for 1,2,3,4,6,7,8-HpBDF which was quantified above SDL in all samples at concentrations ranging from 38.725 fg Nm^{-3} in the fire affected sample at (S4) La Pintana on the 18 Jan to 0.4 fg Nm^{-3} in the post-fire (27 Jan) (S3) San Bernardo sample (Table 5.1). Consistently elevated concentrations of 33.9 and 21.9 fg Nm^{-3} were observed at the Ñuñoa site on the 15th and 31st Jan respectively, with the reduced concentrations of this congener remaining consistent across samples from (S1) Cerrillos at 1.1 and 1.7 fg Nm^{-3} on the 12th and 18th Jan respectively. In this sample 1,2,3,4,6,7,8- HpBDF was the only 2,3,7,8- substituted congener detected on both sampling occasions. Relative contributions of this congener to ∑PBDD/F concentrations were not found to be positively correlated with the fire event, at those sites affected, with higher relative contributions observed in both pre- and post fire samples at (S4) La Pintana (5.1 % pre-fire, 3.7 % post-fire and 3.1 % during the fire event). A similar trend was observed at (S3) San Bernardo, where a pre- and post fire contributions of 1,2,3,4,6,7,8-HpBDF were higher than that observed during the fire event (1.9 % pre-fire, 1.8 % post-fire and 1.7 % during the fire event). Despite the appearance of trends, the very small contribution difference observed is likely to be below the precision of the measurements for this compound and therefore cannot be treated as an indication of an actual concentration trend.

Also somewhat prevalent across samples was the 2,3,4,7,8-PeBDF congener, which was quantified above SDLs in 6 of the 10 samples analysed. The highest concentration was observed during the fire at (S4) La Pintana on the 18 Jan with a concentration of 4.9 fg Nm^{-3} contributing just 0.4 % to the total ∑PBDD/F yet 7.8 % to the ∑2,3,7,8- PBDD/F concentration. Consistent concentrations of this congener were also observed in both samples taken at (S2) Ñuñoa with 3.2 and 3.5 fg Nm^{-3} recorded,

contributing 0.4 and 0.3 % to ∑PBDD/Fs and 5.9 and 10.7 % to ∑2,3,7,8- PBDD/Fs in samples taken over the 15th and 31st Jan respectively. This congener was detected at (S3) San Bernardo in the pre-fire 15 Jan sample exclusively at a concentration of 0.4 fg Nm^{-3} and showed a relative contribution of 0.4 % to total ∑PBDD/Fs and 14.9 % to ∑2,3,7,8- PBDD/Fs, somewhat elevated with respect to those recorded at S2 and S3. 2,3,4,7,8- PeBDF was not recorded at (S1) Cerrillos above SDLs in either of the samples quantified.

2,3,7,8-TBDF, despite being the most prevalent of PBDD/F congeners observed in other data sets (see 5.4.4) was recorded above SDL in only a single sample in our data set. A concentration of 4.8 fg Nm^{-3} was recorded in the (S3) fire affected sample at San Bernardo on the 21 Jan. This value represented a contribution of 0.7 % to the ∑PBDD/F concentration, however was observed to contribute 18.6 % to the total 2,3,7,8-PBDD/Fs quantified in this sample.

Interestingly, 2,4,6,8-TBDF was able to be quantified due to its inclusion in calibration standards used in the analysis (CIL-EDF-5407). This congener was observed in all samples at significant concentrations and was present consistently at higher concentrations than the total HpBDF homologue group in all samples with one exception, the (S3) San Bernardo fire affected sample collected over the 21 Jan. Concentrations quantified in samples are presented in Table 5.1 and ranged from 83.1 fg Nm^{-3} in the fire affected (S4) sample (La Pintana; 18 Jan) to 3.2 fg Nm^{-3} at (S1) Cerrillos on the 12 Jan, and in almost all cases was observed as the highest single congener present. Contributions of this congener to ∑PBDD/Fs ranged from 15.3- 1.82 % with both the highest and lowest contribution observed in the (S3) San Bernardo samples during the fire event on the 21 Jan and post-fire on the 27 Jan respectively. Comparison of the presence and concentrations of this congener with previously established data sets is not possible as, as mentioned the majority of studies focus analysis exclusively on 2,3,7,8-substituted PBDD/Fs. However, given the magnitude of the contribution of this congener to ∑PBDD/F concentrations its inclusion in future analysis data sets seems prudent.

Comparisons of congener profiles observed in this data set with the limited number established and presented in literature differ significantly. Previously recorded congener profiles almost always show dominance of the 2,3,7,8-TBDF congener (see 5.4.4), which are not dominant here in any case. If we exclude the presence of this congener in previous data sets the profiles observed in our study tend to agree satisfactorily with congener profiles presented in other studies for example that from the only previous study reporting PBDD/F congener profiles emitted from the burning of municipal waste under atmospheric conditions (Gullett et al. 2010). In the study by Gullett et al (2010), 1,2,3,4,6,7,8- HpBDF was consistently quantified as the dominant contributing congener present in profiles originating from 2 sites in Mexico and found to account for 44.4± 20.5 % (mean± SD) of ∑PBDD/Fs present (range= 70.5- 4.6 %, n= 8). Significantly, the Gullett et al. study was able to account for some of the variability seen in congener profiles, noting that PBDD/F formation was significantly enhanced under smouldering conditions rather than flaming combustion as was likely the case with respect to the fire event studied in our data set (Gullett et al. 2001).

The prevalence of 2,3,4,7,8-PeBDF has been previously established in a handful of previous studies, most notably in Zhang et al. 2012, where 2,3,4,7,8-PeBDF was observed as the highest contributing congener to 2,3,7,8-profiles across 6 different sites composed of 1 of each; residential, industrial, E-waste, suburban, historical E-waste and background sites. Each site was sampled on 3 occasions simultaneously, during winter and summer months. The 2,3,4,7,8-PeBDF average contribution across all sites was reported at 52± 3.7 %, however it was only present above LOQ during summer months. Our values of 5.1-14.9 % contribution for this congener, while lower than those reported in Zhang et al., still represent the second most prevalent single 2,3,7,8-substituted congener across our data set. Du et al. 2010 also noted the prevalence of the 2,3,4,7,8-PeBDF congener in stack emission samples from a municipal waste incinerator. Here a 2,3,4,7,8-PeBDF contributions of 30 % were observed with the dominant congener being 2,3,7,8-TBDF at 40 % [59]. Significantly these data contrasted with those obtained in stack emissions from a variety of other industrial activities, where 2,3,4,7,8-PeBDF was only a minor contributor to 2,3,7,8- congener profiles.

5.4.6 Concentrations and Profiles of PBDEs in PM_{10} Air Samples and Comparisons with PBDD/Fs from Santiago, Chile.

All data pertaining to PBDE were acquired by the Trace Analysis Group of the University of Masaryk, Brno, Czech Republic and provided by Dr. Karla Pozo.

PBDE concentrations, absolute and relative congener profiles are displayed in Table 5.2 and Figures 5.3- 5.6. ∑PBDE concentrations derived from a total of 10 individual congeners were quantified in identical air samples as PBDD/Fs and were observed at concentrations ranging from 13.1 pg Nm^{-3} observed during the fire event at (S3) San Bernardo (21 Jan) to 1.8 pg Nm^{-3} in the pre- fire sample at (S4) La Pintana (12 Jan). For the most part ∑PBDE concentration trends were consistent with those of ∑PBDD/Fs with increased levels obtained in fire affected samples and reduced concentrations observed in samples taken at dates preceding the fire event or after the majority of negative impacts to air quality attributed to the fire event had subsided (Table 5.2). Despite the increased levels of PBDEs observed, values during the entire sampling period remained well within values previously observed for background and urban samples taken from a variety of locations (Table 5.3), reflecting those observed at remote sites in Sweden [165] and lower than those observed at non-industrial and background sites in China (Kuo et al. 2015; Li et al. 2011). Concentrations did not in any sample exceed the ATSDR Minimal Risk Levels (MRLs) of 6.00 µg m^{-3} for inhalation of lower brominated PBDEs [158], with the highest recorded ∑PBDE level from our data set at 13.1 pg Nm^{-3} approximately 5 orders of magnitude lower than this value.

∑PBDE concentrations at (S3) San Bernardo and (S4) La Pintana increased by a factor of 3.7 and 2.6 respectively from pre-fire values to those observed during the fire event. This trend was also observed albeit to a lesser extent at (S1) Cerrillos with an increase of a factor of 1.7 (12- 18 Jan) recorded as well as at (S2) Ñuñoa (15- 31 Jan) showing a concentration factor increase of 1.1. Here concentrations remained elevated (∑PBDE range: 5.4- 5.7 pg Nm^{-3}) with respect to pre- and post- fire samples at (S3; Mean± SD ∑PBDE= 3.51± 0.01 pg Nm^{-3}) and (S4; Mean± SD ∑PBDE= 2.3± 0.8 pg Nm^{-3}).

∑PBDE concentrations were observed to correlate well with ∑PBDD/F in samples at sites which permitted the analysis (S3, S4- where n> 2) and showed significant correlations ($p< 0.05$ Pearson's, Bivariate Correlation) with sum concentrations of PBDD/Fs and PBDEs rising and falling in concert. ∑PBDD/Fs were at all times present in samples at % level concentrations with respect to ∑PBDEs and were recorded over a range of 0.7- 27.0 % ∑PBDEs, the former from the post- fire sample (27 Jan) at (S4) La Pintana and the latter from the fire affected (18 Jan) sample taken at (S3) San Bernardo. A mean ∑PBDD/F contribution of 8.8± 8.6 % (mean± SD) to ∑PBDEs was observed across the entire data set. Temporally consistent contributions were recorded at both non-fire affected sites with 1.4± 0.2 % at (S1) Cerrillos and 16.1± 2.3 % at (S2) Ñuñoa. Positive correlations between PBDD/Fs and PBDEs was also reported by Hayakawa et al. 2004 and were attributed to the formation of PBDD/Fs from PBDE during combustion or through evaporation of PBDD/F impurities in PBDEs added to commercial and household products [161].

Congener profiles of PBDEs across all samples remained relatively consistent throughout the sampling period and followed the pattern of BDE- 209 > BDE- 99 > BDE- 47 as is expected from the presence of commercial PBDE mixtures in the combustion feed stock (Gullett et al. 2010; Hayakawa et al. 2004). This profile was observed in all samples, with a notable exception in the fire affected sample at (S3) San Bernardo on the 21st January, which showed statistically significant elevated contributions of higher brominated congeners with the exception of BDE-209. In this sample alone BDE- 153, -154 and -183 were observed at (observed % vs. mean % ± SD) 15.6 vs. 3.4± 4.4 %, 16.2 vs. 3.2± 4.6 % and 24.67 vs. 7.2± 6.9 % respectively. A statistically lower contribution of BDE- 209 was observed in this sample with respect to others in the data set, with a contribution of 30.4 vs. 65.7± 18.3 % (observed % vs. mean % ± SD; Students' t-test, 1 tailed, $p< 0.05$ in all cases). The occurrence of statistically elevated higher brominated species combined with significantly decreased BDE-209 values in this fire affected sample, are consistent with the de-bromination of BDE-209. De-bromination of higher brominated BDE congeners has been previously observed in studies of PBDE congener profiles obtained during fire events. Farrar et al. in 2004 measured the concentrations and

congener contributions of PBDEs in the atmosphere of Lancaster, UK during the year 2000 “Bonfire Festival”. Congener profiles were observed to shift towards higher brominated species as air quality became impacted by the event, with elevated contributions of BDE- 99, -153, -154 observed with respect to concurrently taken background samples. Unfortunately subsequent reductions in BDE-209 was not observed as this congener was not analysed for in this study (BDEs- #> 190,not analysed for; Farrar et al. 2004). Sakai et al. 2003, determined that temperatures exceeding 900°C are required for complete de-bromination of PBDEs to occur and that temperatures below this, such as those typically observed in the burning of municipal waste (500- 700°C; Gullett et al. 2001) are likely to result in de-bromination of the less thermodynamically stable congeners, such as BDE-209 as we postulate was observed in this sample. Interestingly this was not observed in the fire affected sample taken at (S4) La Pintana site where higher brominated BDE congeners were at all times within the standard error of mean values calculated across the data set.

5.5 Conclusions.

In summary, a method based on the full-scan capability afforded on a novel MS system, the GC Q Exactive, was demonstrated for the analysis of PBDD/Fs in air samples. The method showed its suitability for use with samples which have not been extracted for or spiked with PBDD/F internal standards. Accuracy and precision monitoring across the quantification procedure yielded values sufficient to quantify and contrast both PBDD/F homologue groups as well as individual 2,3,7,8-PBDD/F congeners for comparison with potential PBDE precursor concentrations.

It has long known that PBDD/F formation from PBDEs is significantly enhanced during combustion processes however, due to the complex nature of PBDD/F analysis, especially in ambient samples; a very limited amount of literature reporting ambient PBDD/F concentrations is available, less so which contrasts concomitant PBDE concentrations. Accordingly, the method developed was applied to samples taken at several sites across Santiago, Chile during, pre- and post- a large scale fire event

at a municipal waste facility, and was able to detect differences in PBDD/F concentrations and homologue profiles at sites where air quality was and was not significantly impacted by the fire event. Consistent with the majority of previous studies, PBDD congeners were present in vastly lower concentrations with respect to PBDFs, a relationship which was also reflected in 2,3,7,8-substituted congener profiles. Homologue group sum concentrations across the majority of samples showed a pattern of PeBDF > HxBDF > TBDF > HpBDF in concentration, not often observed in literature data sets, which tend to report TBDF as the most dominant congener present. Concentrations of PBDD/Fs were in all cases within levels previously reported in urban and background samples as was found for PBDEs which were analysed externally and presented here for comparative purposes. PBDE concentrations, highest in fire affected samples were at all times well below ASTDR lowest effect levels. Congener profiles of PBDEs followed the pattern of BDE- 209 > BDE- 99 > BDE- 47 as is expected from the presence of commercial PBDE mixtures in the combustion feed stock with the suspected debromination of BDE- 209 demonstrated in a single fire affected sample. Concentrations of PBDEs were found to correlate well with concentrations of PBDD/F homologues in the samples permitting the analysis.

Accordingly, data generated in this study supplements the limited data sets available and provides a useful additional insight to the relationship between these two linked environmental contaminants. In doing so, we provide a baseline procedure which can easily be applied to a wider variety of environmental matrices and target compound groups present in previously quantified sample extracts, providing greater scientific insight and reducing the need for additional matrix sampling.

Chapter 6 Summary and Conclusions.

In this section we present summaries and major outcomes corresponding to each Chapter of this study. Important to note, this section does not provide comprehensive listing or treatment of all project findings, and therefore, the authors recommend referring to the main body of text corresponding to each of the Chapters listed below:

6.1 Summary of Chapter 1: Introduction and Aims and Objectives.

PBDD/Fs and PXDD/Fs are classes of toxic and persistent environmental contaminants. Despite never being deliberately synthesised in any great quantity, their ubiquitous presence has been confirmed across a variety of ambient matrices. While a multitude of plausible sources exist, the limited number of literature reports available indicate a strong contamination source association with PBDEs and other brominated phenolic flame retardants. For the most part, research has focused on the quantification of these compounds in flue gas emissions of thermally intensive industrial processes, as incomplete combustion in the presence of such precursors has been identified as a predominate source of PBDD/F environmental contamination. Laboratory based formation studies have additionally confirmed PBDD/F formation from PBDE precursors and have revealed that reaction conditions, rather than precursor concentrations, are the principle factors controlling levels of PBDD/F emissions. This phenomenon is particularly evident when formation occurs during ‘smouldering’ or insufficient combustion conditions, such as those likely to be observed during ambient combustion of municipal or industrial waste streams.

Despite the weight of evidence linking PBDEs and PBDD/Fs at environmental sources, a conclusive understanding of the magnitude and significance to which these compounds are associated in environmental sinks remains yet to be explored. This remains the case with respect to PXDD/Fs also,

where virtually only anecdotal contamination evidence exists. The paucity of environmental data with respect to these important contaminants can be attributed principally to the high degree of analytical complexity involved in their quantification. Low ambient concentrations, high thermal lability, a large number of relevant individual congeners and mass interferences require their analysis almost exclusively by high resolution mass spectrometry. This coupled with the high costs and scarcity of internal standard solutions has previously hampered analytical efforts.

To address this research gap, the authors took advantage of recent advances in full-ion scanning mass spectrometric analysis technology based on orbital ion trapping. This was favoured over the well established and widely used magnetic sector quantification approach as inherent limitations with respect to the number and mass range of target analyte ions simultaneously acquired would result in the necessity for multiple sample injections. This in turn would result in a compromise between the quantity of target compounds quantified and the availability of sample material for analysis, which in the case of relevant human and environmental samples is often severally limited. Analysis of trace- level environmental contaminants using the orbital ion trapping full-ion scan approach offered by the Thermo Fisher Q Exactive has recently been confirmed as a sensitive and selective alternative for compounds amenable to separation by liquid chromatography, however has not been extensively applied to contaminants such as dioxins and furans for which gas phase analytical separation is required.

Accordingly, the primary objective of this thesis was to evaluate the effectiveness and applicability of the novel Thermo Scientific Q Exactive GC instrument to conduct accurate, selective and reproducible measurements of those contaminants requiring analytical separation in the gas phase exclusively. To achieve this we developed and optimised instrumental parameters to a degree such that all native planar target compounds (PBDD/Fs, PXDD/Fs, PCDD/Fs and dl-PCBs, n= 45) and their corresponding isotopically labelled internal standards (n=32) could be suitably quantified by a single

2µL injection. Non-planar compounds in the target set (PBDEs and NBFRs, n= 39) together with their respective internal standards (n= 16) required a previously performed, thorough wet chemical separation to restrict the degree to which ion crosstalk and mass interferences between these target groups was observed- a typical stipulation almost always employed in these analyses. Accordingly these were analysed by a separate injection employing selective ion monitoring mode (SIM). SIM analysis was the preferred method of acquisition as standards employed in these analyses contained the vast majority of congeners likely present in environmental samples. Accordingly, chromatographic retention times were recorded and the increased sensitivity afforded by this acquisition mode was utilised.

6.2 Summary of Chapter 2: Development and Validation of Analytical Procedures for the Quantification of Halogenated Contaminants by HRGC/HRMS on the Thermo Scientific GC Q Exactive.

Through significant instrumental optimisation, simultaneous quantification of planar analytes was performed using full- ion scan mode on individual congeners present in compound group standards. These analyses yielded instrumental detection limits (IDLs; 1 µL injection) ranging from 0.01- 0.13 pg inj.$^{-1}$ for PBDD/Fs (excl. Octa-BDD, Octa-BDF), 0.001- 0.005 pg inj.$^{-1}$ for PXDD/Fs with PCDD/Fs and dl-PCBs observed at IDLs ranging from 0.003- 0.183 pg inj.$^{-1}$. Octa-BDD and Octa-BDF returned elevated IDLs of 0.96 and 2.26 pg inj.$^{-1}$ respectively, principally due to thermal degradation upon injection. Degradation was minimised for these compounds by employing a programmable temperature and pressure inlet operated with a moderate temperature ramp as well as suitable injection liner selection. These parameters combined to provide IDLs sufficiently low as to quantify these highly thermally labile congeners at levels relevant for environmental analysis. This optimisation represented significant analytical development, as for the reasons stated above, these congeners have remained virtually unreported in scientific literature to date. Non- planar target compounds

including PBDEs and NBFRs, analysed in SIM mode yielded IDLs ranging from 0.01- 0.60 pg inj.$^{-1}$ and were therefore deemed suitable to determination environmental concentrations. In addition to IDL measurements all target compounds measured as standards conformed to the following quality assurance criteria:

1. Calibration curve linearity of R^2 >0.999
2. Calibration curve RRF values (n= 10) to below 10 % RSD
3. Instrumental accuracy of 3.0- 22.6 % (mostly at < 10 % excluding Octa-BDF)
4. No evidence of analyte carryover as observed in sequential high-low calibration standard injections.

As such, the Thermo Fisher Scientific Q Exactive GC was deemed fit-for-purpose and appropriate wet-chemical extraction and purification based on pressurised solvent extraction and column chromatography were developed. Validation of these methods was conducted by the extraction and analysis of standard reference sediment material (SRM- 1944) and yielded mean PBDE and PCDD/F individual congener concentration values consistent with those previously reported (n= 18). Due to the novelty of this method, certified reference values for the majority of PBDEs, NBFRs as well as all analysed PBDD/Fs and PXDD/Fs have as yet not been established, and as such these data represent the first concentrations of their kind reported. To further expand the scope of this investigation, methodology developed for the quantification of these compounds in sediments was, with minimal modification, additionally applied to human breast milk. As was the case for the majority of target compounds quantified in sediments, no standard reference material or certified values have as yet been made available and therefore method trueness against certified values were not established for this matrix.

All target analytes concentrations obtained by the extraction and analysis of SRM sediment as well as human breast milk samples yielded method detection limits (MDLs) of 0.3- 76.8 ng g^{-1} dw (Exc.

BDE- 209), 0.01- 0.46 pg g^{-1} dw (Excl. Octa- BDF) and 3- 7 fg g^{-1} dw for PBDEs, PBDD/Fs and PXDD/Fs respectively. The following validation data was also observed:

1. Clean up recoveries of between 50 – 110 %
2. Method trueness (for PBDEs present in SRM) within 79- 109 % (within standard guidelines)
3. Method reproducibility (1SD of mean concentration in SRM) of < 1 order of magnitude with respect to concentration value.

Mass interferences induced by the ionisation of co-eluting compounds of similar atomic composition were controlled for by the establishment of additional quality control procedures. Traditionally, appropriate individual analyte ion ratios, retention times coupled with sufficient mass spectrometric and chromatographic separation are required for target compound conformation. The quantification of PBDFs requires an additional control as isobaric interferences with PBDE congeners remain unresolved at resolutions feasible on current analytical instrumentation. Accordingly, the observation of PBDF -$COBr^{\bullet+}$ ions, widely accepted to be exclusive to the ionisation of PBDFs, and therefore restricted for PBDEs, is currently accepted as sufficient evidence to confirm PBDF target analytes. During the course of method development undertaken in this study, we have for the first time demonstrated the presence of an unidentified PBDF mass interference derived from the ionisation of PBDEs. This interference produced by the ionisation PBDEs was observed to occur systematically over the identical accurate mass channels typically utilised for the monitoring of PBDF -$COBr^{\bullet+}$ 'confirmation' ions and therfore suggests the potential for false positive qualification of PBDFs. Utilising the full-ion scan mode afforded by analysis on the Q Exactive GC MS we subsequently proposed an alternative confirmation strategy, based on the standardisation of chromatographic conditions for both planar and non-planar sample extract fractions. By standardising retention times for all compounds across the data set, confirmation of PBDFs was only conferred to ions eluting at retention times which were baseline separated from interfering PBDE

molecular ion peaks. These were observed by external injection of PBDE standard solutions, eliminating the potential for false positive PBDF confirmation.

This study also reports on the development of an additional analytical technique for the screening of PBDD/Fs in pre-extracted atmospheric particulate matter samples. Here we describe and provide evaluative data for this method which, through the use of externalised calibration and standardisation aimed to expand the limited quantity of available PBDD/F data sets. This was achieved through the analysis of 'archived' sample extracts, originally intended to provide PCDD/F concentrations alone. Reproducibility and accuracy assessments were conducted through the multiple injection of mid- level PBDD/F calibration standards, in this case treated as 'sample unknowns' for the purpose of evaluation. Individual PBDD/F congener relative % error was used as a proxy for method accuracy. From 5 standard injections accuracy was observed to range from 1.6-21.6 % (excl. OBDF; 31.7 %) . Reproducibility, here reported as the (± 1) standard deviations of mean 'unknown' concentrations were for all congeners at least 1 order of magnitude lower than their respective mean concentration values. Overall, these evaluative data provide evidence to support the suitability of this method for the screening of PBDD/F concentrations in stored sample extracts not previously intended for this purpose and subsequently provides a simple approach to elevate the paucity of reported PBDD/F environmental levels.

6.3 Summary of Chapter 3: Concentrations, Temporal and Spatial Trends of PBDE, PBDD/F and PXDD/F Contamination in Radiometrically Dated English Fresh Water Sediments.

In application of the analytical methodology developed, sediment core samples were collected by the authors from three sites across the UK, each corresponding to varying degrees of surrounding urbanisation and industrialisation. Individual core slices were obtained and radiometrically dated to provide a temporal profile by which sedimentation year could be established and concentrations of

PBDEs, PBDD/Fs and PXDD/Fs contrasted between sites. Our principle findings, based on the UK sediment samples analysed, show:

1. Temporal concentration trends for all target analytes including PBDEs, PBDD/Fs and PXDD/Fs at 3 independent sampling locations across the UK.
2. PBDE concentrations at those environmental sinks sampled, continue to increase with respect to time, over the temporal scope of this investigation (2015- 1935) and are yet to respond significantly to legislative restrictions.
3. First reports of hepta- through nona-PBDE congener concentrations in UK sediments, showing large, contributions to ∑PBDE concentrations which likely has led to a substitutive underestimation in previously reported ∑PBDE data sets.
4. Confirmation of PBDD and PBDF contamination source independence, as evidenced by the observed lack of significant concentration relationships between these compound groups.
5. The presence of several statistically significant temporal relationships between target analyte groups (∑PBDF- ∑PBDE) as well as correlation of the 1,2,3,4,6,7,8- HpBDF with BDE-209.
6. The first quantitative report of temporal contaminant trends for PXDD/Fs reported in the scientific literature to date.
7. The presence of a significant negative relationship between PXDD/F concentrations with respect to time.
8. And the confirmation that PXDD/F trends do not present any clear statistical relationship with PBDD/Fs or PBDEs and therefore indicate the independence of PXDD/F contamination sources.

Accordingly, we were able to confirm within a reasonable degree of certainty that PBDE and PBDF source commonality, as previously reported, does extent to those environmental sinks as measured throughout this investigation and therefore we conclude that:

The increased use of BFRs <u>has</u> led to an increase in environmental contamination of PBDFs.

6.4 Summary of Chapter 4: The use of a Novel HRMS Approach to Determine Infant Dietary Intake and Exposure to Legacy and Novel Flame Retardants, dl-PCBs, Chlorinated, Brominated and Mixed Halogenated Dioxins and Furans.

This chapter aimed to successfully apply the analytical methodology developed and reported in Chapter 2, for the assessment of ultra-trace level environmental contaminants in human breast milk. This matrix was selected due to its complex nature, ease of sampling and high degree of toxicological relevance. Here, analytical methodology developed for fresh water sediments was extended to include the quantification of PBDEs, NBFRs, PBDD/Fs, PCDD/Fs, PXDD/Fs and dl-PCBs in UK human breast milk samples. Through application of these analytical protocols we have provided the most comprehensive contamination assessment conducted on UK human breast milks to date. Additionally this study has provided the following:

1. An expansion of the analytical target analyte set to include NBFRs, PCDD/Fs and dl- PCBs not quantified in sediment core samples.
2. Generation and interpretation of baseline data and for the first time confirming the PBDD/F contamination status in English mothers' milk.
3. Contrastive assessment of relative congener profiles as well as concentration data against established international data sets.
4. Contemporised previously established data sets pertaining to the contamination status of UK mothers for dl- PCBs and PCDD/Fs.
5. Extended concentration data for individual congeners as well as compound group totals to calculate daily contaminant intakes in exclusively breast fed UK infants.
6. Comparison of daily infant intake values against USEPA Chronic Oral Reference Doses (RfDs), ASTDR Minimal Risk Levels (MRLs) and WHO Tolerable Daily Intake (TDIs) values.

Concentration levels observed in our data set were not dissimilar to those previously reported in breast milk collected from other Western European nations or from previous UK studies. For

comparison, concentration data obtained was converted to infant daily uptake values and contrasted against previous UK data sets, USEPA RfDs, WHO TDIs and ASDTR MRLs. No exceedances of USEPA RfD values were observed, however, due to the limited quantity of reference doses provided, intake assessments were performed on only 5 of the 34 individual PBDE congeners quantified. PBDE intakes calculated here were in all cases also observed below both ASDTR MRLs and WHO TDIs however, were present at concentrations associated with a multitude of negative health outcomes. TDI exceedances were observed in at least 2 of the 11 samples for PCDD/F, dl-PCBs and middle and upper bound average intake TEQs of PBDD/Fs, the latter not as yet formally included in guidelines however widely considered to be at least as toxic as their chlorinated counterparts. The limited number of samples provided to the authors (n= 11) prevented an adequate assessment of compound group relationships and this was accordingly not performed.

All breast milk samples analysed here were derived from single samples consisting of less than 50 mL (whole) volumes. As with the methodology developed for sediments, samples were extracted and fractionated to planar and non-planar fractions (1 each) for analysis on the Q Exactive GC MS platform. All values reported conformed to QA/QC protocols described in Chapter 2 and provided meaningful and relevant data. Accordingly, we find this method appropriate, suitable and highly applicable for the multi-residue quantification of ultra-trace level organic contaminants in limited quantities of human breast milk.

6.5 Summary of Chapter 5: A Semi- Quantitative Analysis Method for the Determination of PBDD/Fs in Archived Samples:

Utilising the methodology developed for the analysis of pre- extracted ('archived') samples, PBDD/F concentrations were determined in atmospheric particulate matter (PM_{10}) collected at Santiago, Chile and provided to the authors. These samples, collected prior to, during as well as after an uncontrolled fire event at a municipal waste facility were of particular relevance as such conditions

have been previously shown to significantly enhance PBDD/F formation. As such, PBDD/F data generated here was derived from PM_{10} extracts taken concurrently at 4 separate locations. These data were contrasted between sites as well as between PBDE congener concentration values provided to the authors. In addition to concentration data, air mass back trajectory modelling was conducted which strongly indicated that only 2 of the 4 sites in this study were likely affected by the contaminant plume originating from the fire site located approximately 20 km from the closest sampling station.

The results of the air mass tradectory modelling indicated that 2 of the 4 sites sampled were likely affected by the contaminent plume. This was confirmed by chemical analysis of PBDD/Fs conducted here as well as the PBDE concentrations provided to the authors. PBDD/Fs were, at these sites found to increase over the temporal range of the fire event, with respect to background levels. This phemomoman was not observed at the 2 sites not indicated as affected by air mass modelling. Affected sites showed a rapid response to the cessation of the fire event, with concentrations returning to pre-fire levels within 24 hrs post-fire. Sites indicated as not affected by air mass modelling did not show dynamic concentrations of PBDD/Fs or PBDEs over the period of sampling. PBDD/F concentrations observed across all sites were consistently below ASTDR lowest observed effect levels. A summary of further findings are as follows:

1. The Q Exactive GC instrument is capable of quantifying PBDD/Fs by external calibration in prior extracted and 'archived' samples to within limits suitable for environmental assessment.
2. Air mass back trajectory modelling was capable of indicating sites affected by the contaminant plume as confirmed by analyte concentrations.
3. At those sites affected, increases in both PBDD/Fs and PBDEs were observed and shown to rapidly decline in concert with fire conditions.

4. Analysis showed a distinct lack of PBDDs consistent with theory, indicating this contaminant group is not a predominate product of the combustion of PBDE containing waste products and its presence is likely derived from alternative, as yet undefined sources.
5. Homologue concentrations reflected a consistent pattern in the 2 fire affected sites of [PeBDF] > [HxBDF] > [TBDF] > [HpBDF]- not consistent with previous data sets which tend to show TBDF concentration dominance.
6. 2,3,7,8-PBDF congeners were in all cases observed to represent a low proportion of ∑PBDFs observed, with maximum % contributions across all samples of < 3 %. These contributions were observed to be reduced in those samples affected by the fire event.
7. PBDE congener profiles followed the pattern of [BDE- 209] > [BDE- 99] > [BDE- 47] as is expected from the presence of commercial PBDE mixtures.
8. Concentrations of PBDEs were found to correlate well with concentrations of PBDF homologues in the samples permitting the analysis to be performed.

6.6 Conclusions and Future Perspectives.

This study aimed to assess the suitability of a novel mass spectrometric platform, the Thermo Scientific Q Exactive GC, to provide data adequate for the assessment of ultra-trace level environmental contaminants. In doing so we were successful in providing an instrumental benchmark performance reference as well as fully validated methodology for the extraction, purification and analysis of these compounds in three important environmental matrices: fresh water sediment cores, human breast milks and atmospheric particulate matter.

In application of these methods we were successful in evaluating the environmental dynamics of PBDD/Fs, PXDD/Fs and PBDEs and provided data yielding the following significant findings:

1. PBDE and PBDF source relationships do indeed extent to environmental sinks over the temporal and spatial range of this study.
2. PXDD/F concentrations appear to be declining at these sites, contrary to scientific theory, and by a currently unknown mechanism.
3. PBDD/Fs are present in the human breast milk of UK primipara mothers, at concentrations close to or exceeding relevant guideline values.
4. Concentrations of PBDD/Fs increase in PM_{10} samples taken at sites affected by fire events associated with the combustion of municipal waste.
5. At the point of cessation of such an event, concentrations rapidly decline to background levels.

Here we have established for the first time the suitability of the Thermo Scientific Q Exactive GC instrument to provide accurate and precise measurements of PBDD/F and PXDD/F environmental contaminants. In applying those methods to the above matrices we have outlined the significant advantages of these approaches over traditional analytical procedures by:

1. Quantifying a far larger target analyte set than previously practical
2. Utilising a reduced quantity of sample material than previously required
3. Developing a more comprehensive PBDF quality assurance and control approach than traditionally applied
4. Retaining, or in some cases enhancing method sensitivity and reproducibility with respect to traditional approaches.

In support of those methods developed over the course of this thesis, we have provided relevant and original environmental applications that have yielded significant and novel insights, all of which aim to supplement the limited PBDD/F and PXDD/F data sets currently available. In doing so, we have also afforded a basis for which these methods may be expanded and adapted to include a boarder range of target analytes present in a multitude of other relevant environmental and

biological matrices thus, providing a reduction in analytical complexity and alleviating several of the major bottle-necks constraining future investigations of this nature.

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Appendix A Report on the Radiometric Dating of Sediment Cores HOLTU3, EDGB5 and WAKE4 from England

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A.1 Rationale and methodology

Lead-210 (half-life is 22.3 year) is a naturally-produced radionuclide, derived from atmospheric fallout (termed unsupported ^{210}Pb). Cesium-137 (half-life is 30 years) and ^{241}Am are artificially produced radionuclides, introduced to the study area by atmospheric fallout from nuclear weapons testing and nuclear reactor accidents. They have been extensively used in the dating of recent sediments. Dried sediment samples from three cores HOLTU3, EDGB5 and WAKE4 were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay in the Environmental Radiometric Facility at University College London, using ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. Lead-210 was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. Cesium-137 and ^{241}Am were measured by their emissions at 662keV and 59.5keV (Appleby et al, 1986). The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy gamma rays within the sample (Appleby et al, 1992).

A.2 Results

HOLTU3 from Holt Hall

Lead-210 Activity

It appears that equilibrium of total ^{210}Pb activity with the supported ^{210}Pb occurs at around 76 cm of the core. Unsupported ^{210}Pb activities, calculated by subtracting ^{226}Ra activity (as supported ^{210}Pb) from total ^{210}Pb activity, decline overall irregularly with depth (Figure 1b). In the top 16 cm, unsupported ^{210}Pb activities increase with depth, suggesting an increase in sedimentation rates towards the sediment surface that diluted the ^{210}Pb activity. Small fluctuations in the decline of ^{210}Pb activities with depth from 16.5 cm downwards, imply smooth changes in sedimentation rates.

Artificial Fallout Radionuclides

The ^{137}Cs activity versus depth shows two well-resolved peaks at 55.5 cm and 40.5 cm of the core, respectively (Figure 1c). It is almost certain that the 55.5 cm peak was derived from the atmospheric testing of nuclear weapons with maximum fallout in 1963, while the 40.5 cm peak was from the fallout of the 1986 Chernobyl accident. There are detectable ^{241}Am points. As the activities are low and the points are separate, they are in little use for dating.

Core Chronology

Use of the CIC (constant initial concentration) model was precluded by the non-monotonic variation in unsupported ^{210}Pb activities. ^{210}Pb chronologies were calculated using the CRS (constant rate of ^{210}Pb supply) dating model (Appleby and Oldfield, 1978). The CRS dating model places the 1963 depth at c. 45.5 cm, which is not in agreement with the depth suggested by the ^{137}Cs record. Radiometric chronologies and sedimentation rates of the core were corrected using the CRS model by referring sediments at 55.5 cm as formed in 1963 suggested by the ^{137}Cs record. This ascribed the sediments at 40.5 cm to 1986, which is in agreement with the ^{137}Cs record. The calculated results were given in Table 3 and shown in Figure 2. Sedimentation rates in the core show a gradual increase from c. 0.04 g cm^{-2} yr^{-1} in the 1910s to c. 0.24 g cm^{-2} yr^{-1} in the 1980s, followed by relatively uniform rate till 2000s. There is a sharp increase in the sedimentation rate in the last few years.

EDGB5 from Edgbaston Pool

Lead-210 Activity

Total ^{210}Pb activity reaches equilibrium with the supported ^{210}Pb at a depth around 47 cm of the core. Unsupported ^{210}Pb activities in the top 25 cm decline more or less exponentially with depth, suggesting a relatively uniform sedimentation rate in this section. From 25 cm to 45 cm, the decline has a steeper gradient and the profile follows an approximately exponential relationship, with some small departures, down its rapid disappearance at 47 cm.

Artificial Fallout Radionuclides

The ^{137}Cs activity versus depth shows a well-resolved peak at 41.5 cm of the core (Figure 3c), which was derived from the maximum fallout of the atmospheric testing of nuclear weapons in 1963. In the same depth, ^{241}Am was detected, which supports the 1963 ^{137}Cs peak.

Core Chronology

Again, use of the CIC model was precluded by the small non-monotonic variation in unsupported ^{210}Pb activities. Chronologies and sedimentation rates of the core were calculated by using the CRS dating model. The simply CRS model places the 1963 at 35.5 cm, which is not in agreement with the ^{137}Cs and ^{241}Am records. The chronologies were corrected by referring sediments at 41.5 cm as formed in 1963. The results show that sedimentation rates were relatively uniform with a mean at 0.094 g cm^{-2} yr^{-1} in the last sixty years or so.

WAKE4 from Wake Valley

Lead-210 Activity

Equilibrium of total ^{210}Pb activity with the supported ^{210}Pb occurs at a depth around 70 cm of the core. The unsupported ^{210}Pb activity profile can be featured into two sections. In the top 36 cm, unsupported ^{210}Pb activities decline slowly with depth, suggesting an increase trend in sedimentation rates towards the sediment surface. From 36 cm downwards, the decline in unsupported ^{210}Pb activities has a steeper gradient, and it is more or less exponential with some departures.

Artificial Fallout Radionuclides

The ^{137}Cs activity versus depth shows a well-resolved peak at 48.5 cm of the core (Figure 5c), which was derived from maximum fallout of the atmospheric testing of nuclear weapons in 1963. There is a ^{241}Am peak at the same depth, which confirms the nuclear bomb testing fallout.

Core Chronology

The CIC model could not be used for this core due to the non-monotonic variation in unsupported ^{210}Pb activities. The CRS dating model was used for calculating chronologies and sedimentation rates of the core. The simply CRS model places the 1963 depth at 42 cm, which is not in agreement with the depth suggested by the ^{137}Cs and ^{241}Am records. Again, the final chronologies were corrected by referring sediments at 48.5 cm as formed in 1963. the chronologies and sedimentation rates were given in Table 9 and shown in Figure 6. Sedimentation rates were relatively uniform with a mean at 0.141 g cm^{-2} yr^{-1} from the 1940s to the 1990s, followed by a slow increase trend with some fluctuations.

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Table 1. ^{210}Pb concentrations in core HOLTU3 taken from Holt Hall.

Depth	Dry Mass	Pb-210						Cum Unsupported	
		Total		Supported		Unsupp		Pb-210	
cm	g cm^{-2}	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq m^{-2}	±
0.5	0.0072	100.99	27.14	76.82	7.21	24.17	28.08	1.7	1.4
8.5	0.8416	133.44	17.72	42.36	4.03	91.08	18.17	422.6	142.4
16.5	1.8506	159.71	16.9	43.55	3.59	116.16	17.28	1463	230.1
23.5	2.7048	112.07	18.36	45.4	3.95	66.67	18.78	2224.4	281.4
30.5	3.7592	100	14.25	48.22	3.5	51.78	14.67	2845.6	334.4
35.5	4.6914	93.71	12.8	49.19	3.16	44.52	13.18	3293.6	362.5
38.5	5.3402	80.32	12.98	46.25	2.94	34.07	13.31	3547	374.8
40.5	5.7727	103.89	14.38	71.47	3.63	32.42	14.83	3690.7	380.6
45.5	6.9034	77.23	13.28	50.74	3.31	26.49	13.69	4022.7	404.4
50.5	8.0359	60.58	10.56	39.98	2.45	20.6	10.84	4287.9	430.7
53.5	8.6596	60.08	11.56	37.48	2.7	22.6	11.87	4422.5	438.4
55.5	9.0754	66.19	9.41	34.09	2.07	32.1	9.63	4535.1	441.7
60.5	9.9362	52.1	9.53	38.06	2.45	14.04	9.84	4723.1	447.6
65.5	10.7037	42.24	10.46	27.84	2.38	14.4	10.73	4832.2	454.6
68.5	11.1597	44.26	8.88	32.5	2.09	11.76	9.12	4891.7	458
72.5	11.8212	47.97	10.49	29.35	2.7	18.62	10.83	4990.4	461.8
76.5	12.5378	21.35	10.05	27.16	2.33	-5.81	10.32	5036.3	467.9

Table 2. Artificial fallout radionuclide concentrations in core HOLTU3.

Depth	Cs-137		Am-241	
cm	Bq Kg^{-1}	±	Bq Kg^{-1}	±
0.5	7.91	3.99	0	0
8.5	13.79	2.32	0	0
16.5	17.84	2.42	0	0
23.5	24.25	2.76	2.95	1.38
30.5	29.38	2.3	0	0
35.5	36.04	2.4	0	0
38.5	40.2	2.28	0	0
40.5	49.98	2.68	0	0
45.5	29.19	2.26	0	0
50.5	27	1.76	0	0
53.5	28.14	1.87	0	0
55.5	32.86	1.62	0	0
60.5	24.63	1.59	1.39	0.75
65.5	8.23	1.33	0	0
68.5	4.92	1.06	1.3	0.74
72.5	0	0	0	0
76.5	0	0	0	0

Table 3. ^{210}Pb chronology of core HOLTU3 taken from a Holt Hall.

Depth	Drymass	Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	yr	±	g cm^{-2} yr^{-1}	cm yr^{-1}	± %
0	0	2015	0				
0.5	0.0072	2015	0	2	0.4	4	117
8.5	0.8416	2013	2	2	0.1977	1.716	24.6
16.5	1.8506	2006	9	2	0.1272	1.024	22.8
23.5	2.7048	2001	14	3	0.186	1.364	34.5
30.5	3.7592	1995	20	4	0.2021	1.221	36.6
35.5	4.6914	1991	24	5	0.2037	1.031	39.8
38.5	5.3402	1988	27	6	0.2431	1.124	48.7
40.5	5.7727	1986	29	7	0.174	0.778	54.9
45.5	6.9034	1979	36	7	0.1617	0.714	53.8
50.5	8.0359	1972	43	7	0.146	0.667	55.2
53.5	8.6596	1967	48	8	0.116	0.556	55.6
55.5	9.0754	1963	52	8	0.091	0.5	36
60.5	9.9362	1953	62	13	0.074	0.45	88.5
65.5	10.7037	1941	74	16	0.058	0.38	94.9
68.5	11.1597	1932	83	21	0.046	0.292	98.9
72.5	11.8212	1917	98	24	0.044	0.267	88.5

Table 4. ^{210}Pb concentrations in core EDGB5 taken from Edgbaston, England.

Depth	Dry Mass	Pb-210						Cum Unsupported	
		Total		Supported		Unsupp		Pb-210	
cm	g cm^{-2}	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq m^{-2}	±
0.5	0.0311	278.62	25.37	54.6	6.23	224.02	26.12	69.8	6.7
3.5	0.2424	249.78	16.38	45.28	3.38	204.5	16.73	522.2	43.1
6.5	0.4359	257.67	23.75	46.75	5.18	210.92	24.31	924.1	60.4
9.5	0.6556	252.29	18.87	51.4	4.29	200.89	19.35	1376.4	81.1
12.5	0.8833	224.49	16.78	52.13	3.9	172.36	17.23	1800.5	94
15.5	1.1381	201.83	18.52	50.39	4.27	151.44	19.01	2212.5	105.8
18.5	1.4575	194.95	10.92	48.49	2.39	146.46	11.18	2688.2	120.3
21.5	1.8271	183.05	15.66	35.91	3.5	147.14	16.05	3230.8	131.3
24.5	2.2215	178.63	16.88	52.25	4.03	126.38	17.35	3769.1	148.4
27.5	2.6087	189.36	10.95	57.58	2.55	131.78	11.24	4268.8	162.9
30.5	3.0543	136.64	16.71	52.39	4.02	84.25	17.19	4742.3	174.1
33.5	3.5346	143.31	9.71	47.45	2.34	95.86	9.99	5174.2	190.3
35.5	3.8765	100.3	12.88	51.82	3.48	48.48	13.34	5411.8	194.9
38.5	4.4501	115.96	14.91	43.42	3.33	72.54	15.28	5754.3	208.4
41.5	5.0984	103.78	14.21	51.37	3.3	52.41	14.59	6155.8	229.9
44.5	5.7673	102.93	13.78	47.72	3.2	55.21	14.15	6515.6	249.9
47.5	6.5309	49.42	7.92	52.84	2.12	-3.42	8.2	6713.4	267.5
51	7.4949	60.08	13.58	53.86	3.25	6.22	13.96		
55	8.5964	40.73	10.87	54.92	2.78	-14.19	11.22		

Table 5. Artificial fallout radionuclide concentrations in core EDGB5.

Depth	Cs-137		Am-241	
cm	Bq Kg^{-1}	±	Bq Kg^{-1}	±
0.5	19.43	3.63	0	0
3.5	18.03	1.91	0	0
6.5	18.09	3	0	0
9.5	22.83	2.35	0	0
12.5	25.92	2.27	0	0
15.5	27.43	2.59	0	0
18.5	41.11	1.76	0	0
21.5	55.28	2.93	0	0
24.5	45.3	2.89	0	0
27.5	60.47	2.04	1.58	0.86
30.5	67.23	3.48	0	0
33.5	76.04	2.15	0	0
35.5	85.58	3.17	0	0
38.5	92.24	3.47	0	0
41.5	108.27	3.5	3.1	1.18
44.5	52.34	2.59	0	0
47.5	22.51	1.35	0	0
51	6.92	1.73	0	0
55	4.93	1.32	0	0

Table 6. ^{210}Pb chronology of core EDGB5 taken from Edgbaston, England.

Depth	Drymass	Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	yr	±	g cm^{-2} yr^{-1}	cm yr^{-1}	± %
0	0	2015	0				
0.5	0.0311	2015	0	2	0.1057	1.527	12.8
3.5	0.2424	2013	2	2	0.1089	1.615	9.9
6.5	0.4359	2011	4	2	0.0997	1.447	12.9
9.5	0.6556	2009	6	2	0.0976	1.31	11.4
12.5	0.8833	2006	9	2	0.1061	1.32	12
15.5	1.1381	2004	11	2	0.1123	1.174	14.3
18.5	1.4575	2001	14	2	0.106	0.923	10.8
21.5	1.8271	1997	18	2	0.0941	0.739	13.7
24.5	2.2215	1993	22	2	0.0963	0.739	16.6
27.5	2.6087	1989	26	3	0.0805	0.58	13.6
30.5	3.0543	1984	31	3	0.1084	0.703	23.6
33.5	3.5346	1979	36	4	0.0813	0.494	17.5
35.5	3.8765	1976	39	4	0.1454	0.794	31.4
38.5	4.4501	1971	44	5	0.0825	0.405	27.2
41.5	5.0984	1963	52	6	0.0903	0.411	35
44.5	5.7673	1954	61	9	0.0655	0.274	38.3

Table 7. ^{210}Pb concentrations in core WAKE4 taken from Wake Valley, England.

Depth	Dry Mass	Pb-210						Cum Unsupported	
		Total		Supported		Unsupp		Pb-210	
cm	g cm^{-2}	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq m^{-2}	±
0.5	0.018	151.19	16.93	50.76	5.38	100.43	17.76	18.1	2.4
5.5	0.4782	92.77	13.18	37.03	3.8	55.74	13.72	367.4	55.9
10.5	1.2497	105.54	12.77	32.82	3.69	72.72	13.29	860	111.8
15.5	2.1255	101.01	13.13	36.55	3.8	64.46	13.67	1460	162.3
20.5	3.005	89.42	11.67	37.62	3.92	51.8	12.31	1969.3	201.9
25.5	3.8652	115.16	13.19	40.6	3.67	74.56	13.69	2506.8	231.3
30.5	4.8197	96.79	11.24	44.51	3.52	52.28	11.78	3105.9	263.7
35.5	5.7635	93.19	11.45	35.35	3.49	57.84	11.97	3625.1	287.6
40.5	6.5987	80.63	10.89	43.82	3.52	36.81	11.44	4013.7	305.9
42.5	6.9606	67.04	7.58	40.23	2.54	26.81	7.99	4127.9	310.2
45.5	7.5035	75.36	6.91	46.56	2.33	28.8	7.29	4278.8	312.7
48.5	8.1299	71.58	9.87	35.45	3.02	36.13	10.32	4481.3	316.7
50.5	8.5475	56.59	7.41	37.39	2.36	19.2	7.78	4593.1	320.1
52.5	9.0338	55.83	10.91	35.55	3.19	20.28	11.37	4689.1	322.9
55.5	9.7632	47.97	7.2	40.37	2.36	7.6	7.58	4783.3	330.2
58.5	10.6304	49.69	7.06	37.22	2.22	12.47	7.4	4868.6	336.1
61	11.353	56.97	8.32	35.46	2.66	21.51	8.73	4988.4	341.2
67	13.1548	41.89	6.81	50.79	2.04	-8.9	7.11		
73	14.4115	64.83	5.89	54.17	1.61	10.66	6.11		
79	15.6247	34.01	7.33	47.71	1.92	-13.7	7.58		

Table 8. Artificial fallout radionuclide concentrations in core WAKE4.

Depth	Cs-137		Am-241	
cm	Bq Kg^{-1}	±	Bq Kg^{-1}	±
0.5	16.55	3.24	0	0
5.5	22.5	2.47	0	0
10.5	22.97	2.49	0	0
15.5	17.18	2.28	0	0
20.5	24.44	2.56	0	0
25.5	27.31	2.55	0	0
30.5	39.3	2.63	0	0
35.5	36.71	2.63	0	0
40.5	54.79	2.78	0	0
42.5	56.84	2.18	0	0
45.5	53.62	1.84	1.24	0.67
48.5	74.41	2.99	2.37	0.96
50.5	58.81	2.03	0	0
52.5	16.76	1.98	0	0
55.5	7.07	1.12	0	0
58.5	6.05	1.12	0	0
61	0	0	0	0
67	1.23	0.76	0	0
73	0	0	0	0
79	0	0	1.21	0.72

Table 9. ^{210}Pb chronology of core WAKE4 taken from Wake Valley, England.

Depth	Drymass	Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	yr	±	g cm^{-2} yr^{-1}	cm yr^{-1}	± %
0	0	2015	0				
0.5	0.018	2015	0	2	0.1727	1.986	18.8
5.5	0.4782	2013	2	2	0.2916	2.368	25.4
10.5	1.2497	2010	5	2	0.2025	1.229	19.5
15.5	2.1255	2005	10	2	0.1994	1.136	22.4
20.5	3.005	2001	14	2	0.2175	1.25	25
25.5	3.8652	1996	19	2	0.1287	0.709	20.1
30.5	4.8197	1989	26	3	0.1478	0.779	24.3
35.5	5.7635	1981	34	3	0.1057	0.594	23
40.5	6.5987	1974	41	4	0.1332	0.779	33.2
42.5	6.9606	1972	43	4	0.1696	0.937	32.3
45.5	7.5035	1968	47	4	0.1416	0.726	28.7
48.5	8.1299	1963	52	5	0.0954	0.457	32.6
50.5	8.5475	1960	55	6	0.1614	0.714	44.2
52.5	9.0338	1956	59	6	0.138	0.568	59.3
55.5	9.7632	1953	62	8	0.3297	1.239	102.3
58.5	10.6304	1949	66	9	0.1796	0.622	65.6
61	11.353	1943	72	11	0.0868	0.292	53.1

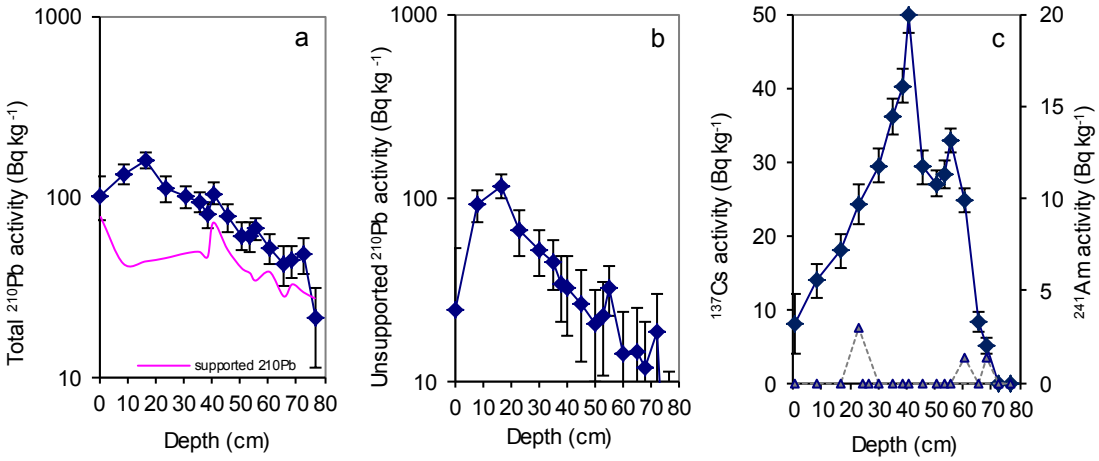


Figure 1. Fallout radionuclide concentrations in core HOLTU3 taken from a Holt Hall, showing (a) total ^{210}Pb, (b) unsupported ^{210}Pb, (c) ^{137}Cs and ^{241}Am concentrations versus depth.

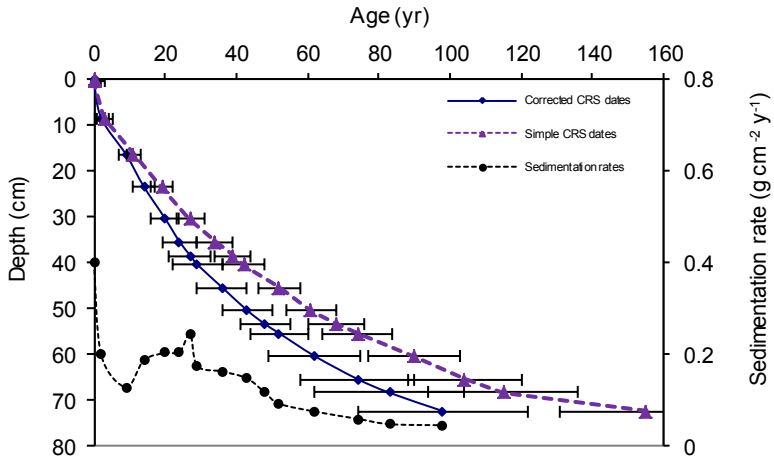


Figure 2. Radiometric chronology of core HOLTU3 taken from a Holt Hall, showing the CRS model ^{210}Pb dates and sedimentation rates.

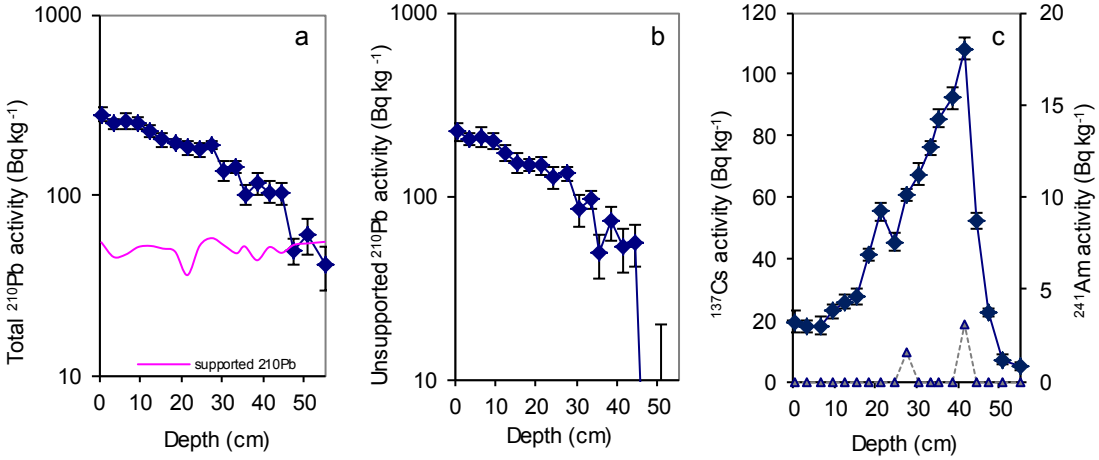


Figure 3. Fallout radionuclide concentrations in core EDGB5 taken from Edgbaston, England, showing (a) total ^{210}Pb and (b) unsupported ^{210}Pb, (c) ^{137}Cs and ^{241}Am concentrations versus depth.

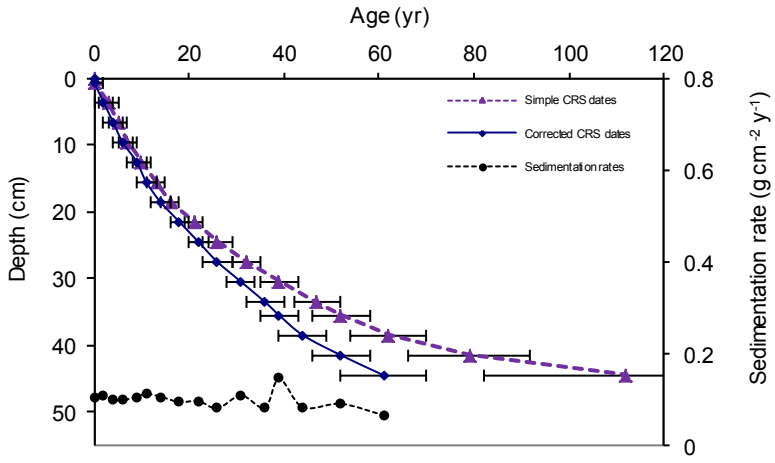


Figure 4. Radiometric chronology of core EDGB5 taken from Edgbaston, England, showing the CRS model ^{210}Pb dates and sedimentation rates.

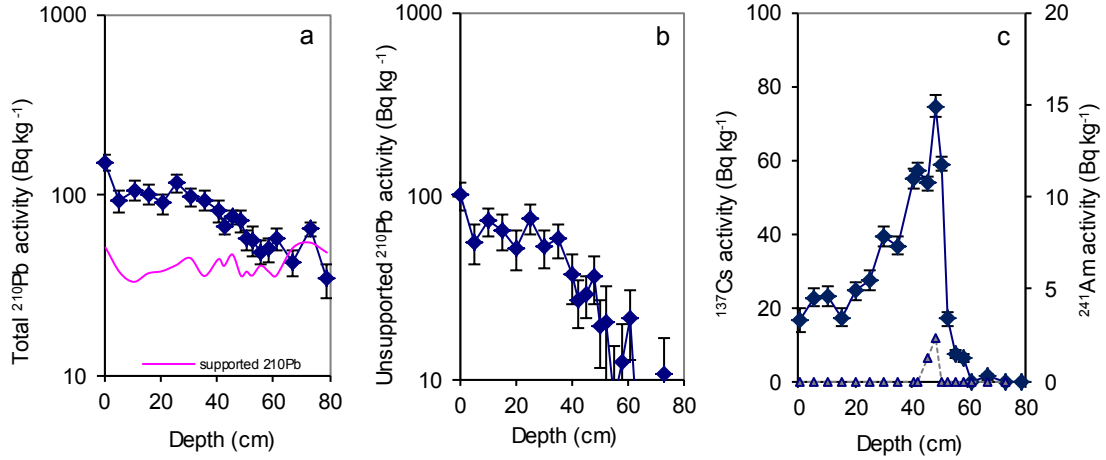


Figure 5. Fallout radionuclide concentrations in core WAKE4 taken from Wake Valley, England, showing (a) total ^{210}Pb, (b) unsupported ^{210}Pb, and (c) ^{137}Cs and ^{241}Am concentrations versus depth.

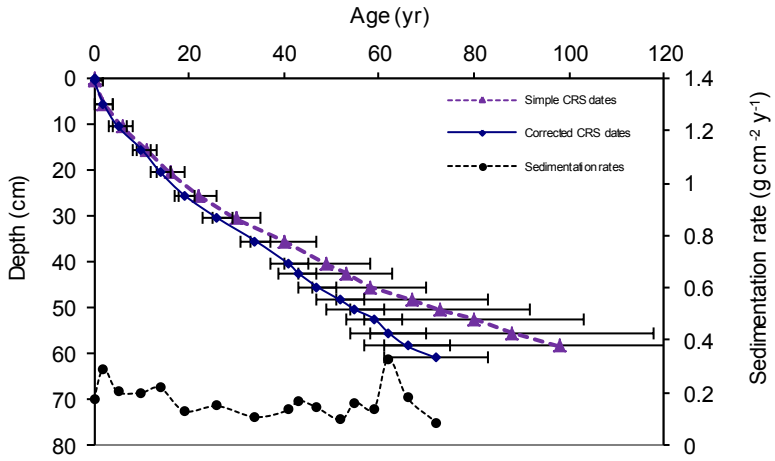
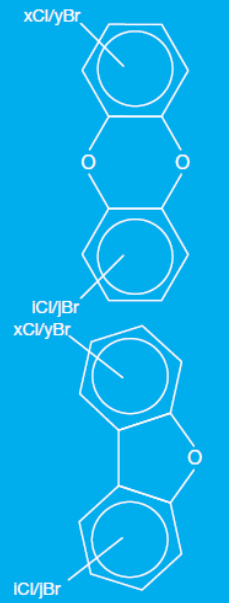


Figure 6. Radiometric chronology of core WAKE4 taken from Wake Valley, England, showing the CRS model ^{210}Pb dates and sedimentation rates.

Appendix B PXDD/F and PBDD/F Target Analyte Ion Mass Simulations and PBDD/F Standard Solutions

Polyhalogenated Dibenzodioxins and -furans

	DIOXINS						FURANS					
	NATIVE		$^{13}C_{12}$ STANDARD		$^{13}C_6$ STANDARD		NATIVE		$^{13}C_{12}$ STANDARD		$^{13}C_6$ STANDARD	
	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]
$BrCl_3$	363.845477	100.00	375.885735	100.00	369.865606	100.00	347.850562	100.00	359.890820	100.00	353.870691	100.00
	365.842526	95.88	377.882784	95.88	371.862655	95.88	349.848515	97.28	361.887870	95.88	355.867741	95.88
	365.843430	97.28	377.883688	97.28	371.863559	97.28	349.847612	95.88	361.888773	97.28	355.868644	97.28
	367.840480	93.27	379.880738	93.27	373.860609	93.27	351.845565	93.27	363.885823	93.27	357.865694	93.27
Br_2Cl_2	407.794961	51.40	419.835219	51.40	413.815090	51.40	391.800047	51.40	403.840305	51.40	397.820176	51.40
	409.792915	100.00	421.833173	100.00	415.813044	100.00	393.798000	100.00	405.838258	100.00	399.818129	100.00
	411.789965	63.92	423.830223	63.92	417.810094	63.92	395.795050	63.92	407.835308	63.92	401.815179	63.92
	411.790868	48.64	423.831126	48.64	417.810997	48.64	395.795954	48.64	407.836212	48.64	401.816083	48.64
Br_3Cl	451.744446	34.27	463.784704	34.27	457.764575	34.27	435.749532	34.27	447.789790	34.27	441.769661	34.27
	453.742400	100.00	465.782658	100.00	459.762529	100.00	437.747485	100.00	449.787743	100.00	443.767614	100.00
	455.739450	31.96	467.779708	31.96	461.759579	31.96	439.744535	31.96	451.784793	31.96	445.764664	31.96
	455.740353	97.28	467.780611	97.28	461.760482	97.28	439.745438	97.28	451.785697	97.28	445.765568	97.28
$BrCl_4$	397.806504	78.22	409.846762	78.22	403.826633	78.22	381.811590	78.22	393.851848	78.22	387.831719	78.22
	399.803554	100.00	411.843812	100.00	405.823683	100.00	383.808639	100.00	395.848898	100.00	389.828768	100.00
	399.804458	76.09	411.844716	76.09	405.824587	76.09	383.809543	76.09	395.849801	76.09	389.829672	76.09
	401.801507	97.28	413.841766	97.28	407.821637	97.28	385.806593	97.28	397.846851	97.28	391.826722	97.28
Br_2Cl_3	441.755989	51.40	453.796247	51.40	447.776118	51.40	425.761074	51.40	437.801333	51.40	431.781203	51.40
	443.753039	49.28	455.793297	49.28	449.773168	49.28	427.758124	49.28	439.798382	49.28	433.778253	49.28
	443.753942	100.00	455.794201	100.00	449.774072	100.00	427.759028	100.00	439.799286	100.00	433.779157	100.00
	445.750992	95.88	457.791250	95.88	451.771121	95.88	429.756078	95.88	441.796336	95.88	435.776207	95.88
$BrCl_5$	431.767532	62.58	443.807790	62.58	439.784711	100.00	415.772617	62.58	427.812875	62.58	421.792746	62.58
	433.764582	100.00	445.804840	100.00	439.785614	60.87	417.769667	100.00	429.809925	100.00	423.789796	100.00
	435.761632	63.92	447.801890	63.92	441.781761	63.92	419.766717	63.92	431.806975	63.92	425.786846	63.92
	435.762535	97.28	447.802793	97.28	441.782664	97.28	419.767621	97.28	431.807879	97.28	425.787750	97.28
Br_2Cl_4	477.714067	51.40	489.754325	51.40	483.734196	51.40	461.719152	51.40	473.759410	51.40	467.739281	51.40
	477.714970	78.22	489.755228	78.22	483.735099	78.22	461.720056	78.22	473.760314	78.22	467.740185	78.22
	479.712020	100.00	491.752278	100.00	485.732149	100.00	463.717105	100.00	475.757363	100.00	469.737234	100.00
	481.709973	48.64	493.750232	48.64	487.730102	48.64	465.715059	48.64	477.755317	48.64	471.735188	48.64
$BrCl_7$	501.686637	100.00	513.726895	100.00	507.706766	100.00	485.691723	100.00	497.731981	100.00	491.711852	100.00
	503.683687	95.88	515.723945	95.88	509.703816	95.88	487.688772	95.88	499.729030	95.88	493.708901	95.88
	503.684591	97.28	515.724849	97.28	509.704720	97.28	487.689676	97.28	499.729934	97.28	493.709805	97.28
	505.681640	93.27	517.721898	93.27	511.701769	93.27	489.686726	93.27	501.726984	93.27	495.706855	93.27
Br_2Cl_6	545.636122	51.40	557.676380	51.40	551.656251	51.40	529.641207	51.40	541.681465	51.40	535.661336	51.40
	545.637026	52.15	557.677284	52.15	551.657155	52.15	529.642111	52.15	541.682369	52.15	535.662240	52.15
	547.634075	100.00	559.674333	100.00	553.654204	100.00	531.639161	100.00	543.679419	100 .00	537.659290	100.00
	549.631125	79.90	561.671383	79.90	555.651254	79.90	533.636211	79.90	545.676469	79.90	539.656340	79.90



The calculated reference masses are based on the following values for isotopic masses:
^{1}H 1.0078250321u,
^{12}C 12.0000000000 u,
^{13}C 13.0033548378 u,
^{16}O 15.9949146221 u,
^{35}Cl 34.9688527100 u and
^{37}Cl 36.9659026000 u.
^{79}Br 78.9183376u and
^{81}Br 80.9162910u.

All listed masses refer to singly positively charged ions. The mass of the electron (0.000548579911u) was taken into account for the calculation of the ionic masses. Reference: Nuclear Phys. A 1995, 595, 409-480; J. Phys.

Chem. Ref. Data 1999, 28 (6), 1713-1852 and references cited therein.

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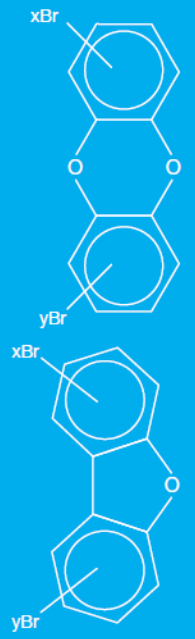
Polybrominated Dibenzodioxins and -furans

	DIOXINS						FURANS					
	NATIVE		$^{13}C_{12}$ STANDARD		$^{13}C_{6}$ STANDARD		NATIVE		$^{13}C_{12}$ STANDARD		$^{13}C_{6}$ STANDARD	
	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]	EXACT MASS [u]	REL INTENSITY [%]
Br_2	339.872906	51.40	351.913164	51.40	345.893035	51.40	323.877991	51.40	335.918249	51.40	329.898120	51.40
	341.870859	100.00	353.911118	100.00	347.890988	100.00	325.875945	100.00	337.916203	100.00	331.896074	100.00
	343.868813	12.98	355.909071	48.64	349.888942	6.49	327.873898	12.98	339.914156	48.64	333.894027	6.49
Br_3	417.783419	34.27	429.823677	34.27	423.803548	34.27	401.788504	34.27	413.828762	34.27	407.808633	34.27
	419.781372	100.00	431.821630	100.00	425.801501	100.00	403.786457	100.00	415.826715	100.00	409.806586	100.00
	421.779325	97.28	433.819583	97.28	427.799454	97.28	405.784411	97.28	417.824669	97.28	411.804540	97.28
	423.777279	31.54	435.817537	31.54	429.797408	31.54	407.782364	31.54	419.822622	31.54	413.802493	31.54
Br_4	495.693931	17.61	507.734189	17.61	501.714060	17.61	479.699017	17.61	491.739275	17.61	485.719146	17.61
	497.691885	68.53	509.732143	68.53	503.712014	68.53	481.696970	68.53	493.737228	68.53	487.717099	68.53
	499.689838	100.00	511.730096	100.00	505.709967	100.00	483.694923	100.00	495.735181	100.00	489.715052	100.00
	501.687791	64.85	513.728049	64.85	507.707920	64.85	485.692877	64.85	497.733135	64.85	491.713006	64.85
Br_5	575.602397	51.40	585.644702	10.57	579.624573	10.57	559.607483	51.40	569.649787	10.57	563.629658	10.57
	577.600351	100.00	587.642655	51.40	581.622526	51.40	561.605436	100.00	571.647741	51.40	565.627612	51.40
	578.603705	12.98	589.640609	100.00	583.620480	100.00	562.608791	12.98	573.645694	100.00	567.625565	100.00
	579.598304	97.28	591.638562	97.28	585.618433	97.28	563.603389	97.28	575.643647	97.28	569.623518	97.28
	581.596257	47.31	593.636515	47.31	587.616386	47.31	565.601343	47.31	577.641601	47.31	571.621472	47.31
Br_6	653.512910	31.70	663.555214	5.43	659.533039	31.70	637.517995	31.70	647.560300	5.43	643.538124	31.70
	655.510863	77.10	665.553168	31.70	661.530992	77.10	639.515949	77.10	649.558253	31.70	645.536078	77.10
	657.508817	100.00	667.551121	77.10	663.528946	100.00	641.513902	100.00	651.556207	77.10	647.534031	100.00
	658.512171	12.98	669.549075	100.00	664.532300	6.49	642.517257	12.98	653.554160	100.00	648.537386	6.49
	659.506770	72.96	671.547028	72.96	665.526899	72.96	643.511855	72.96	655.552113	72.96	649.531984	72.96
	661.504723	28.39	673.544981	28.39	667.524852	28.39	645.509809	28.39	657.550067	28.39	651.529938	28.39
Br_7	731.423422	21.14	743.463680	21.14	737.443551	21.14	715.428508	21.14	727.468766	21.14	721.448637	21.14
	733.421376	61.68	745.461634	61.68	739.441505	61.68	717.426461	61.68	729.466719	61.68	723.446590	61.68
	735.419329	100.00	747.459587	100.00	741.439458	100.00	719.424414	100.00	731.464673	100.00	725.444544	100.00
	737.417282	97.28	749.457541	97.28	743.437412	97.28	721.422368	97.28	733.462626	97.28	727.442497	97.28
	739.415236	56.78	751.455494	56.78	745.435360	56.78	723.420321	56.78	735.460579	56.78	729.440450	56.78
	741.413189	18.41	753.453447	18.41	747.433318	18.41	725.418275	18.41	737.458533	18.41	731.438404	18.41
Br_8	811.331888	42.27	821.374193	12.42	815.354064	12.42	795.336974	42.27	805.379278	12.42	799.359149	12.42
	813.329842	82.24	823.372146	42.27	817.352017	42.27	797.334927	82.24	807.377232	42.27	801.357103	42.27
	815.327795	100.00	825.370100	82.24	819.349971	82.24	799.332880	100.00	809.375185	82.24	803.355056	82.24
	816.331150	12.98	827.368053	100.00	821.347920	100.00	800.336235	12.98	811.373138	100.00	805.353009	100.00
	817.325748	77.82	829.366007	77.82	823.345877	77.82	801.330834	77.82	813.371092	77.82	807.350963	77.82
	819.323702	37.85	831.363960	37.85	825.343831	37.85	803.328787	37.85	815.369045	37.85	809.348916	37.85



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^{16}O 15.9949146221 u,
^{79}Br 78.9183376u and
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All listed masses refer to singly positively charged ions. The mass of the electron (0.000548579911u) was taken into account for the calculation of the ionic masses. Reference: Nuclear Phys. A 1995, 595, 409-480; J. Phys. Chem. Ref. Data 1999, 28 (6), 1713-1852 and references cited therein.

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Polybrominated Dibenzodioxins and -furans

Calibrations Solutions

	All concentrations are in ng/mL				
Native Analytes	**CS1**	**CS2**	**CS3**	**CS4**	**CS5**
2,3,7,8-TeBDD	0.1	0.4	2.0	10	50
1,2,3,7,8-PeBDD	0.2	0.8	4.0	20	100
1,2,3,4,7,8-HxBDD	0.6	2.4	12.0	60	300
1,2,3,6,7,8-HxBDD	0.6	2.4	12.0	60	300
1,2,3,7,8,9-HxBDD	0.6	2.4	12.0	60	300
1,2,3,4,6,7,8-HpBDD	0.8	3.0	15.0	75	375
OBDD	1.0	4.0	20.0	100	500
2,3,7,8-TeBDF	0.2	0.8	4.0	20	100
2,4,6,8-TeBDF	0.2	0.8	4.0	20	100
1,2,3,7,8-PeBDF	0.4	1.6	8.0	40	200
2,3,4,7,8-PeBDF	0.4	1.6	8.0	40	200
1,2,3,4,7,8-HxBDF	0.6	2.4	12.0	60	300
1,2,3,4,6,7,8-HpBDF	0.8	3.0	15.0	75	375
OBDF	1.0	4.0	20.0	100	500
Cleanup Standards					
2,3,7,8-TeBDD ($^{13}C_{12}$,99%)	20	20	20	20	20
1,2,3,7,8-PeBDD ($^{13}C_{12}$,99%)	20	20	20	20	20
1,2,3,4,7,8-HxBDD ($^{13}C_{12}$,99%)	50	50	50	50	50
1,2,3,6,7,8-HxBDD ($^{13}C_{12}$,99%)	50	50	50	50	50
1,2,3,4,6,7,8-HpBDD ($^{13}C_{12}$,99%)	100	100	100	100	100
OBDD ($^{13}C_{12}$,99%)	150	150	150	150	150
2,3,7,8-TeBDF ($^{13}C_{12}$,99%)	20	20	20	20	20
2,3,4,7,8-PeBDF ($^{13}C_{12}$,99%)	20	20	20	20	20
1,2,3,4,7,8-HxBDF ($^{13}C_{12}$,99%)	50	50	50	50	50
1,2,3,4,6,7,8-HpBDF ($^{13}C_{12}$,99%)	100	100	100	100	100
OBDF ($^{13}C_{12}$,99%)	150	150	150	150	150
Syringe Spike					
1,2,3,7,8,9-HxBDD ($^{13}C_{12}$,99%)	50	50	50	50	50
1,2,3,7,8-PeBDF ($^{13}C_{12}$,99%)	20	20	20	20	20
Sampling Spike					
2,4,6,8-TeBDD ($^{13}C_{12}$,99%)	20	20	20	20	20

Cleanup Spike

^{13}C-Labeled Component	All concentrations are in ng/mL
2,3,7,8-TeBDD ($^{13}C_{12}$,99%)	100
1,2,3,7,8-PeBDD ($^{13}C_{12}$,99%)	100
1,2,3,4,7,8-HxBDD ($^{13}C_{12}$,99%)	250
1,2,3,6,7,8-HxBDD ($^{13}C_{12}$,99%)	250
1,2,3,4,6,7,8-HpBDD ($^{13}C_{12}$,99%)	500
OBDD ($^{13}C_{12}$,99%)	750
2,3,7,8-TeBDF ($^{13}C_{12}$,99%)	100
2,3,4,7,8-PeBDF ($^{13}C_{12}$,99%)	100
1,2,3,4,7,8-HxBDF ($^{13}C_{12}$,99%)	250
1,2,3,4,6,7,8-HpBDF ($^{13}C_{12}$,99%)	500
OBDF ($^{13}C_{12}$,99%)	750

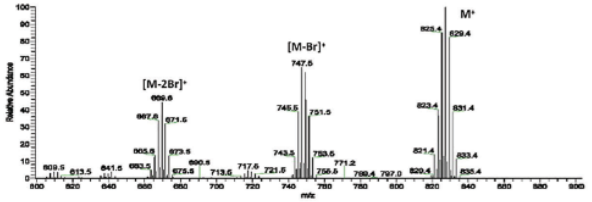
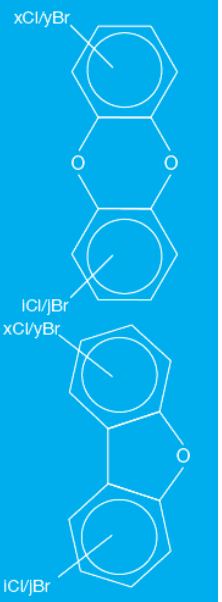


Figure 1. Electron impact ionization spectra acquired @70eV (source temperature 280 °C) for OBDD ($^{13}C_{12}$) showing the relative intensities of the M+, [M-Br]+ and [M-2Br]+ ions. Data was obtained utilising the Thermo Scientific Q Exactive GC Orbitrap system operated in full scan mode. The fragmentation pattern shown is dependent upon EI source voltage and temperature.



The calculated reference masses are based on the following values for isotopic masses:
^{1}H 1.0078250321u,
^{12}C 12.0000000000 u,
^{13}C 13.0033548378 u,
^{16}O 15.9949146221 u,
^{35}Cl 34.9686527100 u and
^{37}Cl 36.9659026000 u,
^{79}Br 78.918337Bu and
^{81}Br 80.9162910u.

All listed masses refer to singly positively charged ions. The mass of the electron (0.000548579911u) was taken into account for the calculation of the ionic masses. Reference: Nuclear Phys. A 1995, 595, 409-480; J. Phys. Chem. Ref. Data 1999, 28 (6), 1713-1852 and references cited therein.

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