

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

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4 **Historical Trends of PBDEs and HBCDs in Sediment Cores from**
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6 **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 (\sum_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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4 **1. Introduction**
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6 Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDs) have been
7 used extensively as brominated flame retardants (BFRs) worldwide. PBDEs have been used
8 in various consumer goods, including foam-upholstered furniture, and high impact
9 polystyrene (HIPS) casings for electrical goods (Bromine Science Environmental Forum
10 (BSEF) 2007; D'Silva et al. 2004). Global HBCD demand in 2003 was 22,000 tonnes
11 (Health and Environment Alliance 2013). Its major applications were in expanded or
12 extruded polystyrene (EPS/EXPS) building insulation and HIPS (Abdallah et al. 2007).
13 Minor uses include the housing of domestic electrical appliances and car seats, latex binders,
14 and textile coatings (National Industrial Chemicals Notification And Assessment Scheme
15 (NICNAS) 2014).
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18 Whilst the physicochemical behaviour of different PBDE congeners varies based on their
19 level of bromination, both PBDEs and HBCDs are hydrophobic and resistant to degradation
20 (D'Silva et al. 2004; Davis et al. 2005), rendering them environmentally persistent and
21 capable of bioaccumulation (Alaee and Wenning 2002). A combination of these properties
22 and their extensive use has led to substantial contamination of indoor and outdoor
23 environments and exposure to humans and wildlife (Covaci et al. 2006; Darnerud 2003;
24 Toms et al. 2009).
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27 BFRs enter the environment via emissions to air, soil and water from their manufacture
28 through to volatilisation and leaching during their use and disposal (Toms et al. 2008).
29 Sediments are sinks for BFRs and other persistent compounds with previous studies
30 demonstrating that various sediment types (marine, estuarine, freshwater) are contaminated
31 with persistent compounds from both diffuse and point sources (Minh et al. 2007; Taylor et
32 al. 2004; Toms et al. 2008). A potentially important point source of these compounds to
33 aquatic ecosystems is storm water. Storm water contains a mixture of material including
34 sewage overflows and discharge of industrial contaminants and as such, storm water drains
35 have been highlighted as point sources for a variety of pollutants, including PBDEs, to
36 aquatic environments (Birch and Taylor 1999; Richman et al. 2013). Furthermore, urban and
37 industrial activities are important sources of BFRs in the environment (Harrad and Hunter
38 2006; Kohler et al. 2008).
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41 There is a lack of information regarding temporal trends of PBDEs in the Australian
42 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 20th 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 ²¹⁰Pb and ¹³⁷Cs 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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4 All samples underwent combined pressurised liquid extraction and clean-up for PBDEs and
5 HBCDs using an ASE 350 (Dionex) and Dionium® cells (a zirconium alloy able to tolerate
6 highly acidic and basic conditions). The full methods are described elsewhere (Abdallah et al.
7 2013). Between 5-10 g (accurately weighed) of each sample were weighed in disposable
8 measuring boats before being added to 100 mL pre-packed Dionium® cells containing (from
9 the bottom upwards): two microfibre filters (Dionex), silica gel (Sigma Aldrich), 5 g florisil
10 (60-100 mesh, Sigma Aldrich), 3 g diatomaceous earth (Sigma Aldrich, UK), microfibre
11 filter, 10 g acid impregnated silica (44% sulfuric acid), microfibre filter, 5 g copper powder, 2
12 g hydromatrix. The remaining volume of the cell was filled with hydromatrix and spiked with
13 known amounts of internal standards (¹³C labelled BDEs -47, -99, -153, -183, -209 and ¹³C
14 labelled α-, β and γ HBCDs). The ASE cells were extracted with DCM and hexane (1:1 v/v)
15 at 90°C and 1500 psi (heating time 5 minutes, static time 5 mins, 3 static cycles, flush volume
16 – 50%, purge time – 120 s). The extract was concentrated to near-dryness using a hotplate (40
17 °C) under a gentle stream of nitrogen, before being transferred to GC vials and reconstituted
18 in 100 µL of ¹³C-labelled BDE-100 (sediment core samples) or ¹³C₁₂-labelled PCB-141 &
19 ¹³C₁₂-labelled TBBP-A (2014 samples) in methanol as a recovery determination standard
20 prior to instrumental analysis of all compounds excluding BDE-47. After injection on LC-
21 MS/MS (section 2.3) samples were concentrated to dryness and reconstituted in 50 µL
22 hexane for GC/MS analysis.

23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 *2.3 Analysis*

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40 Concentrations of HBCDs (α-, β- and γ-) and most targeted PBDEs (BDEs -99, -100, -153, -
41 154, -183 and -209) were analysed via HPLC-APCI-MS/MS using an ABSciex API5500Q
42 mass spectrometer (ABSciex, Concord, Ontario, Canada) equipped with an atmospheric
43 pressure chemical ionisation (APCI) source coupled to a Shimadzu Prominence HPLC
44 system (Shmadzu Corp., Kyoto Japan). Full details are described in Gallen et al. (2014).

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

55 56 57 58 59 60 61 62 63 64 65 *2.4 Quality Control*

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4 Each batch of samples was run with a blank consisting of approximately 10 g diatomaceous
5 earth. If a target compound was detected in a blank at 5-25% of the level in a sample from the
6 same batch, then the blank concentration was subtracted from that particular sample. If the
7 blank level was below 5% then no correction was applied. No target compounds were
8 detected in blanks at >25% of any corresponding samples. In the absence of a QC sample at
9 the times of analyses, SRM 2585 (n=4) was analysed with sediment cores. For all analytes,
10 good agreement was found with certified/indicative values. Surficial sediment samples were
11 also analysed in duplicate with agreement between results (Table SI-2). Concentrations
12 presented here are the average of these duplicates.
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20 *2.5 Calculation of Doubling Times*

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22 To calculate doubling times, a graph of ln(concentration) against time was plotted (Figure SI-
23 1). The slope of this line was used as the first order rate constant (k) used in the following
24 equation:
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$$28 \text{ Doubling time} = \frac{\ln(2)}{k}$$

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33 Doubling times were only calculated where concentrations increased in three consecutive
34 sediment core layers.
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40 **3. Results and Discussion**

41 *3.1 Temporal Trends*

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44 The concentrations of \sum_6 PBDEs (BDEs -47, -99, -100, -153, -154 and -183), BDE-209 and
45 \sum HBCDs in each layer of sediment is presented in Table 1. Data on individual congeners and
46 isomers is supplied in the supporting information (Table SI-3). Contaminants were detected
47 in low levels in sediments deposited as early as 1950-1960s (\sum HBCDs, average = 0.59 ng/g
48 dry wt) and 1960-1970s (\sum_6 PBDEs (-47, -99, -100, -153, -154 and 183) average= 0.038 ng/g
49 dry wt and BDE-209, average = 0.23 ng/g dry wt). Rapid increases in concentrations were
50 observed between 1980 and 2014, which led to peak average concentrations of 3.5, 1.3 and
51 42 ng/g dry wt for \sum HBCDs, \sum_6 PBDEs and BDE-209 respectively in 2014 surficial
52 sediments.
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4 Figure 1 demonstrates the changes in PBDE concentrations from the oldest sediments in
5 which PBDEs were detected (ca. 1960) to surface samples taken in 2014. BDE-209
6 represented an average of 81% (range: not detected (nd)-100%) of \sum PBDEs. Therefore, in
7 this section, BDE-209 is presented separately to \sum_6 PBDEs.
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11 Our data are consistent with use in Australia of the Penta-BDE commercial formulation, with
12 the sum of BDEs -47, -99 and -100 (each of these representing major congeners found in
13 Penta-BDE) contributing an average of 30% (range: nd-100%) to the total PBDE content
14 (including BDE-209) during the 1970s and 1980s. Although \sum_6 PBDE concentrations increase
15 over time, attaining a maximum in 2014, their overall contribution to total PBDE content
16 decreases due to a rapid BDE-209 increase between 1990-2014 with an average contribution
17 of BDE-209 to \sum PBDEs in 2014 samples of 97% (range: 95-99%). This increase is
18 highlighted by the shorter doubling time of BDE-209 (Table 2) compared to that of \sum_6 PBDEs
19 and HBCDs. This is likely to reflect a high release of the Deca-BDE formulation during the
20 1990s and 2000s in and around Sydney estuary. This is unsurprising, given that the import of
21 Penta- and Octa-BDE observed a reduction in excess of 70% between 1998 and 2004 leaving
22 DecaBDE to represent 86% of the total PBDE import into Australia at 180 tonnes (Toms et
23 al. 2008). Moreover, whilst further importation of Penta- and Octa-BDE was banned in 2005
24 (Toms et al. 2009), DecaBDE usage has not been restricted (although it was listed as a
25 priority existing chemical within Australia in 2005 (National Industrial Chemicals
26 Notification And Assessment Scheme (NICNAS) 2007)). Whilst it is unsurprising that BDE-
27 209 is the dominant PBDE congener, it is interesting that the highest concentrations of Penta-
28 BDE (-47, -99 and -100) and Octa-BDE (BDEs -183 and -153) based congeners were found
29 in the surficial sediments taken in 2014. This is somewhat concerning as the aforementioned
30 restrictions of Penta- and Octa-BDE in 2005 do not appear to have triggered a reduction in
31 PBDE input into Sydney estuary, almost ten years later. This is likely to be due to the
32 relatively long mixing times of sediments compared to other environmental compartments,
33 such as air meaning that it is unlikely that sediment concentrations will reflect any reduction
34 of PBDE use in the last ten years. This has also been demonstrated in the UK by Yang et al.
35 (2014) where similar restrictions of Penta- and Octa-BDE have been in place since 2004.
36 These authors stated that atmospheric concentrations of Penta-BDE congeners have fallen
37 since the turn of the 21st century, however water samples from lakes across the UK have not
38 shown the same reduction, which they attribute to the comparatively long mixing times of
39 freshwater lakes.
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4 HBCDs followed a similar pattern to PBDEs, with sharp increases in concentration during the
5 1990s with maximum Σ HBCD concentrations found in the most recent sediments. In three
6 (IC3, IC5 and NH) out of the four locations studied, Σ HBCD concentrations were highest in
7 the surficial sediments sampled in 2014 (Figure 3). Σ HBCD concentrations at BB, peaked in
8 sediment representative of 1997 (4.5 ng/g dry wt), and declined to 2.6 ng/g dry wt in surficial
9 sediment from 2014. These patterns are consistent with commercial use of HBCD in
10 Australia – importation of HBCDs and its containing products into Australia peaked in 2006-
11 07 (90 tonnes), but decreased to approximately 60 tonnes in 2010, when the import of HBCD
12 as a powder or granules ceased (National Industrial Chemicals Notification And Assessment
13 Scheme (NICNAS) 2014). Whilst HBCD has recently been listed as a POP under the
14 Stockholm Convention, its primary use (cavity wall insulation) is exempt from any ban until
15 2024, meaning that input of HBCDs in this rapidly urbanised estuary is likely to continue for
16 the foreseeable future (Swedish Society for Nature Conservation 2014).

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27 The increases in HBCDs and PBDEs, post 1960 (particularly 1980-2014) may be due to
28 changes in historical land-use in areas adjacent to our sampling sites – with substantial use as
29 landfills until the late 1980s including in areas upstream and close to sampling sites.

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32 Landfilled materials include: construction, demolition, industrial and domestic waste (Birch
33 2007) and have been shown to leach pollutants, such as metals into Sydney estuary (Suh et al.
34 2003a, b; Suh et al. 2004). It is well documented that landfill leachate has been found to
35 contain BFRs, including HBCDs and PBDEs and that it can be considered a source to the
36 environment (Stubbings and Harrad 2014). The land surrounding our sample sites has also
37 undergone large redevelopment and urbanisation since the 1980s. It has also been
38 demonstrated that urbanisation itself can lead to increased release of BFRs into the
39 environment due to high building density and associated BFR sources (Harrad and Hunter
40 2006). A combination of surface run-off, overflowing storm water and possible leaching from
41 within “landfills” are plausible explanations for the large increases of BFRs found in Sydney
42 estuary sediments between 1980 and 2014.

3.2 Global Comparison

PBDEs

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57 The historical changes of PBDE concentrations in sediment from Sydney estuary reflect
58 patterns seen elsewhere. Minimal concentrations before the 1970s followed by sharp
59 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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31 Surface sediments from Sydney estuary contain average PBDE levels towards the top end of
32 the range of concentrations found globally (Figure 4). For example, our measurements appear
33 to be similar to those Laizhou Bay in China, where the average \sum_7 PBDE concentration in
34 sediments taken from the vicinity of a PBDE manufacturing site was 52 ng/g dry wt (Pan et
35 al. 2011). Concentrations in Sydney estuary are also almost ten times higher than those in
36 sediment taken from San Francisco Bay, California (Klosterhaus et al. 2012).
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41 *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 γ -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 α -, β - and γ -
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4 HBCD respectively. This is consistent with findings from studies in China (Feng et al. 2012;
5 YW Zhang et al. 2013), Japan (Minh et al. 2007), UK (Harrad et al. 2009) and USA (Marvin
6 et al. 2006). Furthermore, it is similar to the stereoisomer profile of HBCD technical
7 mixtures, which contain 12.5%, 11.1% and 76.4% α -, β - and γ -HBCD respectively (Crump et
8 al. 2010) – a profile observed in most sediments (Covaci et al. 2006).

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13 Concentrations in sediments from Sydney estuary are similar to those detected in locations
14 not directly impacted by HBCD manufacture. The average (2014) concentration of 3.5ng/g
15 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
16 sediment from urban and industrial areas (as demonstrated by Figure 5), but approximately
17 10-200 times lower than in sediment sampled close to HBCD manufacturing plants.

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21 Furthermore, the concentrations in individual sediment layers from the cores are of a similar
22 level to those in sediment layers representative of similar years in Switzerland (Kohler et al.
23 2008), Tokyo (Minh et al. 2007; Tanabe et al. 2008) and China (Tanabe et al. 2008; L Zhang
24 et al. 2013).

25 26 27 28 29 30 31 **4. Conclusions**

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34 PBDEs and HBCDs were detected in all sediments taken in Sydney estuary from 1960s
35 onwards. Concentrations of both groups of compounds underwent rapid increases from 1980-
36 2000. BDE-209 underwent a further increase from 2000-2014 leading to \sum_7 PBDE
37 concentrations similar to those found in Laizhou Bay, China – close to a PBDE
38 manufacturing plant, suggesting that usage of Deca-BDE increased considerably following
39 restrictions of Penta- and Octa-BDE in 2005. Maximum \sum HBCD concentrations in all
40 sediments (1.8-5.3 ng/g dry wt) are similar to sediment concentrations globally in areas of
41 similar land-use, suggesting that HBCD usage in Australia has been similar to the rest of the
42 world. The intense urbanisation of Sydney estuary catchment since the 1980s is likely to
43 contribute largely to the increases in PBDE and HBCD concentrations in sediments, with a
44 combination of surface run-off and storm water drainage into the river transferring BFRs into
45 Sydney estuary from surrounding highly-developed catchment. This is particularly reflected
46 by dramatic increases in BDE-209 levels – especially considering the known extensive use of
47 DecaBDE in domestic and commercial products in the late 1990s to early 2000s globally, as
48 well as its extensive importation rates into Australia at the beginning of the 21st century. In
49 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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10 11 12 13 14 **Acknowledgements**

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Figures and Tables

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

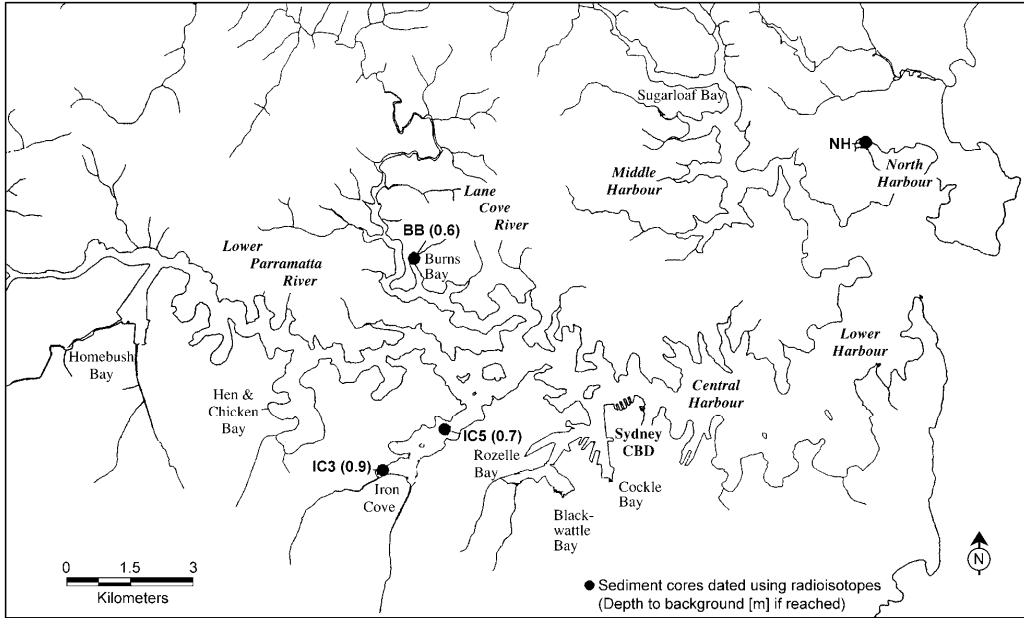
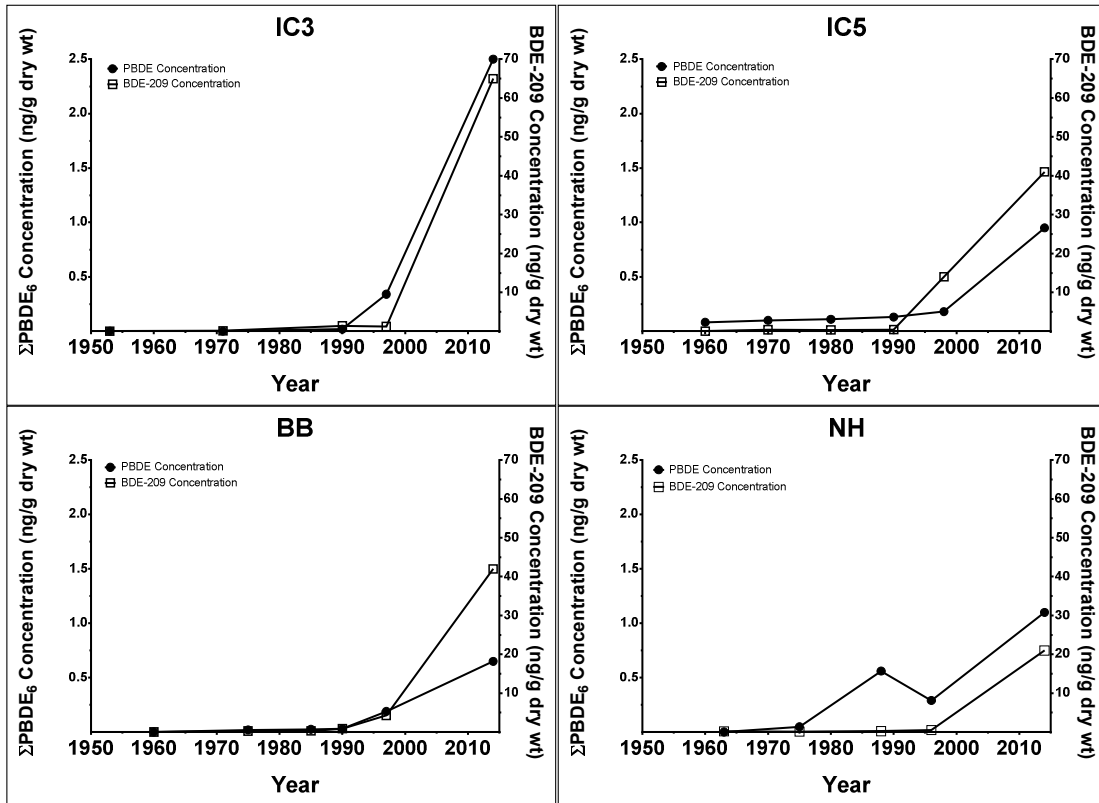
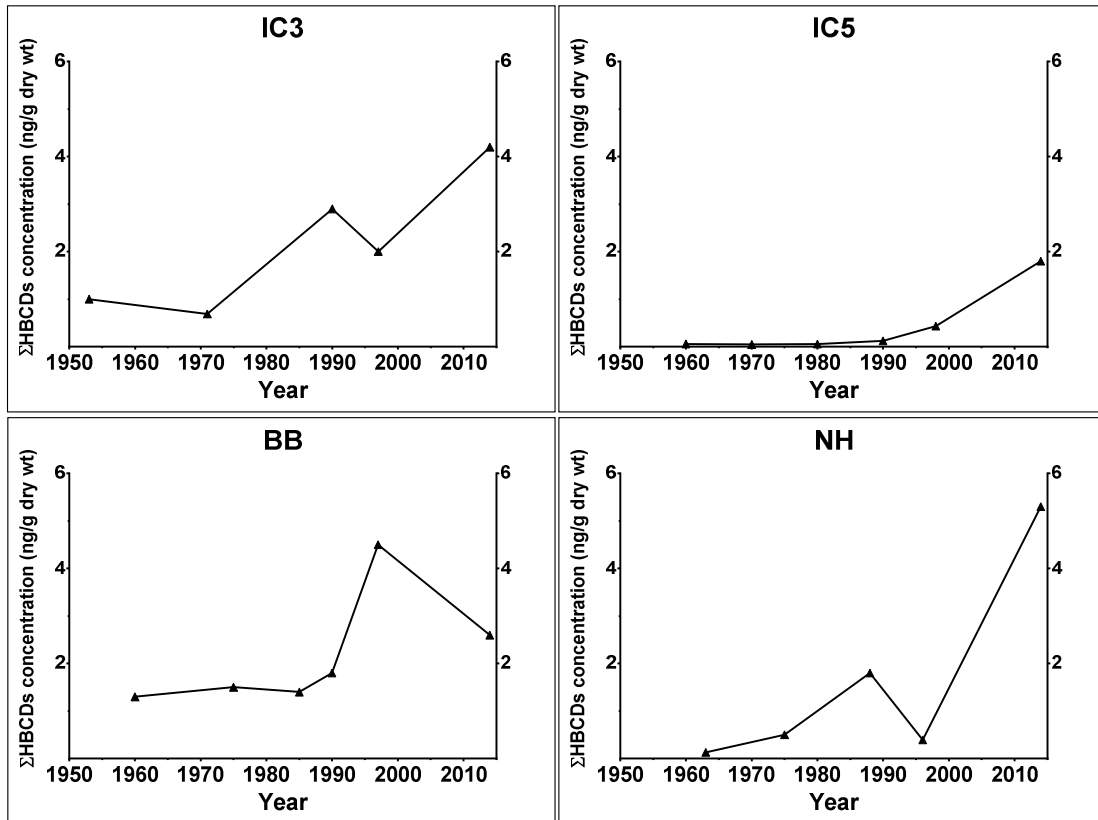


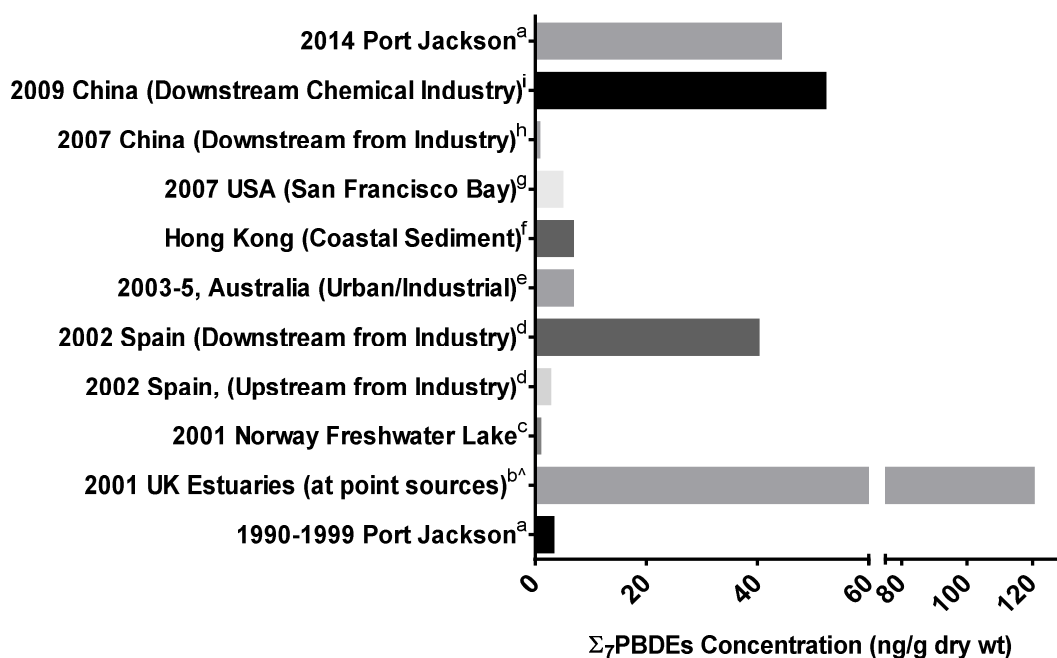
Figure 2 – Σ_6 PBDE and BDE-209 (ng/g dry wt) concentrations in sediments from 4 locations in Sydney Harbour



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4 **Figure 3 – Σ HBCD (ng/g dry wt) concentrations in sediments from 4 locations in Sydney**
5 **Harbour**
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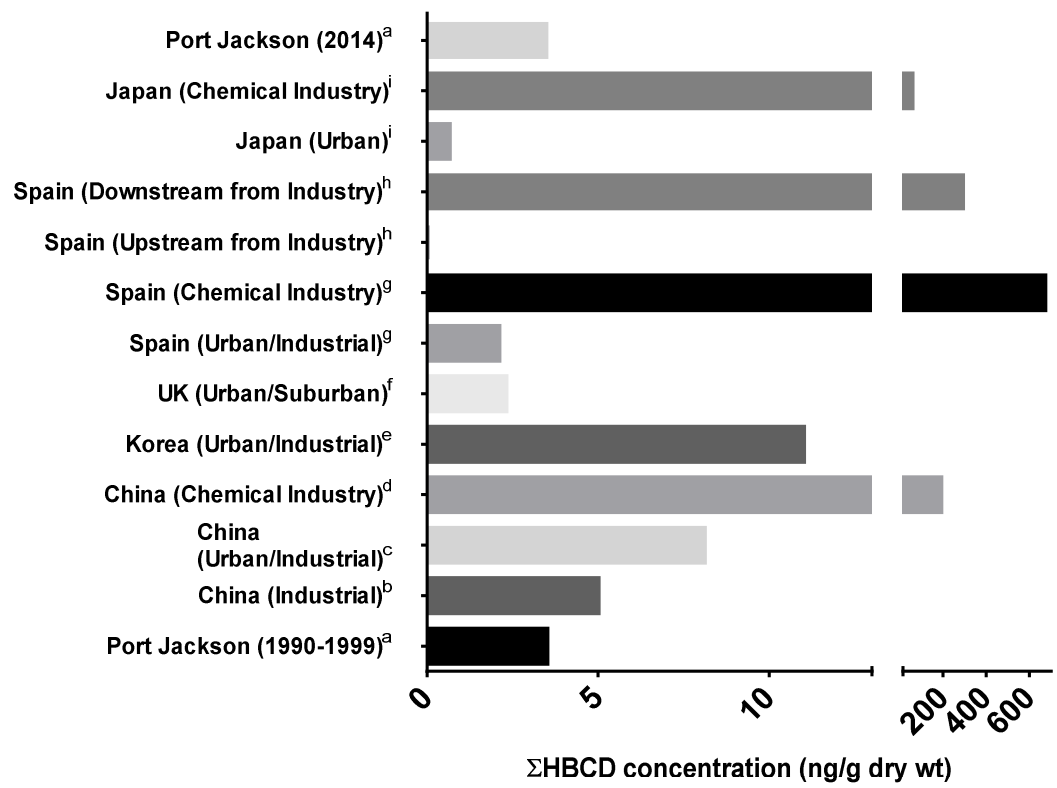
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4 **Figure 4 – Comparison of mean Σ_7 PBDE concentrations from the present study (1990-**
5 **1999 and 2014) with those presented in the literature**
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[^]BDEs -47, -99 and -100 only

^aThis Study, ^bAllchin et al. (1999), ^cEvenset et al. (2007), ^dEljarrat et al. (2004), ^eToms et al. (2006), ^fLiu et al. (2005), ^gKlosterhaus et al. (2012), ^hZhao et al. (2011), ⁱPan et al. (2011)

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



^aAverage 2014 sediments from this study, ^bFeng et al. (2012), ^cYW Zhang et al. (2013), ^dLi et al. (2012), ^eRamu et al. (2010), ^fHarrad et al. (2009), ^gGuerra et al. (2010), ^hEljarrat et al. (2004) ⁱManagaki et al. (2012)

Table 1 – Concentration (ng/g dry wt) of Σ_6 PBDEs, BDE-209 and Σ HBCD concentrations in surficial sediments (2014) and sediment core layers from Sydney estuary

IC3	Σ_6PBDEs	BDE-209	ΣHBCDs	BB	Σ_6PBDEs	BDE-209	ΣHBCDs
2014	2.5	65	4.2	2014	0.65	42	2.6
1997	0.34	1.2	2	1997	0.19	4.3	4.5
1990	0.19	1.4	2.9	1990	0.029	0.86	1.8
1971	nd	0.097	0.69	1985	0.025	0.29	1.4
1953	nd	<0.1	1	1975	0.019	0.27	1.5
1935	nd	<0.1	nd	1960	nd	<0.051	1.3
				1950	nd	<0.089	1.2
IC5	Σ_6PBDEs	BDE-209	ΣHBCDs	NH	Σ_6PBDEs	BDE-209	ΣHBCDs
2014	0.95	41	1.8	2014	1.1	21	5.3
1998	0.18	14	0.43	1996	0.29	0.5	0.39
1990	0.13	0.4	0.12	1988	0.56	0.23	1.8
1980	0.11	0.32	0.056	1975	0.049	0.12	0.5
1970	0.099	0.38	0.046	1963	nd	0.17	0.13
1960	0.082	<0.1	0.057	1926	nd	<0.05	<LOQ
1943	nd	<0.1	nd	1901	nd	<0.098	nd
1925	nd	<0.1	nd	1859	nd	<0.12	nd
1910	nd	<0.1	nd				

Table 2 – Doubling times (years) of Σ_6 PBDEs, BDE-209 and Σ HBCD concentrations in Sydney estuary sediment from 1990-2014

	IC3	IC5	BB	NH[^]
Σ_6PBDEs	6.3	8.1	5.8	N/A
BDE-209	4	5.7	4.4	3.9
ΣHBCDs	N/A	6.3	N/A	N/A

[^]Doubling time for NH calculated from 1988-2014

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4 **Supporting Information**
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6 *Table SI-1 HRGC/HRMS parameters for BDE-47 analysis*
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Injection					
Injection Type			Splitless		
Split Flow			Constant (70 mL/min)		
Inlet Temperature			300 °C		
Injection Volume			1 µL		
GC Program					
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
HRMS Program					
Compound	Quantifying Ion		Qualifying Ion		
BDE-47	483.71310		485.71110		
¹³ C ₁₂ -BDE-47	495.75530		497.75130		

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

Compound	SRM-2585		Duplicate Analyses							
	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^a	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^a	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^a	120 ± 22	123 ± 12	2.62	2.62	1.38	1.28	1.90	2.01	4.12	3.95

^a Indicative values taken from Keller (2007)

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

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

nd = below limit of detection

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Table SI-3 continued

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

nd = below limit of detection

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