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### Hexabromocyclododecanes, polybrominated diphenyl ethers, and polychlorinated biphenyls in radiometrically dated sediment cores from English lakes, ~1950-present

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4 ***Hexabromocyclododecanes, Polybrominated Diphenyl Ethers, and***  
5 ***Polychlorinated Biphenyls in Radiometrically Dated Sediment Cores***  
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7 ***from English Lakes, ~1950-Present***  
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4 **ABSTRACT**  
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6 This paper reports input fluxes between ~1950 and present, of polychlorinated biphenyls (PCBs),  
7 polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecanes (HBCDs) in  
8 radiometrically-dated sediment cores from 7 English lakes. Fluxes of PCBs at all but one location  
9 prone to significant sediment resuspension peaked in the late-1960s/early-1990s, before declining  
10 thereafter. Input fluxes of HBCDs at all sites increased from first emergence in the mid-1960s.  
11 Thereafter, fluxes peaked in the late-1980s/early-2000s, before declining through to the present,  
12 except at the most urban site where HBCD fluxes are still increasing. Trends of PBDEs  
13 predominant in the Penta-BDE and Octa-BDE formulations vary between sites. While at some  
14 locations, fluxes peaked in the late-1990s/early-2000s; at others, fluxes are still increasing. This  
15 suggests the full impact of EU restrictions on these formulations has yet to be felt. Fluxes of  
16 BDE-209 have yet to peak at all except one location, suggesting little discernible environmental  
17 response to recent EU restrictions on the Deca-BDE product. Strikingly, fluxes of BDE-209 in  
18 the most recent core slices either exceed or approach peak fluxes of  $\Sigma$ PCBs, implying substantial  
19 UK use of Deca-BDE. Excepting HBCDs, inventories of our target contaminants correlated  
20 significantly with local population density, implying substantial urban sources.  
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## 1. Introduction

Considerable concern exists about environmental contamination with persistent organic chemicals like polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCD). These widely used compounds possess environmental persistence, potential for long-range atmospheric transport and bioaccumulation, and elicit adverse effects in humans and/or wildlife. Consequently, PCBs, HBCD, and those PBDE congeners that constitute the Penta- and Octa-BDE commercial products, are listed under the United Nations Environment Program's Stockholm Convention on Persistent Organic Pollutants (POPs). The Deca-BDE commercial product is currently under active consideration for listing under the Stockholm Convention. Moreover, manufacture and new use of all of the aforementioned is either banned or restricted by many jurisdictions. Against this backdrop, there is a clear need to monitor the efficacy of such actions; for example, by monitoring temporal trends in environmental contamination.

Monitoring such water bodies can provide information on the spatial distribution of chemical contaminants within a specific region, with study of rural sites generating insights into the influence of factors like population density and industry on levels and patterns of contamination. Moreover, of particular relevance to this study, sediment deposited in lakes over time can represent a record of contaminant inputs into lacustrine systems. Therefore, monitoring chemical contaminants in sediment cores from geographically dispersed lakes can: 1) enhance understanding of their temporal and spatial trends in the environment; 2) permit assessment of differences in the environmental behaviour of different contaminants; and 3) facilitate evaluation of environmental responses to bans and/or control measures. Our hypotheses were that: (a) contamination would correlate positively with the degree of urbanisation, (b) there is significant compound-specific variation in spatial trends of contamination that is at least partly driven by the relative capacity of our target contaminants to undergo long-range atmospheric transport, and (c) temporal trends of our target chemicals will reflect trends in their manufacture and use. To test these hypotheses, we studied temporal trends of PCBs, tri-through-deca-BDEs, and HBCDs in sediment cores from seven English lakes, representing a mix of urban and rural sites.

## 2. Experimental

### 2.1 Sampling locations

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4 A map of our sampling locations is given in Figure S1 as supporting information (SI), with  
5 additional information about individual sites supplied in Table S1. Locations studied are the same  
6 seepage lakes for which we have previously reported concentrations of HBCDs in water, surficial  
7 sediment, and fish (Harrad et al., 2009), and tri-through-hexa-BDEs in water (Yang et al., 2014).  
8 For cost and operational reasons (e.g. shallow lakes were preferred as this facilitates coring),  
9 sediment cores were taken from only seven out of the nine sites depicted in Figure S1.  
10 Specifically: Crag Lough, Edgbaston Pool, Fleet Pond, Holt Hall Lake, Marton Mere, Slapton  
11 Ley, and Wake Valley Pond. One sediment core from each lake was collected in July 2011 (March  
12 2012 for Marton Mere), covering sedimentation from ~1950 to the date of sampling.  
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## 21 *2.2 Sampling & sectioning*

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24 Sediment core sampling was conducted from a boat using a push corer polycarbonate tube of  
25 inner diameter 71 mm. After collection from a flat area of the lake basin near the deepest point,  
26 sediment cores (varying in diameter from about 30 cm at SLT to about 100 cm at EDGB, HOLT,  
27 and WAKE) were kept vertical and sectioned on site with an extruding interval of 1 cm. Each  
28 segment was divided into two during the sectioning procedure: two thirds kept for analysis of our  
29 target contaminants; with the remaining one third used for radiometric dating and determination  
30 of sediment density, water and total organic carbon (TOC) content. After freeze-drying, each 1 cm  
31 core slice was homogenized. Thereafter, based on information from our radiometric dating results,  
32 we combined 1 cm core slices from the same core to generate a series of pooled core slice  
33 samples that each represented around five years of sedimented material. In total, we analyzed 74  
34 such pooled samples. A further core slice was analyzed from the bottom of the core taken from 4  
35 of our lakes, to provide an indication of concentrations of our target contaminants prior to ~1950.  
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## 46 *2.3. Sediment chronologies and sedimentation rates*

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49 Radionuclide data for all sites is given as Appendix in SI. Sedimentation chronology versus depth  
50 varied between cores, i.e. sediments formed in the last century range between the top 20 cm at  
51 Fleet Pond to the top 70 cm at Holt Hall Lake (Figure S2A). Sedimentation rates in these cores  
52 exceed considerably those from remote UK locations, where the top 10 to 18 cm in most cores  
53 equates to ~150 years sedimentation (Yang and Rose, 2003). Generally, sedimentation rates have  
54 increased 3 to 6 fold in most of our cores over the last 100 years or so, up to 11 and 17 times at  
55 Marton Mere and Crag Lough. Figure S2B shows such changes in sedimentation rates in  
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4 individual cores are not smooth, incorporating occasional peaks of rapid and greatly increased  
5 sediment accumulation, which may be attributable to associated changing anthropogenic impact on  
6 individual catchments.  
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#### 9 10 *2.4. Analytical methods*

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13 Details of methods used to radiometrically date (using  $^{210}\text{Pb}$ ) and measure sediment density,  
14 water and loss on ignition (LOI), are given as SI. For determination of concentrations of target  
15 contaminants in sediment samples, 5 g each of both hydromatrix and sodium sulfate (both  
16 pre-cleaned with hexane and acetone) were loaded into pre-cleaned 40 mL extraction cells. An  
17 aliquot of each freeze-dried and homogenized sediment core slice sample (typically 5 g,  
18 accurately weighed) were treated with  $^{13}\text{C}$ -labeled BDE-28, BDE-47, BDE-99, BDE-153, and  
19 BDE-209 (Wellington Laboratories, Canada), PCBs 34, 62, 119, 131, and 173 (Dr. Ehrenstorfer  
20 GmbH, Germany), and  $^{13}\text{C}_{12}$ -labelled  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCDs (Wellington Laboratories, Canada) as  
21 internal (or surrogate) standards. Samples were extracted using a Speed Extractor (E-916 mode,  
22 BÜCHI, Switzerland) with hexane and acetone (1:1, v/v) at 100 °C and 120 bar for 3 cycles of 5  
23 min per cycle. Extracts were collected in 240 mL glass collection vials containing 5 g pre-cleaned  
24 copper wire (for sulfur removal) and stored overnight.  
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36 Detailed descriptions of the procedures used to purify sediment core extracts prior to instrumental  
37 analysis are available as SI. In summary, concentrated crude extracts (1 mL) were passed through  
38 a hydrophilic PTFE filter before purification via gel permeation chromatography, followed by  
39 florisil chromatography and concentration for instrumental analysis.  
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### 43 **3. Instrumental analysis**

#### 44 *3.1 GC-MS*

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47 Concentrations of tri-through-hexa-BDEs and PCBs were determined using an Agilent 6850-5975  
48 GC-MSD operated in electron ionization, selective ion monitoring mode fitted with a VF-5ms  
49 capillary column (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ). For PCB #s 28, 52, 101, 118, 153, 138 and 180,  
50 the oven temperature program was 140 °C for 2 mins, ramped to 215 °C at 5 °C  $\text{min}^{-1}$  and held for  
51 5 mins, then 5 °C  $\text{min}^{-1}$  to 280 °C before a ramp at 4 °C  $\text{min}^{-1}$  to 290 °C for 13 mins. Ions  
52 monitored were: m/z 255.95, 257.95, 289.95, 291.95, 325.90, 327.90, 359.90, 361.90, 393.85,  
53 and 395.85. The analytical method for tri to hexa-BDEs (BDE- 17, -28, -49, -47, -66, -100, -99,  
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4 -85, -154, and -153) was as reported previously (Harrad and Hunter, 2006). Brief details of  
5 GC-MS conditions are given as SI.  
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### 7 8 9 *3.2 LC-MS/MS*

10 HBCDs as well as BDEs-183 and -209 were determined via LC-ESI-MS/MS and  
11 LC-APPI-MS/MS respectively, using a dual pump Shimadzu LC-20AB Prominence liquid  
12 chromatograph interfaced with a Sciex API 2000 triple quadrupole mass spectrometer (Harrad et  
13 al., 2009; Abdallah et al., 2009). Further details are provided as SI.  
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### 19 *3.3 QA/QC*

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21 Method accuracy was assessed via triplicate analysis of NIST SRM2585 (Organics in House  
22 Dust). Results agreed well with certified (PCBs and PBDEs) and indicative (HBCDs) values – see  
23 Table S2. Recoveries of the <sup>13</sup>C<sub>12</sub>-labeled BDE-28, BDE-47, BDE-99, BDE-100,  
24 BDE-153, BDE-154, BDE-183, BDE-209 internal (or surrogate) standards ranged from 92 to 107%  
25 with an average of 97%. Recoveries of PCB and HBCD internal standards were not determined.  
26 However, in every sample, the signal-to-noise ratio of PCB and HBCD internal (or surrogate)  
27 standards exceeded substantially the minimum 20:1 ratio stipulated elsewhere as acceptable  
28 (Ambidge et al., 1990).  
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37 One method blank consisting of sodium sulfate and hydromatrix was analysed alongside each  
38 batch of 11 samples. None of the target PCBs, PBDEs, and HBCDs were found at detectable  
39 levels in any blanks. Assuming a 5 g sample mass; method detection limits (MDL) were: 0.001,  
40 0.001, 0.002 ng g<sup>-1</sup> dw (0.003, 0.002, 0.005 ng g<sup>-1</sup> TOC) for α-, β-, and γ-HBCD, respectively;  
41 0.003-0.05 ng g<sup>-1</sup> dw (0.01-0.13 ng g<sup>-1</sup> TOC) for PBDEs; and 0.03 ng g<sup>-1</sup> dw (0.08 ng g<sup>-1</sup> TOC) for  
42 PCBs. These values were calculated as described in SI. As the recoveries of HBCDs and PCBs  
43 were not determined, MDLs for these contaminants were estimated assuming a recovery of  
44 100%.  
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### 53 *3.4 Statistical methods*

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55 All statistics in this study were conducted using IBM SPSS Statistics 21, and Microsoft Excel  
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## 59 **4. Results and discussion**

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#### 4.1 Temporal trends

To compensate for within-core variations in sedimentation rates, concentrations were converted to input fluxes ( $\text{ng cm}^{-2} \text{ year}^{-1}$ ) thus:

Input flux =  $[(\text{Concentration (dry mass basis)} * \text{Dry Mass}) / \text{Sedimentation Years}] / \text{Surface Area of corer tube (39.59 cm}^2)$

Where “Sedimentation Years” = the period of time (e.g. 5 years) represented by each pooled core slice analyzed. It should be noted that possible *in-situ* contaminant degradation, introduces some unquantifiable uncertainty into our estimates of input flux.

Overall, highest input fluxes were generally found at Edgbaston Pool and Marton Mere, with the lowest detected at Crag Lough and Slapton Ley. Data on input fluxes and concentrations of target contaminants in each sediment core slice analysed are provided as SI (Figure S3 and Table S3, respectively).

Sediment profiles of input fluxes of our contaminants over time at Edgbaston Pool and Crag Lough are shown in Figure 1. These sites were chosen as they are respectively the most urban and most remote sites (Table S1) monitored. Figure S3 depicts data for other sites. Each contaminant class displayed different temporal trends. In all instances, concentrations of target contaminants in core slices dated to decades prior to ~1950 were below detection limits for all the compounds, consistent with the lack of UK production and widespread use of these chemicals prior to the second half of the 20<sup>th</sup> century. The only exception was PCBs, which were found in a core slice from Edgbaston dated to the early 1900s, at a concentration ( $15.7 \text{ ng g}^{-1} \text{ TOC}$ , or  $4.03 \text{ ng g}^{-1} \text{ dw}$ ) that ranged between 3.4-21% (average 7.6%, TOC basis); or 3.1-17% (average 6.8%, dry weight basis) of that determined in later sediment core samples from the same site. This could reflect some minor usage of PCBs in the UK prior to the onset of UK production and extensive use in 1954 (Harrad et al, 1994).

**PCBs** Contrary to PBDEs and HBCDs, temporal trends of PCBs in UK lake sediment cores are comparatively well-characterised (Gevao et al., 1997; Sanders et al., 1992; Rose and Rippey, 2002). Our data show PCB contamination at all lakes in this study increases from the lowest depth slices dated ~1950, peaking generally between the late-1960s and mid-1980s, before declining



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4 steadily thereafter. The one notable exception is Fleet Pond (which experiences significant  
5 resuspension of sediment as it is very shallow and wind-stressed), where PCB fluxes are highest  
6 in surficial sediment. Similar to the peaking time in our lakes, concentrations of PCBs were  
7 reported to start rising in sediments from tidal flats of Haizhou Bay, China in the mid-1950s  
8 following a zig-zag pattern, and peaked in 2005 (Zhang et al., 2014). Another study to compare  
9 with is that of Ruiz-Fernández et al. (2014). In this study, historically consistent increasing trends  
10 were found for both PCB concentrations and input fluxes in two remote lacustrine environments  
11 (EI Tule and Santa Elena lakes) in Mexico, with highest levels observed in surface  
12 sediments. Fleet Pond aside, temporal trend data accords with both those in previous UK studies,  
13 and historical trends in UK manufacture and use. This lends verisimilitude to our  
14 radiometrically-assigned core slice dates.

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17 **PBDEs** For the purposes of discussion, we assume the sum of tri-through-hexa-BDE congeners  
18 are representative of the Penta-BDE formulation, BDE-183 represents the Octa-BDE product,  
19 and BDE-209 represents Deca-BDE. In each case, the date at which PBDEs were first detected in  
20 our samples was between the mid-1960s to around 1970, with the precise date varying according  
21 to location and compound.

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Fluxes of Penta-BDE appear to have peaked in the late 1990s/early 2000s at three out of seven  
English lakes in this study. In cores from our other locations, fluxes are still increasing. There are  
no obvious discernible reasons for this spatial variation – for example, while discussed later  
(Table 1), Penta-BDE inventories are positively correlated with the local population density, the  
variable temporal trends in input fluxes are not related to the population density of the site. While  
the apparent peak at some locations may be interpreted as an encouraging sign of a positive  
response to the introduction of EU control measures in 2004 on new production and usage of  
Penta-BDE; the continuing increase in fluxes at other locations suggests the full beneficial impact  
of these control measures has yet to be felt.

Temporal trends in BDE-183 input fluxes varied between sites. Its first emergence at all sites in  
this study was always (with the exception of Crag Lough) later than that of BDE-209 and either  
at the same time or later than Penta-BDE. While fluxes of BDE-183 appear to have peaked at  
most sites in the late-1990s/early-2000s; at other sites, fluxes peak in surficial sediment. In  
general, these trends suggest that – while there are encouraging signs of a recent reduction in

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4 BDE-183 inputs, the 2004 EU restrictions on manufacture and use of the Octa-BDE product has  
5 not yet been fully successful in reducing environmental contamination.  
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9 In contrast to BDE-183, input fluxes of BDE-209 generally increased smoothly following its  
10 initial emergence at most sites around 1960, and showed no obvious decline in more recent layers  
11 except at Marton Mere, the most contaminated lake. The continuing increase in input fluxes of  
12 BDE-209 at all but one location, implies strongly that recent (2008) EU restrictions on  
13 manufacture and use of Deca-BDE have yet to translate into reduced contamination of the UK  
14 environment. This is not inconsistent with a “lag time” between introduction of emissions  
15 controls and environmental response, and continued monitoring of PBDE temporal trends is  
16 required.  
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20 By comparison, historically increasing contamination trends of PBDEs (BDE-209 not analyzed)  
21 and input fluxes were observed in two remote lakes (EI Tule and Santa Elena) in Mexico  
22 (Ruiz-Fernández et al., 2014). While interestingly, variable temporal trends were observed in  
23 concentrations of BDE-209 and  $\Sigma_{16}$  penta-nona-BDEs in six sediment cores collected in 2002/3  
24 from the highly industrialized inner Clyde Estuary in Scotland, UK (Vane et al., 2010). The highly  
25 industrialized nature of the Clyde river was reflected by the fact that the upper range  
26 concentrations detected, exceed significantly those observed in this study.  
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30 **HBCDs** At most of our locations, HBCD input fluxes increased rapidly following their first  
31 emergence in the 1960s. While at the most urban site (Edgbaston Pool, Birmingham), HBCD  
32 fluxes increased throughout the monitored core and showed no sign of decreasing or levelling off;  
33 fluxes at most sites peaked earlier at various points between the late-1980s and early-2000s,  
34 followed by a clear decline. While to our knowledge, ours is the first published study reporting  
35 temporal trends of HBCD in UK lake sediments, Law et al. (2012) reported a sharp increase in  
36 concentrations of HBCDs in the blubber of harbour porpoises originating from UK waters  
37 between 2000 and 2001, followed by a rapid decrease between 2003 and 2004. The authors  
38 attributed this to the closure in 2003 of an HBCD production facility in northeast England  
39 coupled with reduced HBCD sales in the UK leading up to that point.  
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#### 56 *4.2 Relative abundance of target contaminants*

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59 Fluxes of BDE-183 (Octa-BDE) at all sites are lower than those of tri-through-hexa-BDEs  
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4 (Penta-BDE) and BDE-209 (Deca-BDE). This is consistent with previous observations based on  
5 indoor dust contamination (Harrad et al., 2008a, 2008b), that UK use of Octa-BDE was  
6 modest. We examined our data for further such insights. While more abundant than BDE-183,  
7 input fluxes of  $\Sigma$ tri-through-hexa-BDEs across all sites are either lower than, or of similar  
8 magnitude to those of  $\Sigma$ HBCDs, and are exceeded substantially by those of BDE-209 and PCBs.  
9 This is consistent with available information about the relative use volumes of our target  
10 contaminants (BSEF 2003; Harrad et al., 1994).  
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18 In sediment samples dated up until the late-20<sup>th</sup> century/early-21<sup>st</sup> century, PCBs were the  
19 dominant contaminant. Since then (the precise timing varies between locations), input fluxes of  
20 BDE-209 have increased substantially relative to those of  $\Sigma$ PCBs. As a result, fluxes of BDE-209  
21 exceed those of  $\Sigma$ PCBs in the top 2 core slices at Edgbaston, Marton Mere, and Fleet Pond - the  
22 three most urban locations in our study. At the other less urban sites of Crag Lough, Holt Hall  
23 Lake, and Wake Valley Pond; fluxes of BDE-209 are either yet to exceed those of  $\Sigma$ PCBs, or - in  
24 the case of Slapton Ley - exceed  $\Sigma$ PCBs in surficial sediment only. We hypothesize the higher  
25 BDE-209: $\Sigma$ PCB ratios at more urbanized locations, arise because the largely urban contemporary  
26 emissions of BDE-209 exceed those of PCBs. In time, as BDE-209 undergoes environmental  
27 transport from urban source regions, we suggest BDE-209: $\Sigma$ PCB ratios in more rural/remote sites  
28 will increase. To our knowledge, this study provides the first comparison of BFR and PCB  
29 temporal trends in the same lake sediment samples outside North America; our findings are  
30 consistent with observations that in the early 2000s, concentrations of BDE-209 in Lake Superior  
31 had reached or even exceeded the historic peak PCB concentrations recorded (Song et al., 2004).  
32 In contrast, sediment concentrations of PCBs were found five times lower than that of BDE-209  
33 in Lake Thun, Switzerland (Bogdal et al., 2010).  
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#### 48 49 *4.3 Contaminant inventories*

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51 Contaminant inventories ( $\text{ng cm}^{-2}$ ) were calculated to quantify the total mass deposited since  
52 ~1950 normalized to surface area of each of our target contaminants in each lake in this study.  
53 Inventories were calculated using equation 1:  
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$$56 \text{Inventory} = \Sigma [\text{Concentration (dry mass basis)} * \text{Dry Density} * \text{Core Slice Thickness}] \quad (1)$$

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59 Figure 2 (note the different scale for  $\Sigma$ PCBs) shows  $\Sigma$ PCBs are dominant at all but one of our  
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4 locations, followed by BDE-209,  $\Sigma$ HBCDs, Penta-BDEs, and BDE-183. This is consistent with  
5 our observations about the relative abundance of target contaminants in individual core slices. The  
6 one exception in this study was Fleet Pond, where the inventory of BDE-209 ( $49 \text{ ng cm}^{-2}$ )  
7 slightly exceeded that of PCBs ( $48 \text{ ng cm}^{-2}$ ). Consistent with our findings, the total accumulated  
8 mass of POPs in sediment cores from Lake Thun, Switzerland, followed the order:  
9  $\Sigma$ PCBs > BDE-209 >  $\Sigma$ HBCDs ~ tri-hepta-BDEs (Bogdal et al., 2008). Also in agreement with our  
10 study, historical concentrations of BDE-209 in two sediment cores from the Western Scheldt,  
11 Belgium, consistently exceeded those of tri-hexa-BDEs by between one and three orders of  
12 magnitude (Covaci et al., 2005). However, this same Belgian study reported concentrations of  
13 BDE-209 to exceed those of PCBs by one to two orders of magnitude. This higher contribution of  
14 BDE-209 in the Western Scheldt was hypothesized to result from the heavily industrial nature of  
15 the catchment area, which may lead to a slower decline in PCB inputs, coupled with a  
16 concomitantly rapid increase in those of BDE-209 (Covaci et al., 2005). Meanwhile, in sediment  
17 cores from Lake Michigan (n=3) and Lake Huron (n=3), inventories of BDE-209  
18 exceeded slightly those of  $\Sigma_{36}$ PCBs in 5 cores, and were about one order of magnitude higher  
19 than that of  $\Sigma_9$ PBDEs (BDE-28 to -183) (Song et al., 2005a).

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*4.4 Spatial variation in contamination*

Inventories of all target contaminants were greatest at the most urbanized lakes of Edgbaston Pool and Marton Mere, with inventories at the latter exceeding those at Edgbaston Pool because of substantially higher sedimentation rates at Marton Mere (on average  $0.232$  against  $0.054 \text{ g cm}^{-2} \text{ year}^{-1}$  at Edgbaston Pool). These two sites have the lowest catchment ratios (defined as the ratio of lake area to lake catchment area) (both  $0.01$ ), and highest local population densities (both  $>2500 \text{ km}^{-2}$ ) of our studied lakes. By comparison, inventories were consistently lowest at Slapton Ley and/or Crag Lough, which possess both the highest catchment ratios ( $0.05$  and  $0.03$  respectively) and lowest local population densities (both  $\leq 100 \text{ km}^{-2}$ ). Given these apparent relationships, the potential influence on inventories, of lake depth, perimeter, surface area, catchment area, catchment ratio, and population density (both within the area covered by the unitary authority within which the lake is situated (i.e. local) and within a  $25 \text{ km}$  radius of each site) was thus investigated. Due to limited sample size, the Spearman rank correlation coefficient rather than the Pearson correlation coefficient was used.

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4 Such analysis (Table 1) revealed inventories of some contaminants to be correlated significantly  
5 (p<0.01) with local population density, and for BDE-209(p<0.05)with the population density  
6 within a 25 km radius. This is consistent with previous studies of airborne contamination with  
7 PBDEs (Harrad and Hunter, 2006; Sun et al., 2007). Given these observations, coupled with the  
8 abundant use of our target contaminants in consumer goods and construction materials and the  
9 greater prevalence of these in densely-populated areas; we believe contamination in these lakes  
10 results largely from diffuse emissions from the built environment.  
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18 Our statistical analysis also revealed significant (p<0.05 or <0.01) negative linear correlation  
19 between inventories of all target contaminants and lake catchment ratio. This is consistent with  
20 elevated contamination in lakes with surface areas that are small relative to their catchment area.  
21 No significant relationships were detected between contaminant inventories and lake depth,  
22 perimeter, and area.  
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27 While we reported previously the existence of significant spatial variation between  
28 concentrations of Penta-BDEs in water sampled between 2008 and 2012 from 9 English lakes  
29 (including all those sampled here), we did not observe any significant relationship between  
30 Penta-BDE concentrations in water and any of the lake characteristics or population density  
31 metrics used here (Yang et al., 2014). We hypothesize this is because concentrations in lake water  
32 are more susceptible to short-term variations in inputs than our sediment inventory data.  
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39 Consistent with the hypothesis that BDEs-209 and -183 are less susceptible to long range  
40 environmental transport than other contaminants targeted in this study; the ratios of highest to  
41 lowest lake inventories observed were: 7, 28, and 54 for  $\Sigma$ HBCDs,  $\Sigma$ tri-hexa-BDEs, and  $\Sigma$ PCBs,  
42 respectively. These were all exceeded by the values for BDE-209 (82), and BDE-183 (99);  
43 revealing these two PBDEs to display the greatest inter-site variability. We have previously  
44 observed a similarly low inter-site variability (ratio of highest-to-lowest average concentrations =  
45 3.4) in concentrations of HBCDs in water from the same English lakes (Harrad et al., 2009).  
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#### 52 53 *4.5PBDE congener profiles* 54

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56 The relative contribution of BDE-209 to  $\Sigma$ BDE concentrations in all 72 sediment core samples in  
57 which it was detected ranged from 0.331 to 0.995, with mean and median values of 0.86 and 0.92,  
58 respectively. ANOVA revealed average $\pm\sigma_{n-1}$  BDE-209: $\Sigma$ PBDE ratios at Edgbaston Pool  
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(0.93±0.02), Marton Mere (0.94±0.02), Fleet Pond (0.93±0.03), Slapton Ley (0.95±0.02), and Wake Valley Pond (0.90±0.04) exceeded significantly those at Crag Lough(0.57±0.13) and Holt Hall Lake (0.75±0.07) (ANOVA,  $p<0.001$ ). Moreover, ANOVA also revealed the average± $\sigma_{n-1}$  Penta-BDEs:ΣPBDEratios at Edgbaston Pool (0.03±0.01), Marton Mere (0.03±0.02), Fleet Pond (0.06±0.03), Slapton Ley (0.05±0.02), and Wake Valley Pond (0.08±0.03)are significantly ( $p<0.001$ )lower than those detected at Holt Hall Lake(0.23±0.06) and Crag Lough (0.42±0.13). Such variations in the relative abundances of congeners representing the Penta-BDE and Deca-BDE formulations, may suggest spatial variation in local inputs of these formulations (e.g. generally lower inputs of Deca-BDE at Crag Lough and Holt Hall Lake than elsewhere). Alternatively (or perhaps additionally), these spatial differences in PBDE pattern may be attributable to differences between the environmental fate and behaviour of PBDEs associated with the Penta-BDE and Deca-BDE formulations. For example, the hypothesized lower capacity of BDE-209 to undergo long-range atmospheric transport is consistent with its lower relative abundance at more remote/rural sites like Crag Lough and - to a lesser extent - Holt Hall Lake. As a caveat to this, the local population density of the Slapton Ley site (<99 km<sup>-2</sup>) is similar to Crag Lough's; thereby indicating the observed congener pattern at each site is an integral of more than one factor.

While BDE-209 has consistently been the predominant PBDE in our English lake sediments since its emergence, the extent of its dominance has fluctuated over time. The contribution of BDE-209 decreased from around 1960 reaching its lowest in the 1980s at most sites. This appears not because of a decline in Deca-BDE use at that point, but rather the emergence of congeners associated with the Penta-BDE and Octa-BDE commercial formulae.

Concentrations of BDE-99 exceeded BDE-47 in 39 out of 55 samples in which the former was detected, with the ratio of BDE-47:99 ranging from 0.23-2.08 (mean=0.86, median=0.79). For comparison, BDE-99≥BDE-47 in 49 out of 71 sediment core slices from the inner Clyde Estuary in the UK (Vane et al., 2010). In the Great Lakes,BDE-47 exceeded BDE-99 in 62% of Lake Superior sediment core samples collected between 2001 and 2002, with a similar pattern detected in sediments from Lakes Michigan, Huron, and Ontario in 2002 (Song et al., 2005a, 2005b). In contrast, the contribution of BDE-47 was slightly lower than that of BDE-99 in Lake Erie sediment in 2002; while the BDE-47:99 ratio estimated based on the data of Dodder et al.

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4 (2002) was only 0.5 for Lake Hadley, IN. (Song et al., 2004). The evidence from these various  
5 studies of North American lakes is therefore consistent with the variable patterns observed in this  
6 study, whereby BDE-99 exceeds BDE-47 in many samples, but with the reverse observed in a  
7 significant minority of samples. Our observations are also indicative of a slight “weathering” of  
8 the BDE-47:99 ratio found in the Penta-BDE commercial formulation. Specifically, two technical  
9 Penta-BDE mixtures, Bromkal DE-71 and 70-5DE, display BDE-47:99 ratios of 1.09 and 0.88  
10 respectively (La Guardia et al., 2006).  
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#### 18 *4.6 Factors influencing on HBCD diastereomer profiles*

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20 Contributions of  $\alpha$ - and  $\gamma$ - to  $\Sigma$ HBCDs in this study ranged from zero (i.e. not detected) to 0.51  
21 ( $\alpha$ -HBCD), and 0.24 to 1.0 ( $\gamma$ -HBCD), with mean (median) values of 0.18 (0.17), and 0.72 (0.74),  
22 respectively, in the 70 sediment core samples where at least one of the  $\alpha$ - and  $\gamma$ -diastereomers  
23 were detected.  $\beta$ -HBCD consistently displayed the lowest contribution to  $\Sigma$ HBCD. The  
24 diastereomer profile of HBCD in our English freshwater lakes was consistent with those observed  
25 in most sediments from western European estuaries including the Netherlands, Dublin Bay in  
26 Ireland, the Scheldt basin in Belgium, and the Western Scheldt, as well as most riverine and  
27 estuarine sediments at various UK sites (Morris et al., 2004). In these samples, the profile was  
28 dominated by  $\gamma$ -HBCD, thereby closely resembling the commercial HBCD formulation (10-13%  
29  $\alpha$ -, and 75-89%  $\gamma$ -HBCD, respectively; Becher et al., 2005).  
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39 Relevant parameters that may affect HBCD isomeric profiles were investigated across all our  
40 sites (Figure 3). Interestingly, the contribution of  $\gamma$ -HBCD to  $\Sigma$ HBCD (i.e. its relative abundance)  
41 increased significantly ( $R=0.35$ ,  $p=0.003$ ) with increasing year of deposition. The increased  
42 relative abundance of  $\gamma$ -HBCD in more recently sedimented material is consistent with fresher  
43 input of HBCD, given the commercial product is predominantly  $\gamma$ -HBCD. Lower  
44  $\gamma$ -HBCD: $\Sigma$ HBCD ratios in older core slices are likely due to within-core, post-depositional  
45 isomerization favouring  $\alpha$ -HBCD formation in older sedimented material. Potential differences in  
46 degradation rates of HBCD isomers could also have influenced the historical HBCD isomeric  
47 profile. For example, a freshwater sediment microcosm study using  $^{14}\text{C}$ -labelled HBCD isomers  
48 revealed degradation of  $\beta$ -HBCD was the most rapid, while  $\alpha$ -HBCD degradation rates were  
49 28-47% slower than those for  $\gamma$ -HBCD (Davis et al., 2006).  
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## 5. Conclusion

The input fluxes of PCBs, PBDEs, and HBCDs in radiometrically-dated sediment cores from English lakes between ~1950 and present are presented. Temporal trends for PCBs accord with both those in previous UK studies, and historical trends in UK manufacture and use, while PBDE temporal trends suggest the full impact of EU restrictions on these formulations has yet to be felt. Strikingly, fluxes of BDE-209 in the most recent core slices either exceed or approach peak fluxes of  $\Sigma$ PCBs, implying substantial UK use of Deca-BDE. Excepting HBCDs, inventories of our target contaminants correlated significantly with local population density, implying substantial urban sources.

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## Supporting Information

Available as supporting information are additional tables, figures, and descriptions about sampling locations, and analytical methods and results (as noted in the text).



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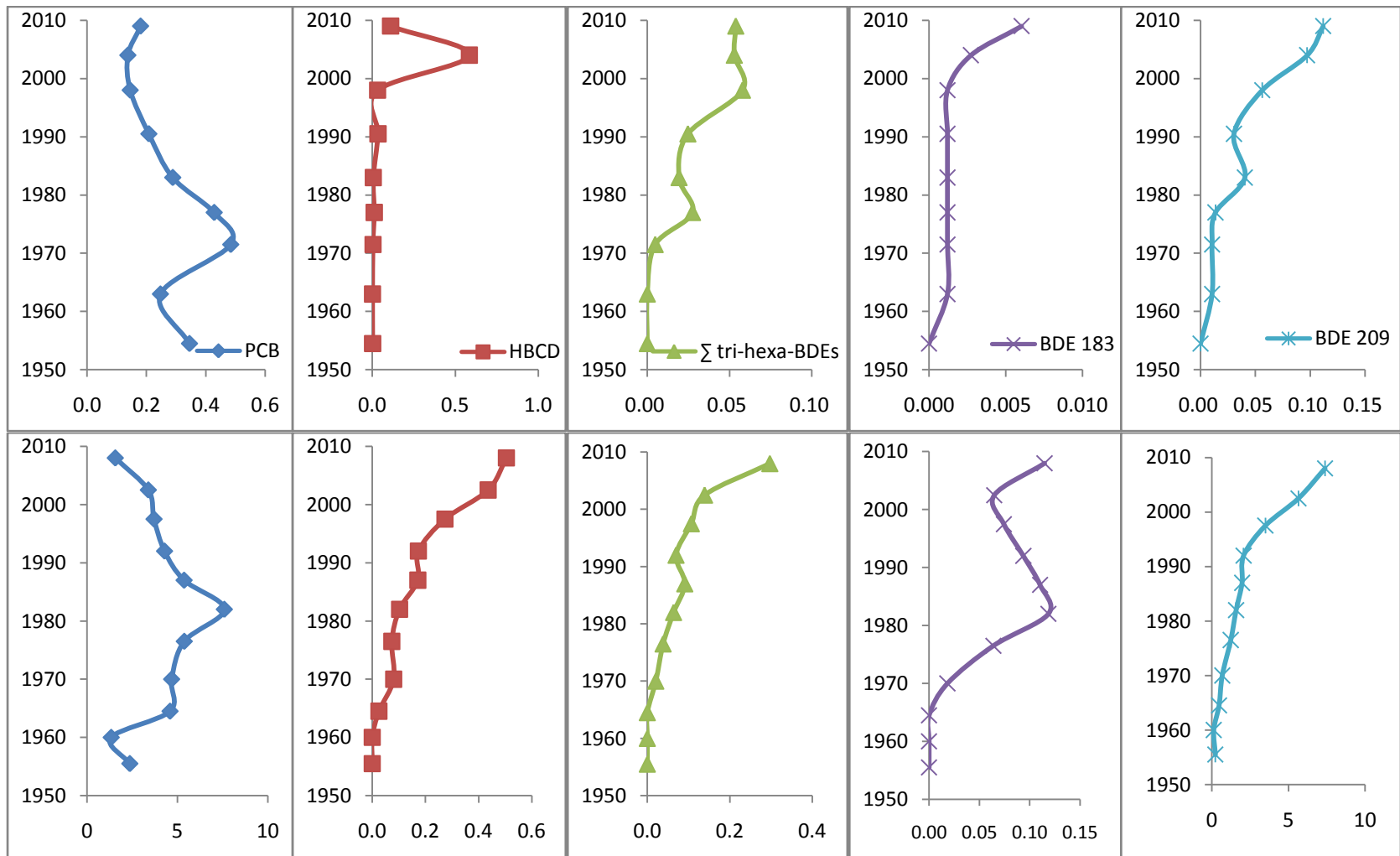
**Table 1: Correlation Coefficients and Significance Levels (p values) of Relationships between Target Contaminant Inventories and Potentially Influential Parameters**

<b>Compound</b>	<b>Local Population Density</b>	<b>Population Density within a 25 km Radius</b>	<b>Lake Catchment Ratio</b>
<b>Σ PCBs</b>	0.918(p=0.002)**	0.667 (p=0.051)	-0.767(p=0.022)*
<b>Σ HBCDs</b>	0.606 (p=0.075)	0.111 (p=0.406)	-0.898(p=0.003)**
<b>Σ tri-hexa-BDEs</b>	0.863(p=0.006)**	0.334 (p=0.232)	-0.898(p=0.003)**
<b>BDE-183</b>	0.898(p=0.003)**	0.505 (p=0.124)	-0.784(p=0.019)*
<b>BDE-209</b>	0.973(p<0.001)**	0.704(p=0.039)*	-0.748(p=0.026)*

\*Significant at p<0.05

\*\*Significant at p<0.01

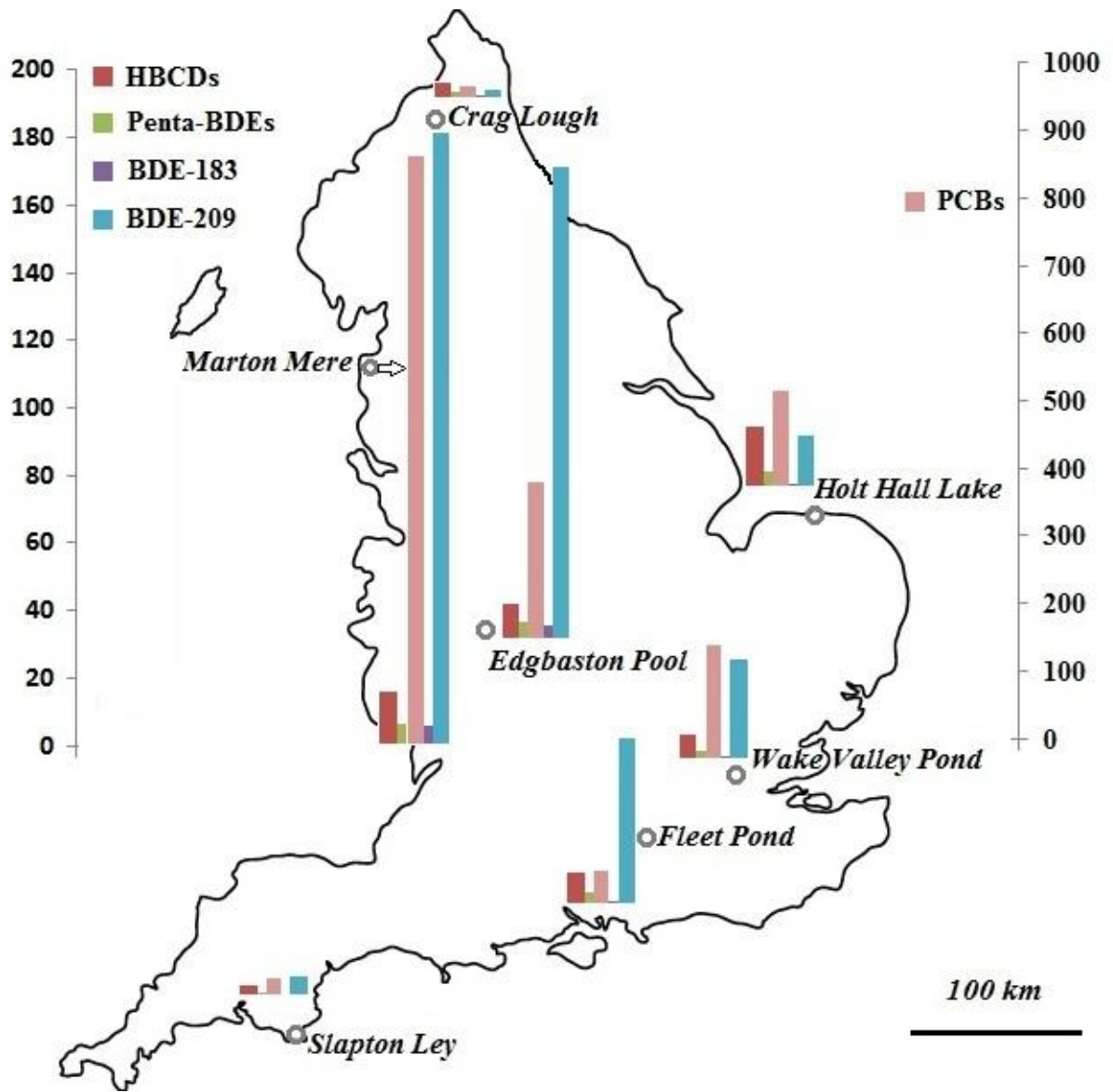
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**Figure 1: Temporal Trends of Input Fluxes ( $\text{ng cm}^{-2} \text{yr}^{-1}$ ; x axis) of PCBs<sup>a</sup>, HBCDs<sup>b</sup>,  $\Sigma$ tri-hexa-BDEs<sup>c</sup>, BDE-183, and BDE-209 in Sediments from the Most Rural (Crag Lough, Top) and Urban (Edgbaston Pool, Bottom) English Freshwater Lakes in This Study, ~1950-2011/2; Average Year of Sedimentation for Each Core Slice Plotted on Chronological Axis.**

<sup>a</sup>sum of PCB-28, -52, -101, -118, -153, -138, -180; <sup>b</sup>sum of  $\alpha$ -,  $\beta$ -,  $\gamma$ -HBCDs; <sup>c</sup>sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, -153

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**Figure 2: Inventories (ng cm<sup>-2</sup>) of Target Contaminants in English Freshwater Lakes, ~1950 to Present. Note Different (Five Times Greater) Scale on Right Hand Axis for PCBs.**

