

# Historical trends of PBDEs and HBCDs in sediment cores from Sydney estuary, Australia

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**Historical Trends of PBDEs and HBCDs in Sediment Cores from  
Sydney Estuary, Australia.**

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4 **Abstract:**  
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6 This paper presents the first historical data on the occurrence of polybrominated diphenyl  
7 ethers (PBDEs) and hexabromocyclododecane (HBCDs) in estuarine sediment from  
8 Australia. Sediment cores and surficial sediment samples were collected from four locations  
9 within Sydney estuary, Australia. Large increases in concentrations were observed between  
10 1980 and 2014, especially for BDE-209 (representative usage of Deca-BDE commercial  
11 mixture), which was found in surficial sediment at an average concentration of 42 ng/g dry wt  
12 (21-65 ng/g dry wt). PBDE congeners representative of both the Penta- and Octa-BDE  
13 commercial mixtures ( $\Sigma_6$ PBDEs) were also found in their highest concentrations in surficial  
14 sediments (average: 1.3 ng/g dry wt; range: 0.65-2.5 ng/g dry wt) suggesting that their input  
15 into the Sydney estuary has not decreased. After a sharp increase in the 1990s, HBCD  
16 concentrations peaked at an average of 3.5 ng/g dry wt (1.8-5.3 ng/g dry wt) in surficial  
17 samples. With global legislation on HBCDs allowing its usage for the next 10 years, it is  
18 expected that its input into the estuary is likely to continue.  
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## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDs) have been used extensively as brominated flame retardants (BFRs) worldwide. PBDEs have been used in various consumer goods, including foam-upholstered furniture, and high impact polystyrene (HIPS) casings for electrical goods (Bromine Science Environmental Forum (BSEF) 2007; D'Silva et al. 2004). Global HBCD demand in 2003 was 22,000 tonnes (Health and Environment Alliance 2013). Its major applications were in expanded or extruded polystyrene (EPS/EXPS) building insulation and HIPS (Abdallah et al. 2007). Minor uses include the housing of domestic electrical appliances and car seats, latex binders, and textile coatings (National Industrial Chemicals Notification And Assessment Scheme (NICNAS) 2014).

Whilst the physicochemical behaviour of different PBDE congeners varies based on their level of bromination, both PBDEs and HBCDs are hydrophobic and resistant to degradation (D'Silva et al. 2004; Davis et al. 2005), rendering them environmentally persistent and capable of bioaccumulation (Alaee and Wenning 2002). A combination of these properties and their extensive use has led to substantial contamination of indoor and outdoor environments and exposure to humans and wildlife (Covaci et al. 2006; Darnerud 2003; Toms et al. 2009).

BFRs enter the environment via emissions to air, soil and water from their manufacture through to volatilisation and leaching during their use and disposal (Toms et al. 2008). Sediments are sinks for BFRs and other persistent compounds with previous studies demonstrating that various sediment types (marine, estuarine, freshwater) are contaminated with persistent compounds from both diffuse and point sources (Minh et al. 2007; Taylor et al. 2004; Toms et al. 2008). A potentially important point source of these compounds to aquatic ecosystems is storm water. Storm water contains a mixture of material including sewage overflows and discharge of industrial contaminants and as such, storm water drains have been highlighted as point sources for a variety of pollutants, including PBDEs, to aquatic environments (Birch and Taylor 1999; Richman et al. 2013). Furthermore, urban and industrial activities are important sources of BFRs in the environment (Harrad and Hunter 2006; Kohler et al. 2008).

There is a lack of information regarding temporal trends of PBDEs in the Australian environment, whilst there are only a handful of studies examining historical levels of HBCDs

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4 around the world. Data from sediment cores also provide information on temporal trends and  
5 the impact of mitigation strategies. The objective of this study was thus to determine  
6 concentrations of PBDEs and HBCDs in sediment cores and surficial sediment samples from  
7 Sydney estuary, Australia in order to assess trends in their release to the environment.  
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11 These data are used to elucidate temporal trends in deposition of PBDEs and HBCDs  
12 between the middle and the end of the 20<sup>th</sup> century at which point restrictions were  
13 introduced on the manufacture and use of the Penta- and Octa-BDE formulations.  
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15 Comparison with concentrations determined in recent surficial sediments provides an  
16 indication of the impact of these restrictions. To our knowledge this is the first report of  
17 HBCD concentrations in Australian sediments and also the first study to investigate temporal  
18 trends of PBDEs and HBCDs in Australia using sediment cores.  
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## 24 **2. Experimental Section**

### 25 *2.1 Sampling*

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27 Sediment cores were taken in 1998/99 (Taylor et al. 2004). Cores were taken from Sydney  
28 estuary in shallow-water areas (<8 m) in locations close to storm water drains (<0.5 km,  
29 except IC5, 1.5 km), which have been identified previously as a major source of storm water-  
30 derived contaminants (Birch and Taylor 1999). A piston corer (up to 1.5 m) was used to  
31 recover sub-surface samples to reduce compaction, provide good core recovery and to avoid  
32 physical disturbance. Four sediment cores were analysed in this study (Figure 1) – two from  
33 Iron Cove (IC3 and IC5), one from Burns Bay (BB) and one from North Harbour (NH). Each  
34 core was subsampled at 2 cm intervals to 10 cm depth, and thereafter subsampled at intervals  
35 of 10 cm. Samples were freeze-dried and sieved to less than 62.5 µm. Sediment age was  
36 determined by Taylor et al. (2004) using <sup>210</sup>Pb and <sup>137</sup>Cs dating techniques (Goldberg 1963;  
37 Nriagu et al. 1979) and sedimentation rates (cm/year) were calculated from sediment  
38 thickness and age.  
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50 In May 2014, a single surficial sediment sample was taken from each of the above locations.  
51 Each surficial sediment sample consisted four grab sub-samples which were collected at each  
52 location. The top 5 centimetres from each sub-sample were combined and homogenised in a  
53 250 mL glass jar. Samples were freeze-dried and sieved in the same manner as above.  
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### 58 *2.2 Extraction & Clean-up*

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All samples underwent combined pressurised liquid extraction and clean-up for PBDEs and HBCDs using an ASE 350 (Dionex) and Dionium® cells (a zirconium alloy able to tolerate highly acidic and basic conditions). The full methods are described elsewhere (Abdallah et al. 2013). Between 5-10 g (accurately weighed) of each sample were weighed in disposable measuring boats before being added to 100 mL pre-packed Dionium® cells containing (from the bottom upwards): two microfibre filters (Dionex), silica gel (Sigma Aldrich), 5 g florisil (60-100 mesh, Sigma Aldrich), 3 g diatomaceous earth (Sigma Aldrich, UK), microfibre filter, 10 g acid impregnated silica (44% sulfuric acid), microfibre filter, 5 g copper powder, 2 g hydromatrix. The remaining volume of the cell was filled with hydromatrix and spiked with known amounts of internal standards (<sup>13</sup>C labelled BDEs -47, -99, -153, -183, -209 and <sup>13</sup>C labelled α-, β and γ HBCDs). The ASE cells were extracted with DCM and hexane (1:1 v/v) at 90°C and 1500 psi (heating time 5 minutes, static time 5 mins, 3 static cycles, flush volume – 50%, purge time – 120 s). The extract was concentrated to near-dryness using a hotplate (40 °C) under a gentle stream of nitrogen, before being transferred to GC vials and reconstituted in 100 µL of <sup>13</sup>C-labelled BDE-100 (sediment core samples) or <sup>13</sup>C<sub>12</sub>-labelled PCB-141 & <sup>13</sup>C<sub>12</sub>-labelled TBBP-A (2014 samples) in methanol as a recovery determination standard prior to instrumental analysis of all compounds excluding BDE-47. After injection on LC-MS/MS (section 2.3) samples were concentrated to dryness and reconstituted in 50 µL hexane for GC/MS analysis.

### 2.3 Analysis

Concentrations of HBCDs (α-, β- and γ-) and most targeted PBDEs (BDEs -99, -100, -153, -154, -183 and -209) were analysed via HPLC-APCI-MS/MS using an ABSciex API5500Q mass spectrometer (ABSciex, Concord, Ontario, Canada) equipped with an atmospheric pressure chemical ionisation (APCI) source coupled to a Shimadzu Prominence HPLC system (Shimadzu Corp., Kyoto Japan). Full details are described in Gallen et al. (2014).

For BDE-47, the HPLC-MS method was insufficiently sensitive. Consequently, sediment core samples BDE-47 was analysed via HRGC/HRMS (HP 5890 II GC coupled to a VG AutoSpec mass spectrometer). The full HRGC/HRMS programme is given elsewhere (Hearn et al. 2012). In surficial sediment samples, BDE-47 was determined via HRGC/HRMS (Thermo Trace 1310 GC coupled to a Thermo DFS HRMS) – the parameters for which are presented in Table SI-1 (supporting information).

### 2.4 Quality Control

Each batch of samples was run with a blank consisting of approximately 10 g diatomaceous earth. If a target compound was detected in a blank at 5-25% of the level in a sample from the same batch, then the blank concentration was subtracted from that particular sample. If the blank level was below 5% then no correction was applied. No target compounds were detected in blanks at >25% of any corresponding samples. In the absence of a QC sample at the times of analyses, SRM 2585 (n=4) was analysed with sediment cores. For all analytes, good agreement was found with certified/indicative values. Surficial sediment samples were also analysed in duplicate with agreement between results (Table SI-2). Concentrations presented here are the average of these duplicates.

### 2.5 Calculation of Doubling Times

To calculate doubling times, a graph of  $\ln(\text{concentration})$  against time was plotted (Figure SI-1). The slope of this line was used as the first order rate constant (k) used in the following equation:

$$\text{Doubling time} = \frac{\ln(2)}{k}$$

Doubling times were only calculated where concentrations increased in three consecutive sediment core layers.

## 3. Results and Discussion

### 3.1 Temporal Trends

The concentrations of  $\sum_6$ PBDEs (BDEs -47, -99, -100, -153, -154 and -183), BDE-209 and  $\sum$ HBCDs in each layer of sediment is presented in Table 1. Data on individual congeners and isomers is supplied in the supporting information (Table SI-3). Contaminants were detected in low levels in sediments deposited as early as 1950-1960s ( $\sum$ HBCDs, average = 0.59 ng/g dry wt) and 1960-1970s ( $\sum_6$ PBDEs (-47, -99, -100, -153, -154 and 183) average= 0.038 ng/g dry wt and BDE-209, average = 0.23 ng/g dry wt). Rapid increases in concentrations were observed between 1980 and 2014, which led to peak average concentrations of 3.5, 1.3 and 42 ng/g dry wt for  $\sum$ HBCDs,  $\sum_6$ PBDEs and BDE-209 respectively in 2014 surficial sediments.

Figure 1 demonstrates the changes in PBDE concentrations from the oldest sediments in which PBDEs were detected (ca. 1960) to surface samples taken in 2014. BDE-209 represented an average of 81% (range: not detected (nd)-100%) of  $\sum$ PBDEs. Therefore, in this section, BDE-209 is presented separately to  $\sum$ <sub>6</sub>PBDEs.

Our data are consistent with use in Australia of the Penta-BDE commercial formulation, with the sum of BDEs -47, -99 and -100 (each of these representing major congeners found in Penta-BDE) contributing an average of 30% (range: nd-100%) to the total PBDE content (including BDE-209) during the 1970s and 1980s. Although  $\sum$ <sub>6</sub>PBDE concentrations increase over time, attaining a maximum in 2014, their overall contribution to total PBDE content decreases due to a rapid BDE-209 increase between 1990-2014 with an average contribution of BDE-209 to  $\sum$ PBDEs in 2014 samples of 97% (range: 95-99%). This increase is highlighted by the shorter doubling time of BDE-209 (Table 2) compared to that of  $\sum$ <sub>6</sub>PBDEs and HBCDs. This is likely to reflect a high release of the Deca-BDE formulation during the 1990s and 2000s in and around Sydney estuary. This is unsurprising, given that the import of Penta- and Octa-BDE observed a reduction in excess of 70% between 1998 and 2004 leaving DecaBDE to represent 86% of the total PBDE import into Australia at 180 tonnes (Toms et al. 2008). Moreover, whilst further importation of Penta- and Octa-BDE was banned in 2005 (Toms et al. 2009), DecaBDE usage has not been restricted (although it was listed as a priority existing chemical within Australia in 2005 (National Industrial Chemicals Notification And Assessment Scheme (NICNAS) 2007)). Whilst it is unsurprising that BDE-209 is the dominant PBDE congener, it is interesting that the highest concentrations of Penta-BDE (-47, -99 and -100) and Octa-BDE (BDEs -183 and -153) based congeners were found in the surficial sediments taken in 2014. This is somewhat concerning as the aforementioned restrictions of Penta- and Octa-BDE in 2005 do not appear to have triggered a reduction in PBDE input into Sydney estuary, almost ten years later. This is likely to be due to the relatively long mixing times of sediments compared to other environmental compartments, such as air meaning that it is unlikely that sediment concentrations will reflect any reduction of PBDE use in the last ten years. This has also been demonstrated in the UK by Yang et al. (2014) where similar restrictions of Penta- and Octa-BDE have been in place since 2004. These authors stated that atmospheric concentrations of Penta-BDE congeners have fallen since the turn of the 21<sup>st</sup> century, however water samples from lakes across the UK have not shown the same reduction, which they attribute to the comparatively long mixing times of freshwater lakes.



HBCDs followed a similar pattern to PBDEs, with sharp increases in concentration during the 1990s with maximum  $\Sigma$ HBCD concentrations found in the most recent sediments. In three (IC3, IC5 and NH) out of the four locations studied,  $\Sigma$ HBCD concentrations were highest in the surficial sediments sampled in 2014 (Figure 3).  $\Sigma$ HBCD concentrations at BB, peaked in sediment representative of 1997 (4.5 ng/g dry wt), and declined to 2.6 ng/g dry wt in surficial sediment from 2014. These patterns are consistent with commercial use of HBCD in Australia – importation of HBCDs and its containing products into Australia peaked in 2006-07 (90 tonnes), but decreased to approximately 60 tonnes in 2010, when the import of HBCD as a powder or granules ceased (National Industrial Chemicals Notification And Assessment Scheme (NICNAS) 2014). Whilst HBCD has recently been listed as a POP under the Stockholm Convention, its primary use (cavity wall insulation) is exempt from any ban until 2024, meaning that input of HBCDs in this rapidly urbanised estuary is likely to continue for the foreseeable future (Swedish Society for Nature Conservation 2014).

The increases in HBCDs and PBDEs, post 1960 (particularly 1980-2014) may be due to changes in historical land-use in areas adjacent to our sampling sites – with substantial use as landfills until the late 1980s including in areas upstream and close to sampling sites. Landfilled materials include: construction, demolition, industrial and domestic waste (Birch 2007) and have been shown to leach pollutants, such as metals into Sydney estuary (Suh et al. 2003a, b; Suh et al. 2004). It is well documented that landfill leachate has been found to contain BFRs, including HBCDs and PBDEs and that it can be considered a source to the environment (Stubbings and Harrad 2014). The land surrounding our sample sites has also undergone large redevelopment and urbanisation since the 1980s. It has also been demonstrated that urbanisation itself can lead to increased release of BFRs into the environment due to high building density and associated BFR sources (Harrad and Hunter 2006). A combination of surface run-off, overflowing storm water and possible leaching from within “landfills” are plausible explanations for the large increases of BFRs found in Sydney estuary sediments between 1980 and 2014.

### *3.2 Global Comparison*

#### *PBDEs*

The historical changes of PBDE concentrations in sediment from Sydney estuary reflect patterns seen elsewhere. Minimal concentrations before the 1970s followed by sharp increases (primarily in BDE-209) between 1980 and 1999 have also been observed in

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4 Switzerland where PBDEs were first detected in lake sediments representative of 1975-1980  
5 with a rapid increase to 8.8 ng/g dry weight in 2000 (Kohler et al. 2008). Similar patterns  
6 have also been seen in the UK and Europe (Vane et al. 2010; Zegers et al. 2003), China  
7 (Chen et al. 2007), North America (Song et al. 2004; Song et al. 2005a; Song et al. 2005b), as  
8 well as the Arctic (Evenset et al. 2007) and others.  
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14 Comparison of our observed measurements of surficial samples with data from the literature,  
15 suggests Sydney estuary is highly contaminated with PBDEs in both a national and a global  
16 context. The average  $\sum_7$ PBDE (BDEs -47, -99, -100, -153, -154, -183 and -209)  
17 concentration in the current study (44 ng/g dry wt) is considerably higher than that of  
18 sediments taken in 2003 from around Australia (6.6 ng/g dry wt (Toms et al. 2006)).  
19 Interestingly, Toms et al. (2006) also highlighted the upper estuary (close to IC3 and IC5) as  
20 the most contaminated surficial sediment sample within >40 Australian locations with a  
21 concentration of 23 ng/g for the same congeners as in this study, of which BDE-209  
22 contributed 97%.  
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30 Surface sediments from Sydney estuary contain average PBDE levels towards the top end of  
31 the range of concentrations found globally (Figure 4). For example, our measurements appear  
32 to be similar to those Laizhou Bay in China, where the average  $\sum_7$ PBDE concentration in  
33 sediments taken from the vicinity of a PBDE manufacturing site was 52 ng/g dry wt (Pan et  
34 al. 2011). Concentrations in Sydney estuary are also almost ten times higher than those in  
35 sediment taken from San Francisco Bay, California (Klosterhaus et al. 2012).  
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#### 42 *HBCDs*

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44 Although limited studies are available for comparison, similar historical patterns have been  
45 seen for HBCDs elsewhere with sharp increase in concentrations in the 1980s with peak  
46 concentrations found in the top layers from sediment cores (Bogdal et al. 2008; Kohler et al.  
47 2008), Japan (Minh et al. 2007; Tanabe 2008), China (YW Zhang et al. 2013) and the Great  
48 Lakes, USA (Yang et al. 2012). The sudden increase in concentrations from 1980 onwards  
49 has been attributed to the market release of HBCD technical mixtures during the 1980s and  
50 1990s (Bogdal et al. 2008).  
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57  $\gamma$ -HBCD was the dominant stereoisomer in all sediments examined in this study. In surficial  
58 sediments (in which concentrations were sufficiently high to permit measurement of all 3  
59 isomers), the average stereoisomer contributions were 23%, 5.5% and 72% for  $\alpha$ -,  $\beta$ - and  $\gamma$ -  
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HBCD respectively. This is consistent with findings from studies in China (Feng et al. 2012; YW Zhang et al. 2013), Japan (Minh et al. 2007), UK (Harrad et al. 2009) and USA (Marvin et al. 2006). Furthermore, it is similar to the stereoisomer profile of HBCD technical mixtures, which contain 12.5%, 11.1% and 76.4%  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCD respectively (Crump et al. 2010) – a profile observed in most sediments (Covaci et al. 2006).

Concentrations in sediments from Sydney estuary are similar to those detected in locations not directly impacted by HBCD manufacture. The average (2014) concentration of 3.5ng/g dry wt (range: 1.8-5.3 ng/dry wt) is within the range of 0.2-11 ng/g dry wt found in surface sediment from urban and industrial areas (as demonstrated by Figure 5), but approximately 10-200 times lower than in sediment sampled close to HBCD manufacturing plants.

Furthermore, the concentrations in individual sediment layers from the cores are of a similar level to those in sediment layers representative of similar years in Switzerland (Kohler et al. 2008), Tokyo (Minh et al. 2007; Tanabe et al. 2008) and China (Tanabe et al. 2008; L Zhang et al. 2013).

#### 4. Conclusions

PBDEs and HBCDs were detected in all sediments taken in Sydney estuary from 1960s onwards. Concentrations of both groups of compounds underwent rapid increases from 1980-2000. BDE-209 underwent a further increase from 2000-2014 leading to  $\sum_7$ PBDE concentrations similar to those found in Laizhou Bay, China – close to a PBDE manufacturing plant, suggesting that usage of Deca-BDE increased considerably following restrictions of Penta- and Octa-BDE in 2005. Maximum  $\sum$ HBCD concentrations in all sediments (1.8-5.3 ng/g dry wt) are similar to sediment concentrations globally in areas of similar land-use, suggesting that HBCD usage in Australia has been similar to the rest of the world. The intense urbanisation of Sydney estuary catchment since the 1980s is likely to contribute largely to the increases in PBDE and HBCD concentrations in sediments, with a combination of surface run-off and storm water drainage into the river transferring BFRs into Sydney estuary from surrounding highly-developed catchment. This is particularly reflected by dramatic increases in BDE-209 levels – especially considering the known extensive use of DecaBDE in domestic and commercial products in the late 1990s to early 2000s globally, as well as its extensive importation rates into Australia at the beginning of the 21<sup>st</sup> century. In spite of restrictions being placed on the Penta- and Octa-BDE commercial formulations

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4 almost a decade previously, the levels of  $\sum_6$ PBDEs were at their highest concentrations in the  
5 most recent sediments across all sampling sites, suggesting that legislative action is yet to  
6 reduce their input into Sydney estuary. The presence of landfills close to sampling sites is  
7 also a potential source of BFRs (and other pollutants) to Sydney estuary.  
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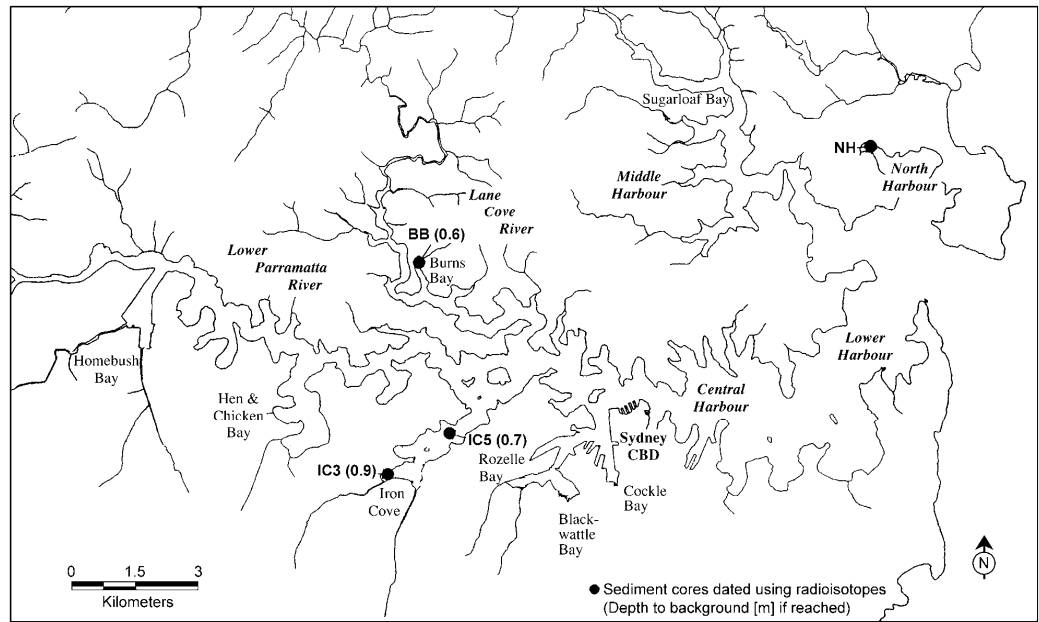
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**Figures and Tables**

**Figure 1 – Sydney estuary sediment core sample names (core depth (m)) and locations**



**Figure 2 –  $\Sigma$ PBDE and BDE-209 (ng/g dry wt) concentrations in sediments from 4 locations in Sydney Harbour**

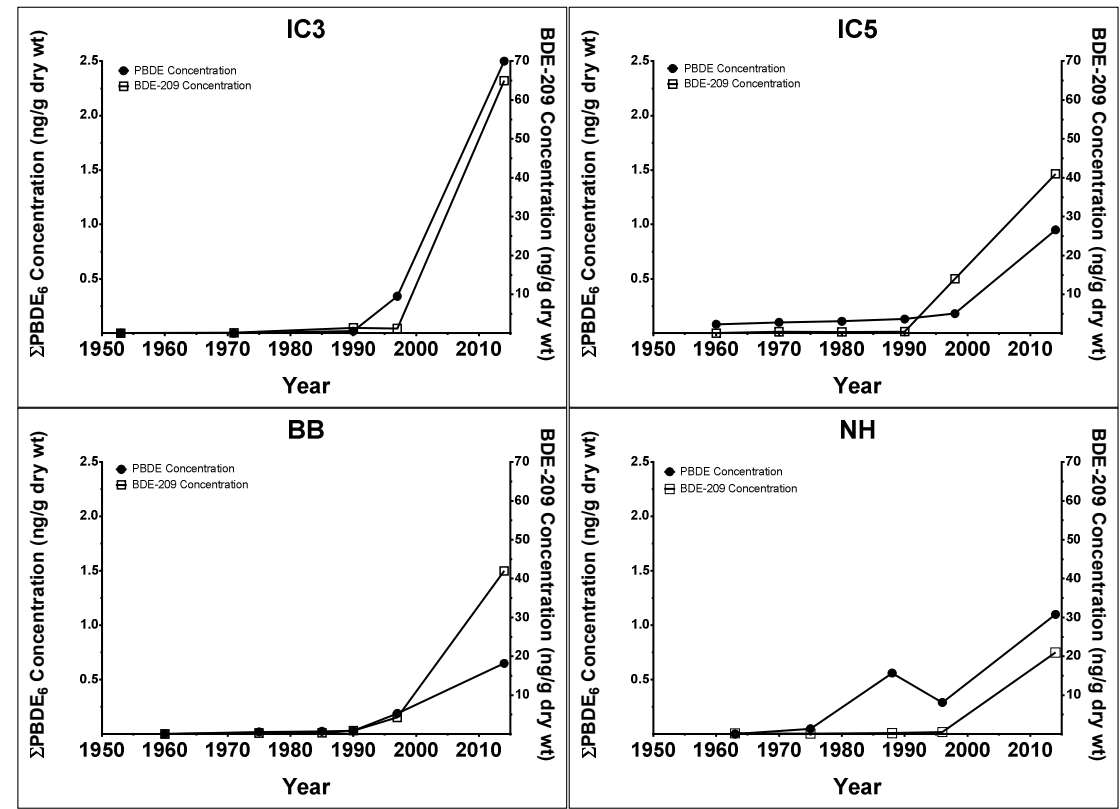
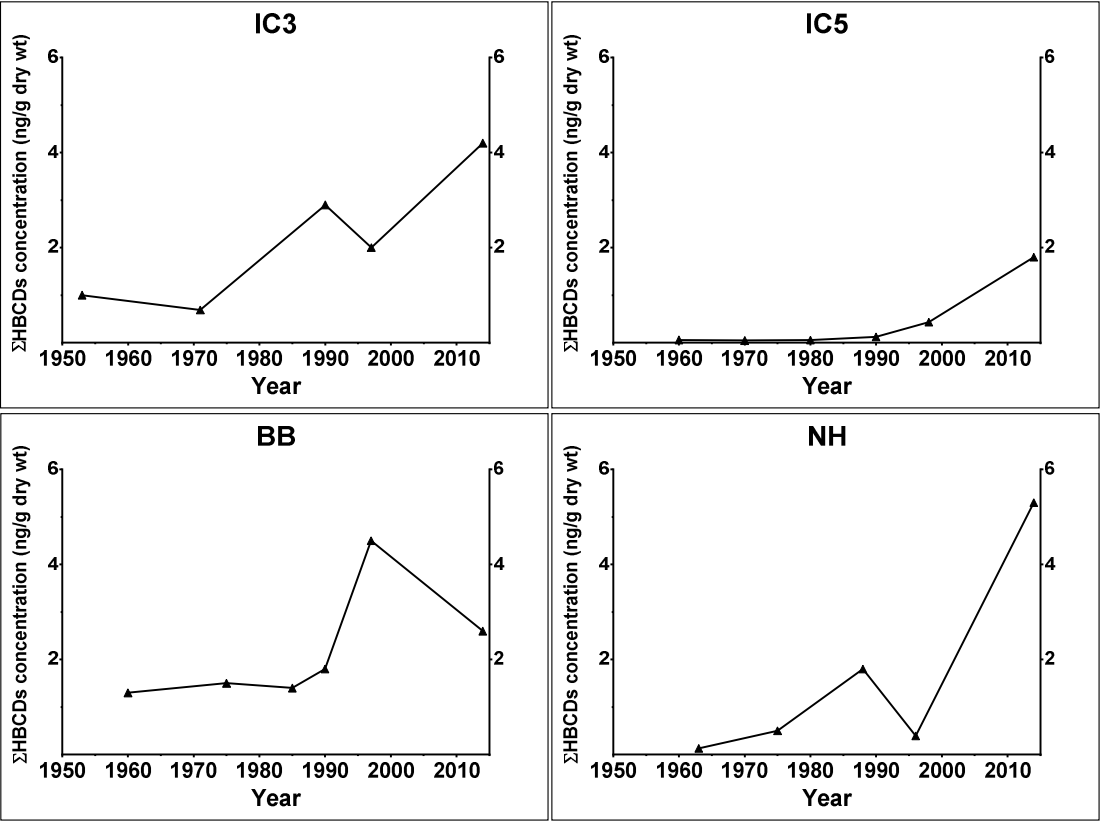
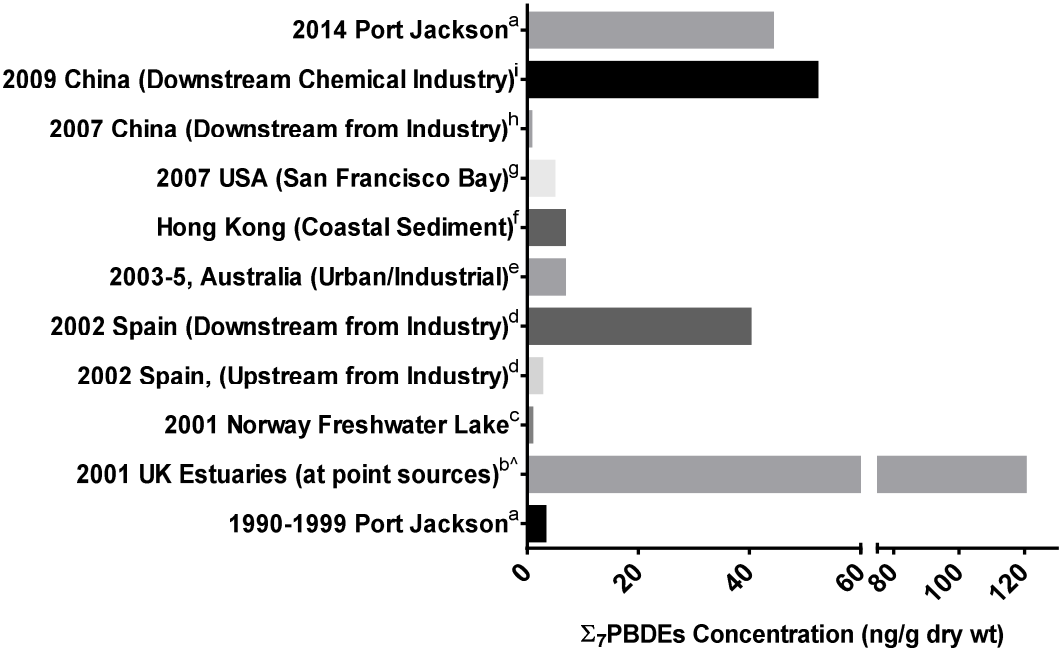


Figure 3 –  $\Sigma$ HBCD (ng/g dry wt) concentrations in sediments from 4 locations in Sydney Harbour



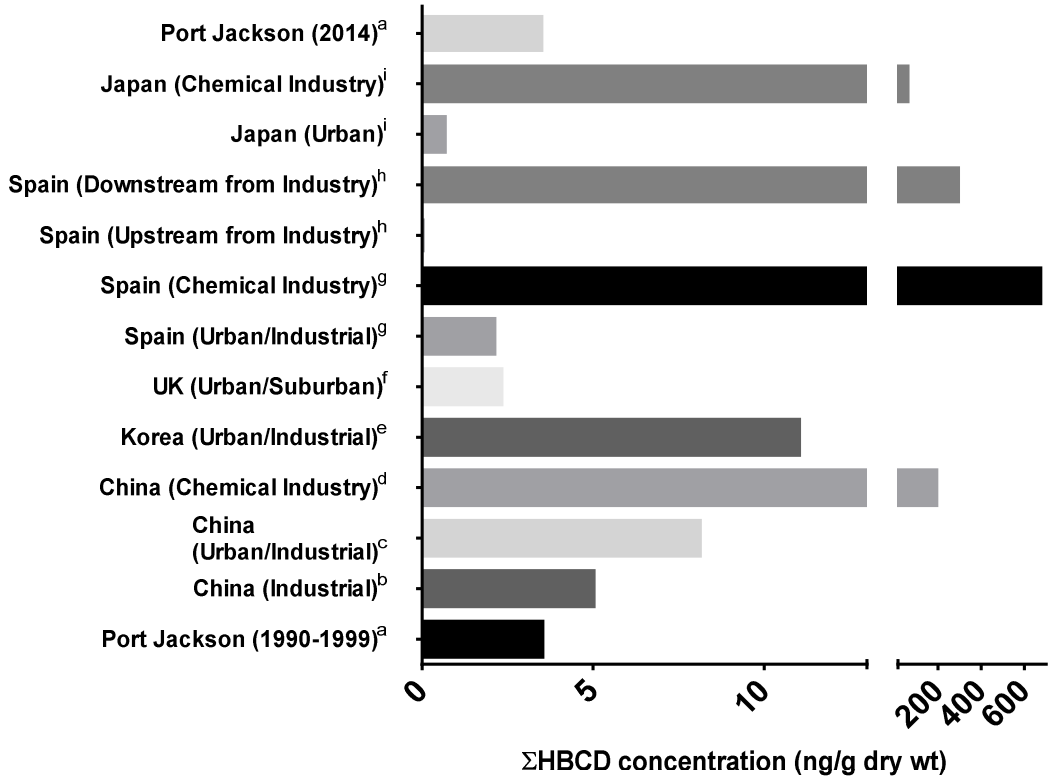
**Figure 4 – Comparison of mean  $\Sigma_7$ PBDE concentrations from the present study (1990-1999 and 2014) with those presented in the literature**



<sup>A</sup>BDEs -47, -99 and -100 only

<sup>a</sup>This Study, <sup>b</sup>Allchin et al. (1999), <sup>c</sup>Evenset et al. (2007), <sup>d</sup>Eljarrat et al. (2004), <sup>e</sup>Toms et al. (2006), <sup>f</sup>Liu et al. (2005), <sup>g</sup>Klosterhaus et al. (2012), <sup>h</sup>Zhao et al. (2011), <sup>i</sup>Pan et al. (2011)

**Figure 5- Comparison of  $\Sigma$ HBCD concentrations (ng/g dry wt) of sediments from the present study with those presented in the literature**



<sup>a</sup>Average 2014 sediments from this study, <sup>b</sup>Feng et al. (2012), <sup>c</sup>YW Zhang et al. (2013), <sup>d</sup>Li et al. (2012), <sup>e</sup>Ramu et al. (2010), <sup>f</sup>Harrad et al. (2009), <sup>g</sup>Guerra et al. (2010), <sup>h</sup>Eljarrat et al. (2004) <sup>i</sup>Managaki et al. (2012)

**Table 1 – Concentration (ng/g dry wt) of  $\Sigma_6$ PBDEs, BDE-209 and  $\Sigma$ HBCD concentrations in surficial sediments (2014) and sediment core layers from Sydney estuary**

| <b>IC3</b>  | <b><math>\Sigma_6</math>PBDEs</b> | <b>BDE-209</b> | <b><math>\Sigma</math>HBCDs</b> | <b>BB</b>   | <b><math>\Sigma_6</math>PBDEs</b> | <b>BDE-209</b> | <b><math>\Sigma</math>HBCDs</b> |
|-------------|-----------------------------------|----------------|---------------------------------|-------------|-----------------------------------|----------------|---------------------------------|
| <b>2014</b> | 2.5                               | 65             | 4.2                             | <b>2014</b> | 0.65                              | 42             | 2.6                             |
| <b>1997</b> | 0.34                              | 1.2            | 2                               | <b>1997</b> | 0.19                              | 4.3            | 4.5                             |
| <b>1990</b> | 0.19                              | 1.4            | 2.9                             | <b>1990</b> | 0.029                             | 0.86           | 1.8                             |
| <b>1971</b> | nd                                | 0.097          | 0.69                            | <b>1985</b> | 0.025                             | 0.29           | 1.4                             |
| <b>1953</b> | nd                                | <0.1           | 1                               | <b>1975</b> | 0.019                             | 0.27           | 1.5                             |
| <b>1935</b> | nd                                | <0.1           | nd                              | <b>1960</b> | nd                                | <0.051         | 1.3                             |
|             |                                   |                |                                 | <b>1950</b> | nd                                | <0.089         | 1.2                             |
| <b>IC5</b>  | <b><math>\Sigma_6</math>PBDEs</b> | <b>BDE-209</b> | <b><math>\Sigma</math>HBCDs</b> | <b>NH</b>   | <b><math>\Sigma_6</math>PBDEs</b> | <b>BDE-209</b> | <b><math>\Sigma</math>HBCDs</b> |
| <b>2014</b> | 0.95                              | 41             | 1.8                             | <b>2014</b> | 1.1                               | 21             | 5.3                             |
| <b>1998</b> | 0.18                              | 14             | 0.43                            | <b>1996</b> | 0.29                              | 0.5            | 0.39                            |
| <b>1990</b> | 0.13                              | 0.4            | 0.12                            | <b>1988</b> | 0.56                              | 0.23           | 1.8                             |
| <b>1980</b> | 0.11                              | 0.32           | 0.056                           | <b>1975</b> | 0.049                             | 0.12           | 0.5                             |
| <b>1970</b> | 0.099                             | 0.38           | 0.046                           | <b>1963</b> | nd                                | 0.17           | 0.13                            |
| <b>1960</b> | 0.082                             | <0.1           | 0.057                           | <b>1926</b> | nd                                | <0.05          | <LOQ                            |
| <b>1943</b> | nd                                | <0.1           | nd                              | <b>1901</b> | nd                                | <0.098         | nd                              |
| <b>1925</b> | nd                                | <0.1           | nd                              | <b>1859</b> | nd                                | <0.12          | nd                              |
| <b>1910</b> | nd                                | <0.1           | nd                              |             |                                   |                |                                 |

**Table 2 – Doubling times (years) of  $\Sigma_6$ PBDEs, BDE-209 and  $\Sigma$ HBCD concentrations in Sydney estuary sediment from 1990-2014**

|                                   | <b>IC3</b> | <b>IC5</b> | <b>BB</b> | <b>NH<sup>^</sup></b> |
|-----------------------------------|------------|------------|-----------|-----------------------|
| <b><math>\Sigma_6</math>PBDEs</b> | 6.3        | 8.1        | 5.8       | N/A                   |
| <b>BDE-209</b>                    | 4          | 5.7        | 4.4       | 3.9                   |
| <b><math>\Sigma</math>HBCDs</b>   | N/A        | 6.3        | N/A       | N/A                   |

<sup>^</sup>Doubling time for NH calculated from 1988-2014

## Supporting Information

Table SI-1 HRGC/HRMS parameters for BDE-47 analysis

|                                       |                 |      |                      |          |             |
|---------------------------------------|-----------------|------|----------------------|----------|-------------|
| <b>Injection</b>                      |                 |      |                      |          |             |
| Injection Type                        |                 |      | Splitless            |          |             |
| Split Flow                            |                 |      | Constant (70 mL/min) |          |             |
| Inlet Temperature                     |                 |      | 300 °C               |          |             |
| Injection Volume                      |                 |      | 1 µL                 |          |             |
| <b>GC Program</b>                     |                 |      |                      |          |             |
| Temperature 1                         | 80 °C           | Rate | -                    | Held for | 2 minutes   |
| Temperature 2                         | 180 °C          | Rate | 20 °C/min            | Held for | 0.5 minutes |
| Temperature 3                         | 300             | Rate | 10 °C/min            | Held for | 8 mins      |
| <b>HRMS Program</b>                   |                 |      |                      |          |             |
| Compound                              | Quantifying Ion |      | Qualifying Ion       |          |             |
| BDE-47                                | 483.71310       |      | 485.71110            |          |             |
| <sup>13</sup> C <sub>12</sub> -BDE-47 | 495.75530       |      | 497.75130            |          |             |

Table SI-2 – Concentrations (ng/g) in SRM-2585 (n=4) and Duplicate samples for Quality Control

|                     | SRM-2585         |                 | Duplicate Analyses |       |       |       |      |      |      |      |
|---------------------|------------------|-----------------|--------------------|-------|-------|-------|------|------|------|------|
| Compound            | Certified Values | Measured Values | IC3-A              | IC3-B | IC5-A | IC5-B | BB-A | BB-B | NH-A | NH-B |
| BDE-47              | 497 ± 46         | 499 ± 27        | 0.80               | 1.17  | 0.26  | 0.26  | 0.26 | 0.43 | 0.71 | 0.77 |
| BDE-100             | 145 ± 11         | 156 ± 14        | 0.18               | 0.13  | 0.03  | 0.05  | 0.03 | 0.04 | 0.03 | 0.03 |
| BDE-99              | 892 ± 53         | 891 ± 30        | 0.74               | 0.69  | 0.12  | 0.12  | 0.14 | 0.14 | 0.14 | 0.18 |
| BDE-154             | 83.5 ± 2         | 79 ± 6.2        | 0.16               | 0.10  | 0.04  | 0.09  | 0.03 | 0.02 | 0.02 | 0.04 |
| BDE-153             | 119 ± 1          | 114 ± 8.4       | 0.21               | 0.14  | 0.36  | 0.36  | 0.02 | 0.03 | 0.03 | 0.06 |
| BDE-183             | 43 ± 3.5         | 44.4 ± 2.6      | 0.35               | 0.28  | 0.11  | 0.10  | 0.08 | 0.07 | 0.08 | 0.07 |
| BDE-209             | 2510 ± 190       | 2490 ± 191      | 83.2               | 46.7  | 41.8  | 40.6  | 50.4 | 34.4 | 21.7 | 19.7 |
| α-HBCD <sup>a</sup> | 19 ± 3.7         | 19.5 ± 4.1      | 1.07               | 1.46  | 0.49  | 0.34  | 0.43 | 0.53 | 0.98 | 0.99 |
| β-HBCD <sup>a</sup> | 4.3 ± 1.1        | 3.94 ± 1.4      | 0.25               | 0.27  | 0.11  | 0.09  | 0.11 | 0.11 | 0.32 | 0.30 |
| γ-HBCD <sup>a</sup> | 120 ± 22         | 123 ± 12        | 2.62               | 2.62  | 1.38  | 1.28  | 1.90 | 2.01 | 4.12 | 3.95 |

<sup>a</sup> Indicative values taken from Keller (2007)



Table SI-3 Concentrations of individual PBDE congeners and HBCD isomers in sediment from Sydney estuary

|      | Concentration (pg/g dry wt) |         |        |         |         |         | Concentration (ng/g dry wt) | Concentration (pg/g dry wt) |        |        |        |
|------|-----------------------------|---------|--------|---------|---------|---------|-----------------------------|-----------------------------|--------|--------|--------|
| IC3  | BDE-47                      | BDE-100 | BDE-99 | BDE-154 | BDE-153 | BDE-183 | BDE-209                     | a-HBCD                      | b-HBCD | g-HBCD | ΣHBCDs |
| 2014 | 980                         | 160     | 710    | 130     | 180     | 310     | 65                          | 1300                        | 260    | 2600   | 4160   |
| 1997 | 154                         | 160     | nd     | nd      | 15      | 11      | 1.2                         | 220                         | nd     | 1800   | 2020   |
| 1990 | 78                          | 91      | nd     | nd      | nd      | 16      | 1.4                         | 200                         | nd     | 2700   | 2900   |
| 1971 | nd                          | nd      | nd     | nd      | nd      | nd      | 0.097                       | nd                          | nd     | 690    | 690    |
| 1953 | nd                          | nd      | nd     | nd      | nd      | nd      | nd                          | nd                          | nd     | 1020   | 1020   |
| 1935 | nd                          | nd      | nd     | nd      | nd      | nd      | nd                          | nd                          | nd     | nd     | nd     |
| IC5  | BDE-47                      | BDE-100 | BDE-99 | BDE-154 | BDE-153 | BDE-183 | BDE-209                     | a-HBCD                      | b-HBCD | g-HBCD | ΣHBCDs |
| 2014 | 260                         | 37      | 120    | 62      | 360     | 110     | 41                          | 420                         | 99     | 1300   | 1819   |
| 1998 | 100                         | 79      | nd     | nd      | nd      | nd      | 14                          | nd                          | nd     | 430    | 430    |
| 1990 | 73                          | 59      | nd     | nd      | nd      | nd      | 0.4                         | nd                          | nd     | 120    | 120    |
| 1980 | 54                          | 51      | nd     | nd      | nd      | nd      | 0.32                        | nd                          | nd     | 56     | 56     |
| 1970 | 50                          | 49      | nd     | nd      | nd      | nd      | 0.38                        | nd                          | nd     | 46     | 46     |
| 1960 | 30                          | 52      | nd     | nd      | nd      | nd      | nd                          | nd                          | nd     | 57     | 57     |
| 1943 | nd                          | nd      | nd     | nd      | nd      | nd      | nd                          | nd                          | nd     | nd     | nd     |
| 1925 | nd                          | nd      | nd     | nd      | nd      | nd      | nd                          | nd                          | nd     | nd     | nd     |
| 1910 | nd                          | nd      | nd     | nd      | nd      | nd      | nd                          | nd                          | nd     | nd     | nd     |

nd = below limit of detection

Table SI-3 continued

| Concentration (pg/g dry wt) |        |         |        |         |         |         |         | Concentration (ng/g dry wt) |        | Concentration (pg/g dry wt) |        |  |  |
|-----------------------------|--------|---------|--------|---------|---------|---------|---------|-----------------------------|--------|-----------------------------|--------|--|--|
| BB                          | BDE-47 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | BDE-183 | BDE-209 | a-HBCD                      | b-HBCD | g-HBCD                      | ΣHBCDs |  |  |
| 2014                        | 350    | 37      | 140    | 25      | 26      | 74      | 42      | 480                         | 110    | 2000                        | 2590   |  |  |
| 1997                        | 120    | nd      | 67     | nd      | nd      | nd      | 4.3     | 150                         | nd     | 4300                        | 4450   |  |  |
| 1990                        | 4      | nd      | 25     | nd      | nd      | nd      | 0.86    | 86                          | nd     | 1700                        | 1786   |  |  |
| 1985                        | 5      | nd      | 20     | nd      | nd      | nd      | 0.29    | nd                          | nd     | 1400                        | 1400   |  |  |
| 1975                        | nd     | nd      | 19     | nd      | nd      | nd      | 0.27    | nd                          | nd     | 1500                        | 1500   |  |  |
| 1960                        | nd     | nd      | nd     | nd      | nd      | nd      | nd      | nd                          | nd     | 1300                        | 1300   |  |  |
| 1950                        | nd     | nd      | nd     | nd      | nd      | nd      | nd      | nd                          | nd     | 1200                        | 1200   |  |  |
| NH                          | BDE-47 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | BDE-183 | BDE-209 | a-HBCD                      | b-HBCD | g-HBCD                      | ΣHBCDs |  |  |
| 2014                        | 740    | 30      | 160    | 29      | 45      | 74      | 21      | 980                         | 310    | 4000                        | 5290   |  |  |
| 1996                        | 65     | 19      | 180    | nd      | 9.2     | 20      | 0.5     | 110                         | 14     | 270                         | 394    |  |  |
| 1988                        | 260    | 26      | 270    | nd      | nd      | 7.7     | 0.23    | 570                         | 61     | 1200                        | 1831   |  |  |
| 1975                        | 25     | nd      | 24     | nd      | nd      | nd      | 0.12    | 76                          | 32     | 390                         | 498    |  |  |
| 1963                        | nd     | nd      | nd     | nd      | nd      | nd      | 0.17    | 83                          | nd     | 49                          | 132    |  |  |
| 1926                        | nd     | nd      | nd     | nd      | nd      | nd      | nd      | nd                          | nd     | nd                          | nd     |  |  |
| 1901                        | nd     | nd      | nd     | nd      | nd      | nd      | nd      | nd                          | nd     | nd                          | nd     |  |  |
| 1859                        | nd     | nd      | nd     | nd      | nd      | nd      | nd      | nd                          | nd     | nd                          | nd     |  |  |

nd = below limit of detection