Temporal Trends in Radiometrically Dated Sediment Cores from English Lakes Show Polybrominated Diphenyl Ethers Correlate with Brominated but not Mixed Bromo/Chloro Dioxins and Furans

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ABSTRACT

This paper reports concentrations between ~1950 and present, of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and furans (PBDD/Fs), in radiometrically-dated sediment cores from three English lakes. Mixed bromo/chloro dibenzo-*p*-dioxins and furans (PXDD/Fs) were measured in two of the same lakes. Concentrations of PXDD/Fs decreased over time to the present. To our knowledge, this is the first report of temporal trends of PXDD/Fs in the environment. In contrast, concentrations of PBDEs increased towards the present and were significantly correlated ($R = 0.88$-0.98; $p < 0.05$) with concentrations of PBDFs in all three lakes. These observations suggest that the sources of PXDD/Fs are not related to PBDEs and differ from those of PBDFs. We also report for the first time the presence of octabromodibenzofuran (OBDF) in the two most recent core slices at one lake. The source of OBDF in these samples is unclear. While OBDF has been reported previously as a significant contaminant of some commercial formulations of Deca-BDE, it is also present in Octa-BDE products and in emissions from a variety of combustion activities. Overall, while the positive correlation between PBDEs and PBDFs suggests increased use of PBDEs has contributed substantially to environmental contamination with PBDFs; examination of PBDF homologue patterns implies emissions from combustion activities are likely also important.

Keywords

PBDD/Fs; PXDD/Fs; PBDEs; Time Trends; Sources; Lakes

Introduction

Polybrominated diphenyl ethers (PBDEs) are industrial chemicals that have found extensive global use as flame retardants added to a wide range of consumer items such as electrical and electronic equipment and furniture fabrics and foams. As a consequence of their environmental persistence, potential for long-range atmospheric transport and bioaccumulation, and adverse effects on humans and/or wildlife, PBDEs are listed under the United Nations Environment Program's Stockholm Convention on Persistent Organic Pollutants (POPs). Moreover, manufacture and new use of PBDEs is either banned or restricted by many jurisdictions. Against this backdrop, there is a clear need to evaluate the efficacy of such actions; for example, by monitoring temporal trends in environmental contamination. Several studies worldwide have previously delineated the increase in concentrations of PBDEs in the environment from the onset of their widespread use in the 1980s to mid-2000s when the first restrictions on them were introduced (Kohler et al, 2008; Zegers et al, 2003; Vane et al, 2010; Webster et al, 2008). Subsequent trends up to the present, point to concentrations levelling off and even declining as actions to eliminate PBDEs take effect (Yang et al, 2016). One concern with respect to PBDEs is that commercial PBDE products have been shown to contain polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) as contaminants at levels that amount to a substantial mass (0.43 - 2.2 t globally) of PBDD/Fs (Hanari et al, 2006; Ren et al, 2011). This is consistent with a recent report that temporal trends of PBDFs correlate with those of PBDEs in sediment cores from Tokyo Bay (Goto et al, 2017). This is concerning owing to evidence of the toxicity of PBDFs that is considered by the WHO to be on a par with that of their chlorinated analogs (Van den Berg et al, 2013). Moreover, there exists emerging concern about environmental contamination with mixed bromo-/chloro-dibenzo-*p*-dioxins and furans (PXDD/Fs) (Wall et al, 2015). Although little is known about the toxicity of PXDD/Fs, their structural similarity to

PBDD/Fs means that establishing the level at which they are present in the environment and elucidating their sources is desirable. Studies exist that demonstrate that combustion activities such as iron ore sintering and waste incineration are sources of PXDD/Fs (Chatkittikunwong and Creaser, 1994; Weber et al, 2003), with their presence in air in Japan (Hayakawa et al, 2004) as well as soil impacted by a recycling plant fire (Myers et al, 2012) and by informal e-waste handling reported (Leung et al, 2007; Ma et al, 2008; Tue et al, 2013; Yu et al, 2008; Zennegg et al, 2009). Currently however, very few data exist on concentrations of PXDD/Fs in sediments. Concentrations of ΣPXDD/Fs were between 0.03-0.1 ng/g dry weight in freshwater sediment taken from a former chlor-alkali plant in the USA, with monobromoheptachloro dibenzo-*p*-dioxin the only congener detected (Kannan et al, 1998). In Osaka Bay, Japan, a wider range of PXDD/Fs were detected in marine sediment, most prominently 2-Br-3,7,8-ClCDD detected between 0.84-6.5 pg/g dry weight (Ohta et al, 2002), while concentrations of monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans which ranged between below detection limit and 1.8 ng/g dry weight were reported for marine surficial sediments from Hong Kong and Korea (Terauchi et al, 2009).

In this study we exploit the fact that sediment deposited in lakes over time can provide a reliable record of contaminant inputs into lacustrine systems. We thus collected sediment cores from three English lakes for which data on concentrations of PBDEs, hexabromocyclododecane (HBCDD), and polychlorinated biphenyls (PCBs) have been measured previously (Yang et al, 2016) and used radiometric techniques to assign dates to core slices representing different depths. Concentrations of PBDEs, PBDD/Fs, and PXDD/Fs were measured in individual core slices and the data used to test the hypothesis that these contaminant classes will display similar temporal trends.

2. Experimental

2.1 Sampling locations

A map of our sampling locations is given as supplementary data (Figure SD-1), with additional information about individual sites supplied in Table SD-1. Locations studied were 3 of the same seepage lakes for which we have previously reported temporal trends in concentrations of PBDEs, HBCDD, and PCBs in sediment cores (Yang et al, 2016). These were: Edgbaston Pool, Holt Hall Lake, and Wake Valley Pond. These lakes were selected from locations with a range of population densities as a surrogate indicator of anthropogenic inputs. One sediment core from each lake was collected between 23rd – 26th June 2015, covering sedimentation from at least ~1950 to the date of sampling. Consistent with our previous study of these lakes (Yang et al, 2016), each core was collected from a flat area of the lake basin near the deepest point.

2.2 Sampling and sectioning of lake sediment cores

Cores were sampled from a flat area close to the maximum depth at each site and were collected from a purpose built pontoon to a depth of between 0.75-0.95 m below the benthic surface using a large diameter sediment core apparatus (‘Big-Ben’) (Patmore et al, 2014). The sediment corer, piston and core covers were all thoroughly decontaminated with hexane before and after use. The ‘Big-Ben’ corer having an internal diameter of 140 mm, is considerably larger than conventional piston corers (typically 50 - 80 mm i.d.) and provides sediment cores with a cross-sectional area of 154 cm^2 resulting in far greater sample for analysis, and facilitating the analysis of PBDD/Fs and PXDD/Fs at the anticipated ultra-trace levels. Sediment cores were extruded vertically in the field at 10 mm intervals, with each sample stored at -20° C in individually sealed Whirl-Pack$^{\text{TM}}$ sampling bags until extraction analysis. Sample contamination derived from use of Whirl-Pack$^{\text{TM}}$ 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 with PBDEs.

Each sediment sample was divided into two during the core-sectioning procedure: two thirds kept for analysis of our target contaminants; with the remaining one third used for radiometric dating and determination of sediment water and total organic carbon (TOC) content. The latter two metrics were determined gravimetrically by mass loss from a 2 g (wet weight) sample, oven dried at 105 °C for 3 h to determine water content and a further 2 h at 550 °C to determine TOC by loss-on-ignition. After freeze-drying, each 10 mm core slice was homogenized. Thereafter, based on information from our radiometric dating results, we combined 10 mm core slices from the same core to generate a series of pooled core slice samples that each represented around five years of sedimented material. In total, 31 such pooled samples were prepared for analysis. A further core slice was analyzed from the bottom of the core taken from each of our lakes, to provide an indication of concentrations of our target contaminants prior to ~1950.

Analytical methods

Details of methods used to radiometrically date (using ^{210}Pb) sediment core slices are given as SD, with sediment chronologies and sedimentation rates provided as Tables SD-2-SD-4 and Figures SD-2-SD-7. For determination of concentrations of target contaminants in sediment samples, 5 g each of both hydromatrix and sodium sulfate (both pre-cleaned) were loaded into pre-cleaned stainless steel extraction cells, along with an aliquot of freeze-dried and homogenized sediment core slice (typically 5 g, accurately weighed). This was treated with ^{13}C-labeled internal standards (details below) and subjected to pressurized liquid extraction using an ASE-350 (Dionex, CA). Extraction was first with hexane:dichloromethane (3:2, v/v; 2 cycles), followed by toluene (2 cycles) at 90°C, 1500 psi and hold time= 5 min. Following concentration to ~ 1 mL using a Turbovap solvent evaporator, crude sediment extracts were purified prior to instrumental analysis via elution through a sequence of acid silica and activated carbon columns (Cape Technologies, Maine, USA). This yielded two concentrated extracts (F1b and F2b) for instrumental analysis of PBDEs (F1b) and PBDD/Fs + PXDD/Fs (F2b) for each sediment core slice. Detailed descriptions of the complex procedures used to purify and fractionate sediment core extracts prior to instrumental analysis are provided as SD (Figures SD-8-10 and accompanying text).

Commercially available standards were used for the analysis of BFRs. These comprised native PBDEs and $^{13}C_{12}$-BDEs 28, 47, 99, 100, 153, 154, 183, 207, and 209 (Wellington Laboratories) and native and $^{13}C_{12}$- analogues of the following PBDD/Fs (Cambridge Isotope Laboratories): 2,3,7,8-TBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, 1,2,3,4,6,7,8-HpBDD, OBDD, 2,3,7,8-TBDF, 2,4,6,8-TBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF, and OBDF. The following native standards of PXDD/Fs were kindly provided by Dr. Alwyn Fernandes, FERA, UK: 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-1,3,7,8-CDD, 2-Br-3,6,7,8,9-CDD, 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. In the absence of $^{13}C_{12}$-labeled PXDD/Fs, $^{13}C_{12}$-2,4,6,8-TBDF was used as internal (surrogate) standard for quantification of PBDD/Fs.

Instrumental Analysis

Quantification of target compounds and congener groups was conducted on a Thermo Scientific GC Q Exactive GC/orbitrap MS. Concentrations of PBDEs were determined via injection of 2 µL of F1 onto a Thermo Fisher Scientific Trace Gold Dioxin capillary column (12 m x 0.25 mm x 0.1 µm), with the GC-MS operated in selected ion monitoring (SIM) mode. Concentrations of PBDD/Fs and PXDD/Fs were determined by injecting 2 µL of F2 onto the same GC column, with the GC-MS operated in full scan mode. For both F1 and F2, extracts were injected via a 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 was deployed. A constant He flow of 1.3 mL/min was deployed with a temperature program of: 120 °C held for 3 min before ramping to 250 °C at 6.5 °C/min, followed by a second ramp from 250 °C to 305 °C at 8 °C/min held for 7 min. The orbitrap MS was operated at 60,000 mass resolution, which facilitated confirmation of analyte identity via accurate mass. In all cases, where a standard for a given compound was included in our calibration standard, identification of that compound was via comparison of retention time to the standard, while quantification of that compound was made using its response factor relative to the appropriate internal (surrogate) standard. For PBDD/F and PXDD/F compounds for which we did not have standards, quantification was achieved using an averaged relative response factor for compounds of the same homologue group. For example, hexabromo-PBDFs were quantified using the relative response factor for 1,2,3,4,7,8-HxBDF. Full details of mass spectrometric parameters are provided as SD.

QA/QC

Recoveries for all target analyte internal standards ranged between 50 and 110 %, with the exception of $^{13}C_{12}$-OBDD and $^{13}C_{12}$-OBDF for which recoveries in some samples were as low as 40%. Method accuracy was assessed for PBDEs by replicate (n=7) analysis of NIST SRM1944

(New York/ New Jersey Waterway Sediment). This revealed good agreement between concentrations measured in this study with the certified values reported by NIST. Full details are provided in SD (Table SD-5). While certified or indicative values have not previously been reported for PBDD/Fs and PXDD/Fs, they are also provided as SD (Tables SD-6 and SD-7) for comparison with future studies.

Statistical methods

All statistics in this study were conducted using IBM SPSS Statistics 21, and Microsoft Excel 2007.

Results and discussion

Concentrations of PBDEs

Concentrations of all target PBDEs and PBDD/Fs in each individual core slice from each sampling location are provided as supporting data (Tables SD-8 – SD-13). Table 1 provides a summary of concentrations of ΣPBDEs detected in this study together with those reported in selected relevant previous studies for comparison. Most pertinently, concentrations of ΣPBDEs reported for surficial sediments for our three lakes match closely with those reported previously by our group for surficial sediments (albeit dating from 6-7 years earlier) for the same lakes (Yang et al, 2016). While the lake situated in the local authority with the highest population density (Edgbaston Pool) displayed the greatest concentrations of ΣPBDEs, concentrations at Wake Valley Pond and Holt Hall Lake are similar despite Wake Valley Pond being located in a more densely populated local authority area (Table SD-1 – i.e. Edgbaston Pool 2,500 people/km^2 >Wake Valley Pond 250-499 people/km^2 >Holt Hall Lake 100-249 people/km^2). This is partly consistent with previous findings showing higher concentrations of PBDEs in air and soil from more densely populated areas due to emissions from the built environment (Harrad and Hunter, 2006). Concentrations of ΣPBDEs in this study at Edgbaston Pool ca 3 km from the center of the city of Birmingham are close to the average reported for surficial sediments collected in 2011 from 45 locations along the River Thames in the UK (Ganci et al, 2019). By comparison, those at Holt Hall Lake and Wake Valley Pond are around an order of magnitude lower than at Edgbaston Pool. When compared to ΣPBDE concentrations in surficial sediments collected in 2002-2003 as part of two studies conducted in industrial areas of the River Clyde in Scotland (Vane et al, 2010; Webster et al, 2008), concentrations at all three lakes in our study are substantially lower.

Relative Abundance of PBDE Congeners

The PBDE congener pattern in all our samples is dominated by BDE-209. This is consistent with industry figures that in Europe, Deca-BDE production far exceeded that of both Penta- and Octa-BDE (BSEF, 2003). It is also in line with previous reports for the same lakes (Yang et al, 2016), with sediment cores from the Clyde Estuary in Scotland, UK (Vane et al, 2010; Webster et al, 2008), and with surficial sediments from the River Thames running through London, UK (Ganci et al, 2019). Consistent with the Clyde Estuary, the relative contribution of the nona-BDEs-206, -207, and -208 to ΣPBDEs in this study exceeds that observed in commercial formulations of Deca-BDE. Specifically, in the top three core slices from all three locations, Σnona-BDEs comprises 8-27% of ΣBDEs. This compares to 2.5 and 9.3% respectively in the commercial Deca-BDE formulations Saytex 102E and Bromkal 82-0DE (La Guardia et al, 2006). While the contribution of Σnona-BDEs to ΣBDEs is higher in the commercial Octa-BDE products DE-79 and Bromkal 79-8DE at 12.1 and 18.9% respectively (La Guardia et al, 2006); the contribution of the main indicator congener for Octa-BDE (BDE-183) to ΣPBDEs in our sediments is much lower (0.45-2.1% in the top three slices at all lakes) than in DE-79 and Bromkal 79-8DE (42%

and 12.6% respectively). On this evidence, the presence of the three nona-BDEs in this study seem most likely attributable to debromination of BDE-209. This is supported by the fact that BDE-209 and Σnona-BDEs are positively correlated ($p < 0.05$ at Edgbaston Pool; $p < 0.1$ at Wake Valley Pond and Holt Hall Lake) at each lake studied here. Similar conclusions were drawn based on the observation that nona-BDEs were the second most abundant homologue group after BDE-209 in river sediments from China (Mai et al, 2005; Zhang et al, 2009). However, we note a report of elevated abundances of BDE-208 relative to BDE-209 in TV/PC display casings, and PC components sampled in South China. In this study the authors attributed to the decomposition of higher brominated PBDEs during the process of manufacturing use and/or recycling of PBDE-containing products (Chen et al., 2010). Specifically, the ratios of average concentrations of BDE-208: average concentrations of BDE-209 in TV and PC housing were 5.4% and 2.8% respectively. By comparison, BDE-208:BDE-209 ratios in the uppermost 4 core slices in our study ranged from 0.2% to 0.6% at Edgbaston Pool; 1.3% to 2.0% at Wake Valley Pond; and 1.3% to 9.5% at Holt Hall Lake. It is thus possible that the nona-BDEs detected in our study have arisen at least in part to emissions from treated products as well as any post-emission debromination (Law et al., 2008).

Temporal Trends in PBDEs in English Lake Sediments

Figure 1 plots the temporal trends in concentrations of ΣPBDEs at all three locations. Given the predominant contribution of BDE-209 to ΣPBDEs, the trends in ΣPBDEs reflect those of BDE-209. Importantly, BDE-209 concentrations in the cores from Edgbaston Pool and Wake Valley Pond do not peak in the uppermost core slice (2015); instead the highest concentrations are found in the slice immediately below (2012 and 2009 for Edgbaston Pool and Wake Valley Pond respectively). The situation differs for Holt Hall Lake, where the highest BDE-209 concentration is in the surficial sediment (2015). Overall, this suggests that while the full impact of recent restrictions on the manufacture and use of Deca-BDE has yet to manifest itself at the lakes studied here; there are tentatively encouraging signs that contamination is levelling off.

Concentrations, Relative Abundance, and Possible Sources of PBDD/Fs in English Lake Sediments

PBDD/Fs were detected in all samples in this study at concentrations two orders of magnitude below those of PBDEs. Table 1 compares ΣPBDD/F concentrations in this study compared to those reported in a variety of previous studies from other locations. Concentrations in sediment core slices from the less urbanised Wake Valley Pond and Holt Hall Lake are in line with those reported for Swedish lakes and rivers (Hagberg et al, 2005; Lundstedt, 2016). However, those at Edgbaston Pool exceed those reported elsewhere. Similar to the situation for PBDEs, while the lake situated in the local authority with the highest population density (Edgbaston Pool) has noticeably the highest ΣPBDD/F concentrations; levels of these contaminants are similar at Wake Valley Pond and Holt Hall Lake despite the former being located in a more densely populated local authority area. PBDFs were overwhelmingly dominant, with OBDD the only PBDD detected and that only in the uppermost two layers in the cores taken at Wake Valley Pond and Holt Hall Lake. This is consistent with previous observations for surficial sediments and atmospheric deposition (Goto et al, 2017; Hayakawa et al, 2004), as well as in emissions from waste incinerators (Wang et al, 2010), and iron ore sintering (Drage et al, 2014). It is also pertinent to note that while OBDD and to a far lesser extent penta- and tetra-BDDs have been detected in commercial PBDE formulations (Ren et al, 2011), PBDFs – especially OBDF and 1,2,3,4,6,7,8-HpBDF - were in comparison detected in such products at far higher concentrations (Hanari et al, 2006; Ren et al, 2011).

Figure 2 shows the homologue profiles of PBDFs in sediment core slices from each lake. It is interesting to note the spatial variation in these profiles, for example TBDFs are far less abundant at Edgbaston Pool than at the other two lakes. A striking observation is that OBDF was detected at Wake Valley Pond - albeit only in the two uppermost core slices (2015 and 2009). To our knowledge, this is the first report of OBDF in sediments. The low detection frequency of OBDF in sediments is perhaps surprising given previous data that reports OBDF to be an impurity in both Octa-BDE and Deca-BDE commercial formulations (Hanari et al, 2006; Ren et al, 2011). However, this may be because OBDF has been reported to be easily debrominated (Goto et al, 2017). Overall, the PBDF homologue pattern in our sediment cores (expressed as a percentage of ΣPBDFs) more closely resembles that reported for the Octa-BDE formulation which comprises 0.3 % TBDFs, 1.8 % PeBDFs, 44.9 % HxBDFs, 27.1 % HpBDFs, and 25.8 % OBDF, than the Deca-BDE formulation which comprises 0.1% for each of TBDFs, PeBDFs, and HxBDFs, 3.6% for HpBDFs, and 96.1% OBDF. While this might suggest the Octa-BDE commercial formulation is a more significant source of the PBDFs observed in our sediments than the Deca-BDE product; as noted above, the major PBDE formulation used in the UK was Deca-BDE. Moreover, we note that concentrations of ΣPBDFs are more strongly correlated with those of BDE-209 ($R=0.96$, $p<0.05$ and $R=0.85$, $p<0.1$) than those of BDE-183 at both Edgbaston Pool and Wake Valley Pond ($R=0.48$, $p>0.1$ and $R=0.64$, $p>0.1$) - no meaningful inference could be drawn in this regard at Holt Hall Lake as there were too few samples in which PBDFs and both BDEs-183 and -209 were detected.

In addition to the potential contribution of PBDE use, both OBDF and 1,2,3,4,6,7,8-HpBDF (the predominant HpBDF detected in this study) have been reported to be emitted from combustion processes (Wang et al, 2015). We also note that we did not target 2,7-/2,8-dibromodibenzo-p-dioxins or 1,3,7-/1,3,8-tribromodibenzo-p-dioxins, which have been identified as being of biogenic origin (Goto et al, 2017) and can therefore not rule out possible contributions from biogenic sources to the burden of PBDD/Fs in our lakes. In summary, drawing firm conclusions about PBDD/F source attribution based on homologue and congener patterns in environmental matrices like lake sediments, is complicated by post-emission modification of such profiles by weathering processes that favour some PBDD/Fs more than others. Notwithstanding this, the evidence of congener/homologue profiles presented here, suggests that the PBDD/Fs detected in this study are predominantly a complex integral of combustion source emissions and their presence as contaminants of the Deca-BDE formulation.

Temporal Trends in concentrations of ΣPBDFs and PBDF homologue patterns

Temporal trends in concentrations of ΣPBDFs are shown in Figure 1. Overall, they reveal a steady rise in concentrations from the 1980s onwards, peaking at the surface (2015) at Edgbaston Pool and Wake Valley Pond, and in the second most recent core slice (dated to 2009) at Holt Hall Lake. Prior to the onset of rising concentrations in the 1980s, concentrations were much lower. Inspection of Figure 1 suggests temporal trends in ΣPBDEs and ΣPBDFs are positively correlated and indeed the correlation coefficient for the three sites is significant, ranging between 0.88-0.98 ($p<0.05$ at each site). With respect to changes in the homologue pattern over time, Figure 2 reveals no clear trend at Holt Hall Lake. In contrast, there is a marked shift from HpBDFs to HxBDFs in more recent sediment layers at Edgbaston Pool. Meanwhile at Wake Valley Pond, there is a noticeable decline in the abundance of TBDFs, along with increased abundance of HpBDFs in more recent core slices, as well as the aforementioned presence of OBDF in the top two layers (dated to 2009 and 2015) only. These variable homologue patterns and temporal trends suggest that changes in the relative contributions of different sources of PBDFs over time differ between our three lakes. To our knowledge there is only one study with which our data on PBDF homologue patterns in sediment cores can be compared. In this study of a sediment core from Osaka Bay in Japan that covered the period 1904-2000, OBDF was not detected and in declining order of abundance the other homologues followed the order HpBDF>HxBDF>PeBDF>TBDF (Takigami et al, 2005). This homologue pattern most closely resembled that observed in this study at Holt Hall Lake.

Concentrations, Relative Abundance, and Temporal Trends of PXDD/Fs in English Lake Sediments

Table 2 reports concentrations of individual PXDD/Fs and homologue groups in each sediment core slice analyzed in this study. Also included in Table 2 are concentrations of 2-Br-3,7,8-CDD, 2-Br-3,6,7,8,9-CDD, 2-Br-2,7,8-CDF, and 1-Br-2,3,7,8-CDF reported previously in surficial sediments collected from Osaka Bay, Japan (Ohta et al, 2002). Concentrations of these PXDD/Fs in our study are of a similar range to those reported for Osaka Bay. As observed for both PBDEs and PBDD/Fs, concentrations of ΣPXDD/Fs at the two lakes studied for these contaminants do not correspond with the population density of the local authority within which the lake was submitted (Table SD-1). Specifically, t-test comparison shows PXDD/F concentrations at Wake Valley Pond to be statistically indistinguishable ($p>0.05$) from those at Holt Hall Lake. For PXDD/Fs, the concentrations detected were typically two orders of magnitude below those of PBDD/Fs. PXDFs were more abundant than PXDDs in every core slice analysed from both locations where PXDD/Fs were determined, with PXDFs typically 2-3 times more abundant. There was no clear temporal trend in the ratio of PXDFs:PXDDs at either lake. Moreover, the homologue pattern is broadly similar at both lakes and does not appear subject to temporal variation.

Temporal trends in concentrations of PXDD/Fs differ between the two lakes in which they were measured. Concentrations at Wake Valley Pond peak in the oldest slice (1954) analyzed at this location and then steadily decrease through to the present (2015). In slight contrast, concentrations at Holt Hall Lake rise from 1935 to 1976, before declining through to the uppermost layer (2015). In contrast to the significant positive correlation between ΣPBDEs and ΣPBDFs at all three lakes, concentrations of ΣPBDEs are not significantly correlated ($p>0.05$) with those of ΣPXDD/Fs. Likewise, ΣPBDD/Fs are not correlated with ΣPXDD/Fs ($p>0.05$). Overall, this suggests that the sources of PXDD/Fs are different to those of PBDD/Fs, and that the manufacture and use of PBDEs does not appear to be a source of PXDD/Fs.

Conclusions

Concentrations of PXDD/Fs in radiometrically-dated sediment cores from 3 English lakes decreased over time to the present. In contrast, concentrations of PBDEs increased towards the present and were significantly correlated with concentrations of PBDFs in all three lakes. These findings suggest that PBDEs do not appear to be a source of PXDD/Fs and that the sources of PXDD/Fs are different to those of PBDFs. Moreover, while the correlation between PBDEs and PBDFs implies that increased use of PBDEs has contributed substantially to environmental contamination with PBDFs; examination of PBDF homologue patterns implies emissions from combustion activities such as waste incineration and iron ore sintering are likely also important. Concentrations of PBDEs in all samples are dominated by BDE-209 which is the main consitutent of the Deca-BDE formulation most widely used in the UK. At two of the three lakes studied, the concentrations of BDE-209 were highest in the sediment layers dated to 2012 and 2009, rather than in the surface layer dated to 2015. This may indicate that recent bans and resrtictions on the manufacture and use of Deca-BDE may be starting to take effect and reduce concentrations in the environment.

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Supplementary Data

Supplementary data to this article can be found online at

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Table 1: Concentrations of ΣPBDEs and ΣPBDD/Fs (ng/g dry weight) in surficial sediments from this study with those in soil and sediments from selected other studies

Matrix, Location	ΣPBDD/F	ΣPBDE	Reference
Fresh water sediments			
Edgbaston Pool, UK	7.1	210	This Study
Holt Hall Lake, UK	0.49	18	This Study
Wake Valley Pond, UK	0.49	21	This Study
Edgbaston Pool, UK[a]	-	120	Yang et al, 2016
Holt Hall Lake, UK[a]	-	10	Yang et al, 2016
Wake Valley Pond, UK[a]	-	9.8	Yang et al, 2016
Surficial Sediments, River Thames, UK	-	180 (mean)	Ganci et al, 2019
Clyde Estuary, UK (core slices)	-	1-2,600	Vane et al, 2010
Scotland, UK (core slices)	-	2.3-98,000	Webster et, 2008
Rural/urban lakes, Sweden	0.44-0.54	-	Hagberg et al, 2005
Urban river, Sweden	0.41-1.7	29-62	Lundstedt, 2016
Rural lake Sweden	0.082-0.085	4.4-16	Lundstedt, 2016
Urban lake, China	0.00048-0.0057	-	Zhou et al, 2012
Stream at dump site, Peru	0.012-0.074	3.7-6.1	Naturvårdsverket, 2011
Lake, industrial area, Thailand	0.037-1.5	3.4-58	Naturvårdsverket, 2011
Marine sediments			
Hong Kong/Korea	nd.-0.46	-	Terauchi et al, 2009
Tokyo Bay, Japan	0.0052-0.070	10-78,050	Choi et al, 2003
Osaka, Japan	0.0041-0.077	8.0-352	Ohta et al, 2002
Osaka, Japan	0.0024-0.59	53-910	Takigami et al, 2005
Coastal and offshore, Sweden	0.050-10	-	Lundstedt, 2016
Rural Soil			
Lanna, Sweden	0.028-0.054	0.065-1.3	Lundstedt, 2016
Urban soil			
Umeå and Norrköping, Sweden	0.0011-0.22	0.18-66	Lundstedt, 2016
Bangalore and Chennai, India	0.0060-0.31	-	Ramu et al, 2008
Kyoto, Japan	0.28	-	Hayakawa et al, 2004
Industrial area, China	nd.-0.43	2.03-269	Ma et al, 2008; Ma et al, 2009
Industrial area, Thailand	0.019-0.16	1.8-13	Naturvårdsverket, 2011
Dump site, Peru	0.0086-0.32	3.6-92	Naturvårdsverket, 2011

[a] Data for core slices dated to 2008 for Edgbaston Pool and for 2009 for both Holt Hall Lake and Wake Valley Pond.

Table 2: Concentrations (pg/g OC) of PXDD/Fs in Sediment Core Slices from Wake Valley Pond and Holt Hall Lake with Comparative Data from Osaka Bay, Japan

Location	**Congener/ Homologue/ Year**	**2015**	**2009**	**2005**	**2004**	**1999**	**1993**	**1985**	**1977**	**1969**	**1965**	**1954**	**1935**
Wake Valley Pond	2-Br-7,8-CDD	0.023	0.16	0.24		0.32	0.4	0.035			0.079	<0.032	
Holt Hall Lake	2-Br-7,8-CDD	1.1	2.8		2.6	3.4		1.1	<0.025	<0.024		<0.021	<0.021
Wake Valley Pond	*Total Br-2CDD*	0.73	1.9	1.9		2.7	2.3	3.6			0.8	9.3	
Holt Hall Lake	*Total Br-2CDD*	1.8	4.1		4.0	5.3		2.2	11	7.1		2.3	<0.021
Wake Valley Pond	2-Br-3,7,8-CDD	0.081	<0.028	<0.027		0.12	0.22	0.22			0.29	<0.047	
Holt Hall Lake	2-Br-3,7,8-CDD	0.02	0.049		0.054	0.16		0.08	1.4	<0.035		<0.031	<0.03
Osaka Bay, Japan[a]	2-Br-3,7,8-CDD	0.84-6.5											
Wake Valley Pond	*Total Br-3CDD*	1.5	2.2	2.8		3.8	3	3.5			6.2	9.3	
Holt Hall Lake	*Total Br-3CDD*	0.77	2.1		2.4	2.7		2.4	18	<0.027		<0.019	<0.018
Wake Valley Pond	2,3-Br-7,8-CDD	<0.015	<0.017	<0.016		<0.016	<0.017	<0.016			<0.016	<0.029	
Holt Hall Lake	2,3-Br-7,8-CDD	<0.013	0.095		0.062	<0.018		0.034	<0.022	<0.021		<0.019	<0.018
Osaka Bay, Japan[a]	2,3-Br-7,8-CDD	Not detected											
Wake Valley Pond	*Total 2Br-2CDD*	0.48	0.64	0.87		1.2	1.5	1.8			1.2	4.4	
Holt Hall Lake	*Total 2Br-2CDD*	0.33	0.79		0.82	1.1		0.97	5.0	2.2		0.62	<0.017
Wake Valley Pond	1-Br-2,3,7,8-CDD + 2-Br-1,3,7,8-CDD*	<0.018	<0.021	0.37		<0.02	<0.021	<0.02			<0.021	<0.032	
Holt Hall Lake	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
Osaka Bay, Japan[a]	1-Br-2,3,7,8-CDD	Not detected											
Wake Valley Pond	*Total Br-4CDD*	1.7	1.8	2.8		3.8	5.9	4.6			7	5.7	
Holt Hall Lake	*Total Br-4CDD*	0.47	1.9		1.0	1.9		<0.021	<0.022	<0.021		0.71	<0.018
Wake Valley Pond	2-Br-3,6,7,8,9-CDD	<0.015	<0.017	<0.016		<0.016	<0.017	<0.016			<0.016	<0.029	
Holt Hall Lake	2-Br-3,6,7,8,9-CDD	<0.013	<0.015		<0.016	<0.018		0.6	<0.022	<0.021		<0.019	<0.018
Osaka Bay, Japan[a]	2-Br-3,6,7,8,9-CDD	Not detected - 0.32											
Wake Valley Pond	*Total Br-5CDD*	1	0.82	3.5		2.2	5.1	7			7.5	15	
Holt Hall Lake	*Total Br-5CDD*	<0.018	0.11		<0.01	<0.012		0.6	<0.022	<0.021		<0.019	<0.018

Location	**Congener/ Homologue/ Year**	**2015**	**2009**	**2005**	**2004**	**1999**	**1993**	**1985**	**1977**	**1969**	**1965**	**1954**	**1935**
Wake Valley Pond	2-Br-7,8-CDF	0.77	1	0.88		<0.01	2	2.7			<0.01	<0.018	
Holt Hall Lake	2-Br-7,8-CDF	<0.008	<0.01		<0.01	<0.012		0.53	<0.014	<0.013		<0.012	<0.012
Wake Valley Pond	*Total Br-2CDF*	6.9	16	16		26	17	25			22	62	
Holt Hall Lake	*Total Br-2CDF*	4.7	7.9		7.7	12		9.6	88	89		15	9.5
Wake Valley Pond	2-Br-6,7,8-CDF + 3-Br-2,7,8-CDF[*]	<0.012	0.13	0.17		0.3	0.65	0.46			0.076	<0.023	
Holt Hall Lake	2-Br-6,7,8-CDF + 3-Br-2,7,8-CDF[*]	0.07	0.28		0.18	0.40		1.3	5.1	<0.017		0.63	<0.015
Osaka Bay, Japan[a]	3-Br-2,7,8-CDF	Not detected-2.0											
Wake Valley Pond	*Total Br-3CDF*	4.3	6	6.4		8.4	8.7	10			11	57	
Holt Hall Lake	*Total Br-3CDF*	2.5	4.8		5.3	8.8		5.0	44	49		6.6	3.1
Wake Valley Pond	1-Br-2,3,7,8-CDF	0.022	<0.014	0.047		0.042	0.66	<0.012			<0.012	<0.021	
Holt Hall Lake	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
Osaka Bay, Japan[a]	1-Br-2,3,7,8-CDF	Not detected											
Wake Valley Pond	*Total Br-4CDF*	1.5	1.6	2.6		3.6	6.4	5.8			2	20	
Holt Hall Lake	*Total Br-4CDF*	1.8	5.0		2.4	5.2		0.81	7.3	<0.016		3.5	4.4
Wake Valley Pond	∑PXDD	5.4	7.5	12		14	18	20			23	43	
Holt Hall Lake	∑PXDD	3.3	9.1		8.2	11		6.0	34	9.3		7.1	<0.03
Wake Valley Pond	∑PXDF	13	24	25		38	32	41			34	140	
Holt Hall Lake	∑PXDF	9.0	18		15	26		15	140	140		25	17
Wake Valley Pond	∑PXDD/F	18	31	37		51	50	61			57	180	
Holt Hall Lake	∑PXDD/F	12	27		24	37		21	170	150		32	17

[a] Range (pg/g dry weight) surficial sediments from Osaka, Japan (n=6) (Ohta et al, 2002) – detection limits not reported

Figure 1: Temporal Trends in Concentrations (ng/g OC) of ΣPBDE, ΣPBDF, and ΣPXDD/F in 3 English Lake Sediment Cores

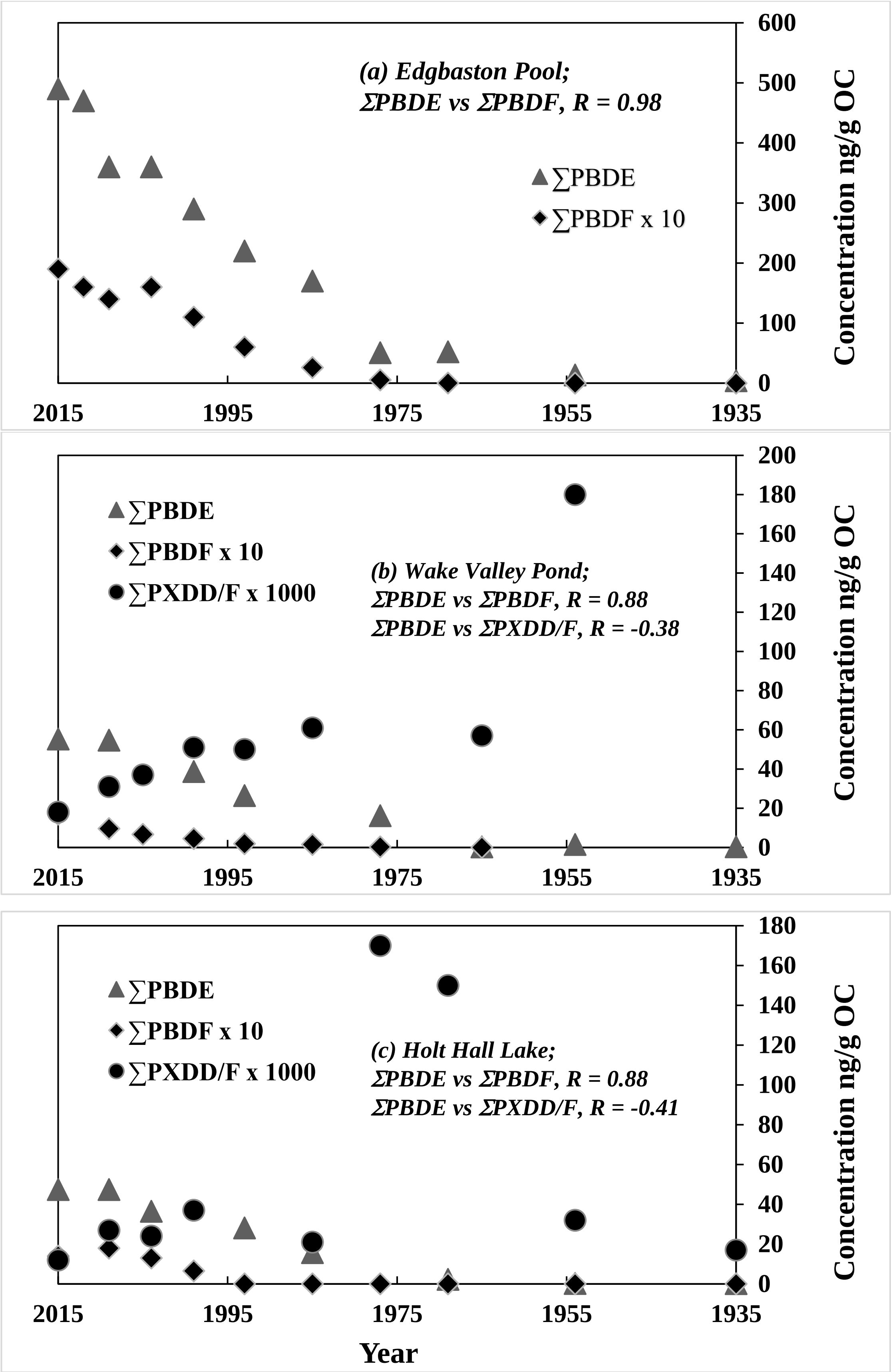
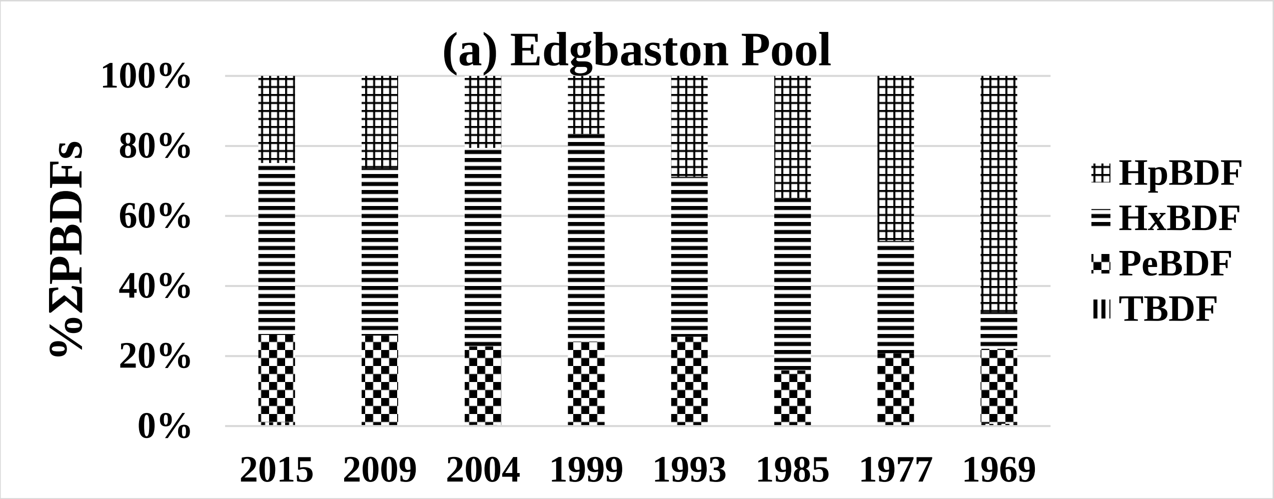
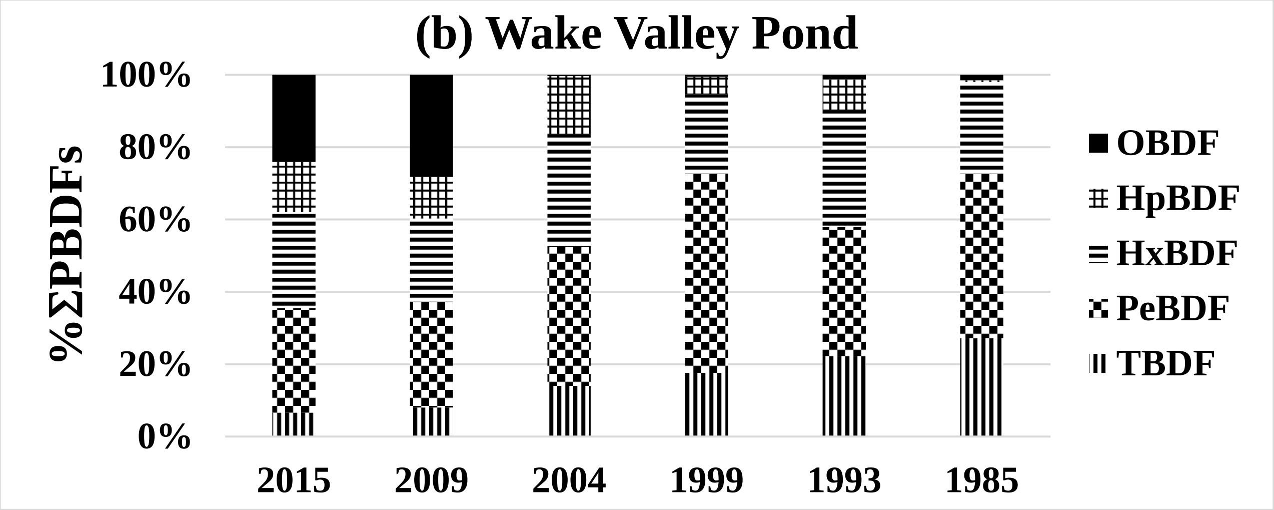
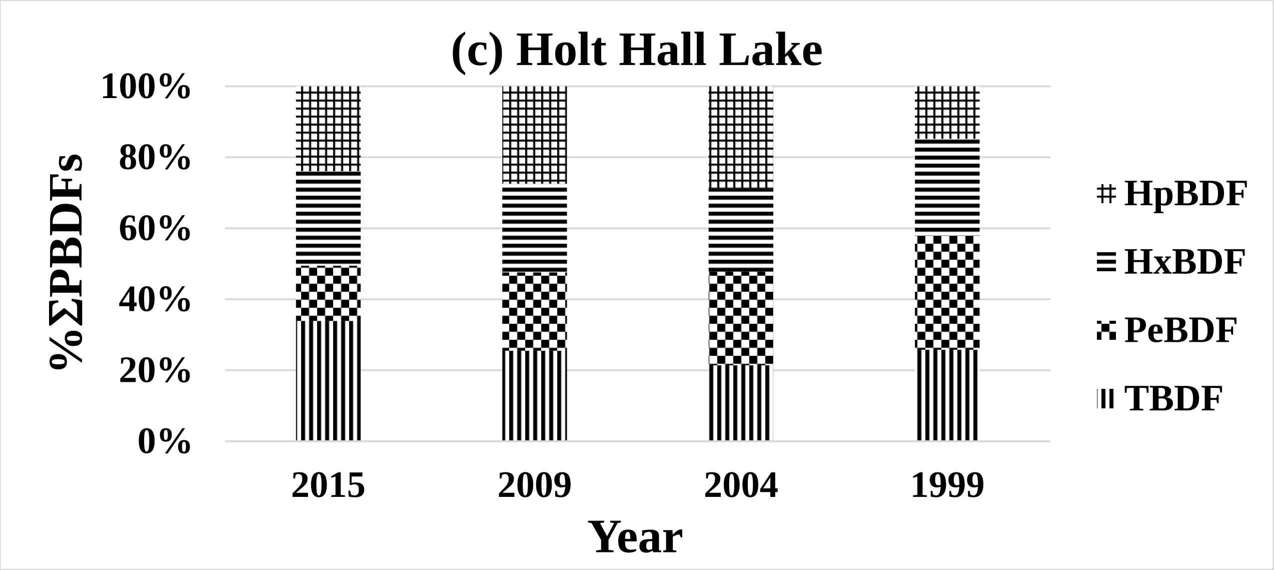


Figure 2: Temporal Trends in Relative Contributions of PBDF Homologues to ΣPBDF Concentrations in 3 English Lake Sediment Cores


(a) Edgbaston Pool


(b) Wake Valley Pond


(c) Holt Hall Lake