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Trends in Hexabromocyclododecanes in the UK and North America

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1. Abstract. Water samples (n=107) taken from nine English freshwater lakes from a mix of urban, rural, and remote locations on 12 occasions between August 2008 and February 2012, and archived suspended sediment samples (n=39) collected over the period 1980-2012 at the mouth of the Niagara River in Lake Ontario were analysed to assess the temporal trends in contamination by the three main hexabromocyclododecane (HBCD) diastereomers (α-, β-, and γ-HBCD). HBCDs (45 to 890 pg L^{-1}, n=107) were generally equally distributed between the operationally defined freely dissolved and particulate phases in English lake water. Concentrations of HBCDs declined over the sampling period with half-lives of 5.1 years in English water, with a significantly decreasing trend also observed for Niagara River suspended sediments (NRSSs). With respect to seasonal trends, significantly higher concentrations were found in colder compared to warmer periods at 5 out of 9 English lakes, while NRSSs in this study revealed no statistically significant seasonal trends. The maximum HBCD concentration in NRSSs was about 3 orders of magnitude lower than those detected in English lake water, which is plausible given the greater *per capita* use of HBCD in Europe than North America. While γ-HBCD was consistently dominant (35-86%; mean=56%) in English lake water samples, and dominated in NRSSs collected prior to 2002 inclusive (13-100%, mean=73%), the abundance of γ-HBCD was significantly lower (3.5-37%; mean=23%) in NRSSs from 2003 onwards.

Keywords: HBCD, suspended sediment, surface water, United Kingdom, North America

2. Introduction

Hexabromocyclododecane (HBCD) has been produced since the 1960s (Marvin et al., 2011), and used as an additive BFR in expanded (EPS) and extruded polystyrene (XPS) foams used as thermal insulation for buildings, as back-coating for upholstery textiles, and in electronic housing (Covaci et al., 2006; de Wit et al., 2010). Since the 1980s, the BFR industry has employed HBCD as an early replacement for Penta-BDE in Europe and more recently in the US (Muir and de Wit, 2010), making it until relatively recently the most abundantly used additive BFR. HBCD was produced in China (9,000-10,000/15,000 tons in 2009/2010), Europe and the USA (combined annual 13,426 tons by the ESEF (Bromine Science and Environmental Forum) member companies in 2009), and Japan (data not available), with as of 2011, known annual worldwide production being approximately 28,000 tons (Report of the persistent organic pollutants review committee on the work of its seventh meeting, 2011). The main share of the market volume was in Europe and China (UNEP, SCOP-HBCD risk management evaluation), with the publicly available data showing that in 2001 - in contrast to PBDEs - 60% of HBCD was consumed in Europe compared to 17% in the Americas (BSEF, 2006).

HBCD can be released into the environment during production and manufacturing, processing, transportation, use, handling, storage or containment, as well as from disposal of the substance or products containing the substance, via either point source discharges or diffuse releases (UNEP, SCOP-HBCD risk management evaluation). HBCD has been found in almost all environmental compartments with considerable concentrations found in aquatic organisms and foodstuffs, providing evidence of its bioaccumulative capacity. Harrad et al., (2009) reported an average bioaccumulation factor (BAF) of 2,100 for ΣHBCDs, with higher values observed for α-HBCD (5,900), than β- (1,300) and γ-HBCD (810). Moreover, food web magnification was reported for α-HBCD and ΣHBCDs, with trophic magnification factors of 2.22, and 1.82, respectively (Wu et al., 2010), indicating both the potential for biomagnification, and its isomer-specificity. As a result of its persistence and potential adverse environmental and ecological impacts, HBCD has attracted the attention of legislators worldwide. It was included in the OSPAR list of chemicals for priority action under their Hazardous Substances Strategy (OSPAR, 2007). This restriction was closely followed by its listing under the Stockholm Convention on POPs. However, time-limited exemptions were granted for its production and use in EPS and XPS building insulation foam (BSEF, 2013).

Freshwater bodies act as sinks for chemical contaminants introduced via direct discharges via anthropogenic activities (e.g. sewage outfalls), dry and wet deposition from the atmosphere, and land surface run-off. Within such freshwater bodies, water plays an important role in POPs circulation within the aquatic system via partitioning with sediment, air, and aquatic organisms. Therefore, the presence and behaviour of POPs in freshwater bodies such as lakes is an important area of study. Previous studies have identified sediment as an important abiotic compartment for assessment of the overall environmental cycling of HBCD (Marvin et al., 2006; Zhao et al., 2017; Webster et al., 2009; Poma et al., 2014).

Studies on HBCDs in the UK water system are rare, and there is a striking gap with respect to knowledge of temporal and spatial trends in HBCD contamination. The Niagara River is the primary watercourse discharging to Lake Ontario, contributing approximately 85% of the total input, and roughly half of the fine-grained sediments entering the lake (Kemp and Harper, 1976). It is of concern due to its severe environmental degradation, and thus the Niagara River was listed as a Great Lakes Area of Concern in 1987 under the Great Lakes Water Quality Agreement between the US and Canada (Niagara River Area of Concern, 2010).

This study evaluates temporal trends in HBCD contamination at the outlet of the Niagara River with the aim of enhancing understanding of historical changes in HBCD inputs into the river and consequent discharges of HBCDs to Lake Ontario, reflecting also the historical changes in discharges of HBCDs from regional population centres along the watershed. Moreover, samples taken in spring and summer over the period 2004-2012 were used to assess seasonal trends of HBCDs in the Niagara River. These temporal and seasonal trends are compared with those observed in English freshwater lakes. We also compare absolute concentrations in the Niagara with those in England in the context of the relative intensity of HBCD use in the two regions. Finally, spatial trends between the 9 English lakes and influences on these are examined.

3. Materials and Methods

3.1 English Lake Water. A map of the sampling locations is provided as Supporting Information (SI) in Figure S1, with more details shown in Table S1. Sampling of 40 L water per sample was conducted on 12 occasions from each of our 9 freshwater lakes throughout England; however one sample for Thoresby Lake was missing due to drought on one sampling occasion, making 107 samples in total for HBCDs. Initially, between August 2008 to July 2010, sampling frequency was quarterly, switching to biannually thereafter until the last sampling event in February 2012 (See Table S2 for sampling dates). Details on water sampling, filtration, extraction, and extraction purification methods were reported previously elsewhere (Harrad et al., 2009).

3.2 Niagara River Suspended Sediments (NRSSs). Suspended sediment sampling was conducted in March, April/May, June, July, and August between 1980 and 2012 at Niagara-on-the-Lake sampling station, which is at the mouth of the Niagara River in Lake Ontario (around 1 km upstream of Lake Ontario) on the Canadian side (see Figure S2). Details on sampling, sample filtration, extraction, and extract purification methods have been reported previously (Marvin et al., 2007). Sample extracts were concentrated to dryness and reconstituted in 50 µL methanol containing $^{13}C_{12}$-labelled α-, β-, and γ-HBCD.

3.3 Instrumental Analysis. Analysis of HBCDs in English lake water was conducted at the University of Birmingham using LC-MS/MS procedures as reported previously (Harrad et al., 2009) In brief, water samples were gravity filtered through glass fibre filter followed by 2 polyurethane foam plugs and treated with ^{13}C-α–,β- and γ-HBCD as internal (surrogate) standards, prior to pressurised liquid extraction (Dionex ASE-350) with hexane:dichloromethane, 1:1 v/v). Crude extacts were partitioned against concentrated sulfuric acid, followed by elution through 1 g florisil with 30 mL hexane:dichloromethane (1:1 v/v). Just prior to LC-MS/MS analysis d_{18}-α- and γ-HBCDs were added as recovery determination (syringe) standards. Chromatographic separation of HBCD isomers was achieved using a dual pump Shimadzu LC-20AB prominence liquid chromatograph equipped with SIL-20A autosampler and DGU-20A3 vacuum degasser. A Varian Pursuit XRS3C18 reversed phase analytical column (150 mm x 2 mm i.d., 3 µm particle size) was used. A mobile phase of (a) 1:1 water/methanol with 2 mM ammonium acetate and (b) methanol at a flow rate of 150 µL min^{-1} was applied for elution of the target compounds; starting at 50% (b) then increased linearly to 100% (b) over 3 min; this was held for 5 min followed by a linear decrease to 65% (b) over 2.5 min and held for 3.5 min. Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass spectrometer operated in the ES negative ion mode. Infusion experiments utilized the built-in Harvard syringe pumpwith a flow rate of 10 µL min^{-1}. MS/MS detection operated in the MRM mode was used for quantitative determination of the HBCD isomers based on m/z 640.6- m/z 79, m/z 652.4-m/z 79, and m/z 657.7- m/z 79 for the native, ^{13}C-labelled, and d_{18}-labelled diastereomers, respectively. Analysis of NRSSs were performed using LC-ESI-MS/MS (Tomy et al., 2005).

In brief, approximately 10 g of freeze-dried suspended sediment was spiked with 13C-labelled, and d18-labelled diastereomers and extracted by Accelerated Solvent Extarction (ASE) in dichloromethane, followed by copper treatement and an open-column florosil (8 g, 1.2% water, 10.5 mm i.d. x 300 mm) eluted with hexane (38 mL) and 50:50 dichloromethane (42 mL) to afford a fraction containing the HBCDs. Extracts were HB were analysed using an Agilent 1200 LC system that equipped with an Agilent Zorbax Eclipse Plus C_{18} column (2.1 mm x 100 mm x 3.5 μm). The injection volume was 5 uL. A mobile phase program based upon (A) water/acetonitrile (1:1, v:v) and (B) methanol at a flow rate of 0.25 mL min^{-1} was applied for the elution of HBCD isomers. Commencing at 60 % (B) for 4 min, the proportion of (B) in the mobile phase was linearly increased to 100 % over 3 min and held for 5 min, then programmed linearly to 60 % (B) over 3 min, and held for 7 min. HBCD isomers were determined using an AB Sciex QTRAP 4500 System equipped with an ESI source operated in negative ion mode. Ion transitions of m/z 640.7/78.9, and m/z 652.7/78.9 were detected in the multiple reaction monitoring mode (MRM) for quantification of native, and $^{13}C_{12}$-HBCD isomers, respectively

3.4 Quality Assurance and Quality Control. Due to the lack of standard reference material (SRM) for HBCD in sediment, the accuracy and precision of the English water sample analysis was evaluated via triplicate analysis of NIST SRM2585 (House Dust; Table S3), which showed very good agreement with certified or indicative values reported previous in literatures, alongside good precision. Information on recoveries of internal standards, analysis of blanks, instrumental limits of detection (LODs), and method limits of quantification (LOQs) in both water and NRSS samples are given in SI.

4. Results and Discussion

4.1 HBCDs in English Water Samples. Concentrations of total HBCDs (sum of α-, β-, and γ-HBCD) in water in this study ranged from 45 to 890 pg L^{-1} (see Table S4), with the highest and lowest average ΣHBCDs concentrations found at Edgbaston Pool (230 pg L^{-1}) and Wake Valley Pond (110 pg L^{-1}), respectively. HBCD was listed as a priority hazardous substance in the WFD (Directive 2013/39/EU), with environmental quality standards for the annual average and maximum allowable concentration for inland surface freshwater of 1.6 ng L^{-1} and 500 ng L^{-1}, respectively. HBCD concentrations in our nine English lakes did not exceed these levels.

Reports on HBCD concentrations in freshwater are relatively rare: (a) HBCD ranged from 96 to 2,900 pg L^{-1} in freshwater (n=5) sampled in 2012 from Denmark (Vorkamp et al., 2014), which was slightly higher than in our English freshwater lakes; Outside Europe, (b) HBCDs detected in water from Yodo river basin in Japan ranged from 190 to 14,000 pg L^{-1} (mean annual, July 2012-May 2013)(Ichihara et al., 2014); (c) γ-HBCD was detected in 2 out of 12 water samples collected in 2010 from Taihu Lake, China, at concentrations of 370 and 180 pg L^{-1}, respectively, while α-, and β-HBCD were not detectable (Xu et al., 2013). HBCD concentrations in Taihu Lake are comparable with our study but at much lower detection frequencies.

4.2 Concentrations of HBCDs in NRSS. HBCDs were detected in 27 out of 39 archived NRSS samples during 1980 and 2012, with relatively higher detection frequency (86 %) of HBCDs in samples collected prior to 2003 (see Table S5 for details of samples with HBCD detected). The maximum ΣHBCD concentration was 1.33 (mean=0.23, median=0.05 across all samples) pg L^{-1}, or 97.9 (mean=38.2, median=19.3 across all samples) pg g^{-1} dw on a TSS normalised basis. Note that suspended sediments represent the particulate phase in bulk water. Given that in English lake water, 47-61% (mean=53%) of ΣHBCDs were found in the particulate phase (Table S6), concentrations of ΣHBCDs in Niagara River bulk water may reasonably be assumed to range between two- and ten-fold that in its suspended sediments. Even allowing for this, concentrations of ΣHBCDs (combined dissolved and particulate phases) in bulk water samples from our English lakes ranging from 45 to 890 (mean=165) pg L^{-1} (water volume normalised concentrations) or 1.4 to 600 (mean=56) ng g^{-1} dw (TSS content normalised concentrations) during 2008 and 2012 were about 3 orders of magnitude higher than those detected in the Niagara River. With respect to sediment core samples taken from 7 of the same lakes as this study (Yang et al., 2016); after its first emergence, ΣHBCD concentrations (0.06-9.76 ng g^{-1} dw) was consistently found above detection limits in English sediment core segments, with mean and median values of 2.02 and 1.30 ng g^{-1} dw, respectively. These exceed by approximately two orders of magnitude the HBCD levels recorded here in archived NRSSs.

The observation of lower HBCD concentrations in the Niagara River than in English lakes is plausible given that in 2001, 60% of commercial HBCD was consumed in Europe compared to 17% in the America (BSEF, 2006), indicating potentially more HBCD could have been released into the European than North American environment. Moreover, HBCD concentrations in North America could be further "diluted" due to the lower population density than in European countries like the UK. Interestingly however, concentrations of ΣHBCDs in surficial sediments collected in 2007 from the Great Lakes (0.04-3.1 ng g^{-1} dw; Yang et al., 2012) were only a few times lower than those recorded in our surficial sediments from English lakes (0.42-7.87 ng g^{-1} dw; mean = 2.50 ng g^{-1} dw). These contrasting findings highlight that the factors influencing environmental contamination with HBCD are complex, and further research is required to account for these intercontinental differences.

4.3 Partitioning of HBCDs between Dissolved and Particulate Phase. Across all sites, 47-61% of ΣHBCDs were found in the particulate phase (Table S6), with an average±□$_{n-1}$ value of 51±6%, 50±9%, 54±5%, and 53±5% for α-, β-, γ-, and ΣHBCDs, respectively; revealing no apparent diastereomer-specific differences in partitioning between the dissolved and particulate phases. This could be due to their relatively similar Log K_{OW} values (5.07, 5.12, and 5.47 for α-, β-, γ- HBCD, respectively). Preliminary results on phase partitioning of HBCDs in some fresh water samples from the same English lakes were reported previously (Harrad et al., 2009); those agree closely with our full dataset reported here.

4.4 Seasonal Impacts on Concentrations of HBCDs in English Lake Water. There is clear potential for POPs concentrations in various environmental matrices to display seasonal variation. Potential influencing factors could include: water temperature, TSS content, and rainfall etc. This section therefore addresses the potential seasonal variations in HBCD levels in English lake water, and its causes. In this study, sampling dates from March 21st to September 20th were defined as warmer periods with an average temperature of 16.4 ˚C; while dates from September 21st to March 20th were defined as colder periods with an average temperature of 6.4 ˚C.

4.5 Seasonal and Temporal Trends. In line with a previous study of the River Seine (Cailleaud et al., 2007), we observed higher TSS contents (mean values) in colder compared to warmer periods at Crag Lough, Edgbaston Pool, Holt Hall Lake, Marton Mere, and Thoresby Lake (by factors of 1.1, 1.8, 1.3, 1.4, and 2.3, respectively). Such winter increments in TSS are likely attributable to greater re-suspension of sediment due to die-back of aquatic plants and increased mixing of the water column due to higher precipitation and wind speeds during colder periods. For Chapman's Pond, Fleet Pond, Slapton Ley, and Wake Valley Pond, TSS contents in colder period were lower than/equal to those in warmer period, by factors of 0.6, 0.5, 0.4, and 1.0, respectively.

Across the monitored period, HBCDs displayed seasonal trends, with higher average concentrations (expressed on both a water volume and TSS content basis) in colder periods at most (but not all) sites, as shown in Figure S3 and S4. Very striking is that, as shown in Figure 1, the ratios of average HBCD concentrations in colder periods relative to those in warmer periods at each individual site displayed a significant positive linear correlation ($p<0.001$) with seasonal ratios for TSS. This indicates that TSS is an important factor driving ΣHBCD concentrations in English lake water. However, linear regression analysis of data for all samples from all sites combined showed no significant positive correlation either between HBCD concentrations and TSS, or a combination of TSS and season or water temperature.

As shown in Figure 2, among the 16 NRSS samples collected in the spring and summer seasons during 2003 and 2012; ΣHBCDs were more frequently detected in samples taken in spring (5 out of 8 samples) than in those taken in summer (3 out of 8 samples). However, while average concentrations of ΣHBCDs expressed on a water volume normalised basis were very similar in spring (0.024 pg L^{-1}) and summer (0.023 pg L^{-1}); TSS normalised concentrations were lower in spring (6.94 pg g^{-1}) than in summer (9.63 pg g^{-1}), but with no statistical significance observed (t-test, $p>0.05$). Note that in our study of English lakes, both operationally defined dissolved and particulate phases were analysed for HBCDs; while for Niagara River, only suspended sediments, which were similar to our operationally defined particulate phase from English lake water, were analysed for HBCDs.

4.5.1 English Lake Water To evaluate temporal trends in concentrations of HBCD in English lake water over the duration of this study, we plotted the natural logarithm of the concentration in each sample against sampling day. The first sampling date was defined as day=0, and the last sampling day=1274. The half-life ($T_{1/2}$) was estimated using the equation:

$T_{1/2}=1/\mathrm{Slope}(k)*\ln(2)$

Where k = the 1st order rate constant for the decline/increase in HBCD concentrations (day^{-1})

When data for individual sites are examined, ln(ΣHBCDs, pg L^{-1}) declined significantly at Chapman's Pond ($R=-0.569$, $p=0.027$; $T_{1/2}$ =1279 days), Marton Mere ($R=-0.731$, $p=0.003$; $T_{1/2}$=648 days), and Slapton Ley ($R=-0.708$, $p=0.005$; $T_{1/2}$ =550 days). Moreover, HBCD concentrations across all sites decreased significantly over the monitoring period ($R=-0.24$, $p=0.006$), with a half-life time of approximately 5.1 years (1875 days; Figure 3). These general trends showed good agreement with that revealed by sediment cores from 7 of the English lakes (Yang et al., 2016).

4.5.2 NRSSs. In total, 39 NRSS samples were analysed. One sample was analysed for each year between 1980~2003, except for 2000 where no archived sample extract was available; with one to two samples analysed each year between 2004 to 2012 inclusive.

Figure 4 shows concentrations of HBCDs on both a water volume and TSS content normalised basis in the Niagara River increased with fluctuations from 1980 onwards, peaking in the at about 1990, respectively, before declining generally thereafter with further fluctuations. HBCDs decreased to extremely low levels after 2002, with concomitantly low detection frequency (47 %). Data for NRSS samples in which HBCDs were detected (n=27) were used to calculate the half-life time ($T_{1/2}$). The estimated $T_{1/2}$ derived was 4.4 years (1989-2012) and 5.1 years (1993-2012 – see Figure S6) for HBCD concentrations on a water volume and TSS content normalised basis, respectively.

4.5.3 The UK vs. North America. Temporal trends of HBCD levels revealed by archived NRSSs were comparable with our observations from most of the English lakes sediment cores we analysed in a previous study (Yang et al., 2016), in which HBCD concentrations have declined or levelled-off from the early 2000s onwards (except at the most urban site where HBCD fluxes are still increasing). About a 10 years lag was observed between the UK and North America though, which would have mirrored the different usages of HBCD formulae in both regions.

4.6 Spatial Trends in Concentrations of HBCDs in English Lake Water. With respect to HBCDs, statistically significant inter-site variability was observed in concentrations normalised for TSS (ANOVA, $p<0.05$), with the highest concentrations seen at Crag Lough and Holt Hall Lake, and the lowest at Fleet Pond (Table S4). This is consistent with our previous observations for PBDE concentrations in the same samples (Yang et al., 2014). This suggests that location does influence the HBCDs concentrations in water in our lakes. We investigated possible causes of this spatial variation via multi-linear regression of average HBCD concentrations at each site against factors such as: lake area, mean depth, lake catchment area, lake catchment ratio (defined as the ratio of lake area to catchment area), lake altitude, and the population density of both: (a) the local authority within which each site was located; and (b) the local authorities within a 25 km radius of each site. No significant relationships were detected. These findings likely reflect the fact that concentrations of HBCDs in water in the lakes in this study are a complex integral of many influential factors.

4.7 Isomeric Profile of HBCDs in English Lake Water and NRSS. In English freshwater lakes, the percentage contributions of α- and γ-HBCD to ΣHBCDs (average±σ_{n-1}) across all English lake water samples ranged from 10 to 43% (28±8%), and 35 to 86% (56±12%), respectively (Figure S5).

In NRSS, γ-HBCD was the dominant isomer overall, with an average relative abundance of 58 % ΣHBCDs across all samples in which HBCD was detected. Interestingly, while γ-HBCD dominated in all NRSS samples collected prior to 2002 inclusive with a relative abundance ranging between 13-100% ΣHBCDs (mean=73%). There are relatively fewer studies to copmare with: (a) γ-HBCD dominated (63-84%), followed by α-HBCD (15-31%) in water from Yodo river basin in Japan (Ichihara et al., 2014); (b) α-HBCD was the main isomer in most freshwater (n=5) and seawater (n=5) samples from Denmark, constituting 40-60% ΣHBCDs; however, α-HBCD was below detection limit in 2 samples, meaning overall that both α- and γ-HBCD accounted for 44% of ΣHBCDs (Vorkamp et al., 2014); (b) while γ-HBCD was detected in 2 out of 12 water samples collected in 2010 from Taihu Lake, α-, and β-HBCD were not detectable (Xu et al., 2013); (c) SPM collected from 5 European rivers (2008-2014) were detected with average 23% α-HBCD (6-58%), 10% β-HBCD (3-32%), and 67% γ-HBCD (31-90%) (Rüdel et al., 2017).

For comparison, γ-HBCD dominates in HBCD commercial mixtures with a reported percentage contribution of γ-HBCD of 75-89%, with α- and β-HBCD present in considerably lower proportions (10-13% and 1-12%, respectively) (Heeb et al., 2005). Clearly, the percentage contribution of γ-HBCD in lake water in the current study is lower than in commercial mixtures. Consistent with this, average α- and γ-HBCD percentage contributions to ΣHBCDs in indoor air (n=25) were 22%, and 66%, respectively, while for matched indoor dust samples, the average contribution of α-HBCD increased significantly to 33%, with that for γ-HBCD decreasing to 56% (Abdallah, 2009). Moreover, the relative abundance of γ-HBCD in water samples was statistically significantly lower/higher (paired sample t-test, $p<0.001$ for both) than in paired surficial sediments/fish samples respectively from the same study reported previously (Harrad et al., 2009).

Interestingly, the HBCD isomer profile shifted in NRSSs collected from 2003 onwards, with γ-HBCD contributing to only 3.5-37% of ΣHBCDs (mean=23%). One possible reason for this statistically significant change in diasteromer pattern (t-test, $p<0.001$) is that post 2002, fresh inputs of HBCDs (in which γ-HBCD dominated) to the Niagara effectively stopped, resulting in a step change shift in the diastereomer pattern potentially due to different environmental processes between diastereomers. This is supported by the significant decrease ($p<0.01$) in ΣHBCD concentrations in NRSS post-2002.

Also, HBCDs have been identified as susceptible to isomerisation at 190 ˚C, with a final composition of 78% α-, 13% β-, and 9% γ-HBCD, regardless of the original composition of the three diastereomers (Peled et al., 1995). As the processes via which HBCDs are incorporated into many applications may involve heat (e.g. adding to molten polymers), this provides a plausible explanation of the higher proportions of α-HBCD observed in water samples in this study. Furthermore, it was also reported that β- and γ-HBCD are degraded more rapidly than α-HBCD under anaerobic conditions (Gerecke et al., 2006).

Temporal changes in HBCD diastereomer patterns at each site over the period of this study were insignificant, indicated by the generally low intra-site standard deviations for the proportions of each diastereomer.

Seasonal trends in the relative proportions of α-, β-, and γ-HBCD were also investigated for all sites. No statistically significant variations were found, supported by both the lack of correlations ($p>0.05$) between the proportions of individual diastereomers and temperature; coupled with similar diastereomer profiles in warmer and colder periods ($p>0.05$ via t-test).

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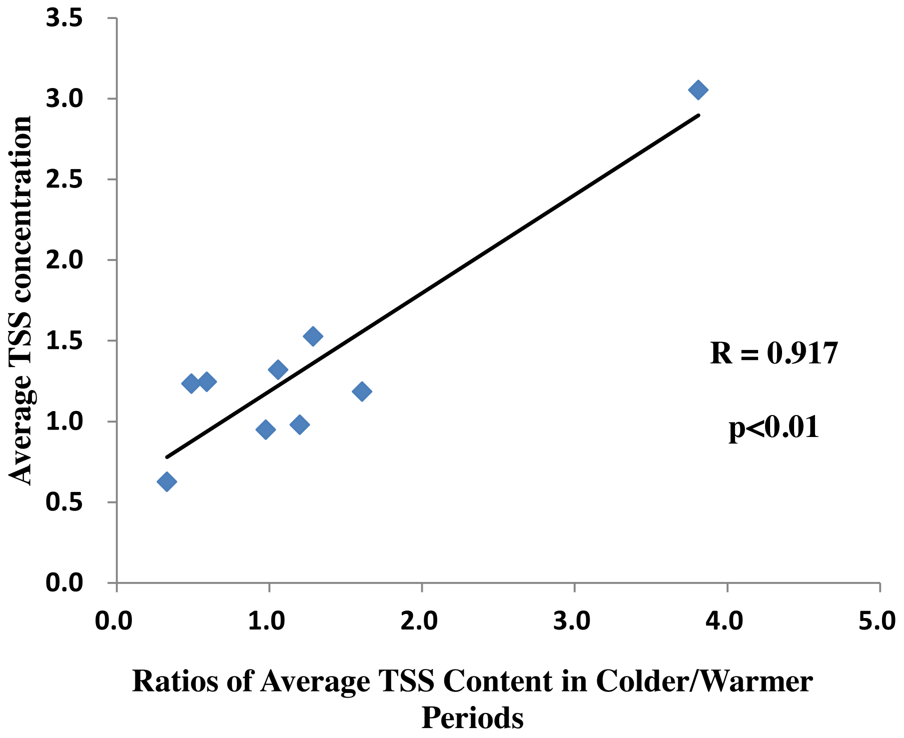

Figure 1: Plots of ratios of average TSS content at individual English lakes in colder/warmer periods against ratios of average concentrations in colder/warmer periods of ΣHBCDs (July 2008-February 2012)

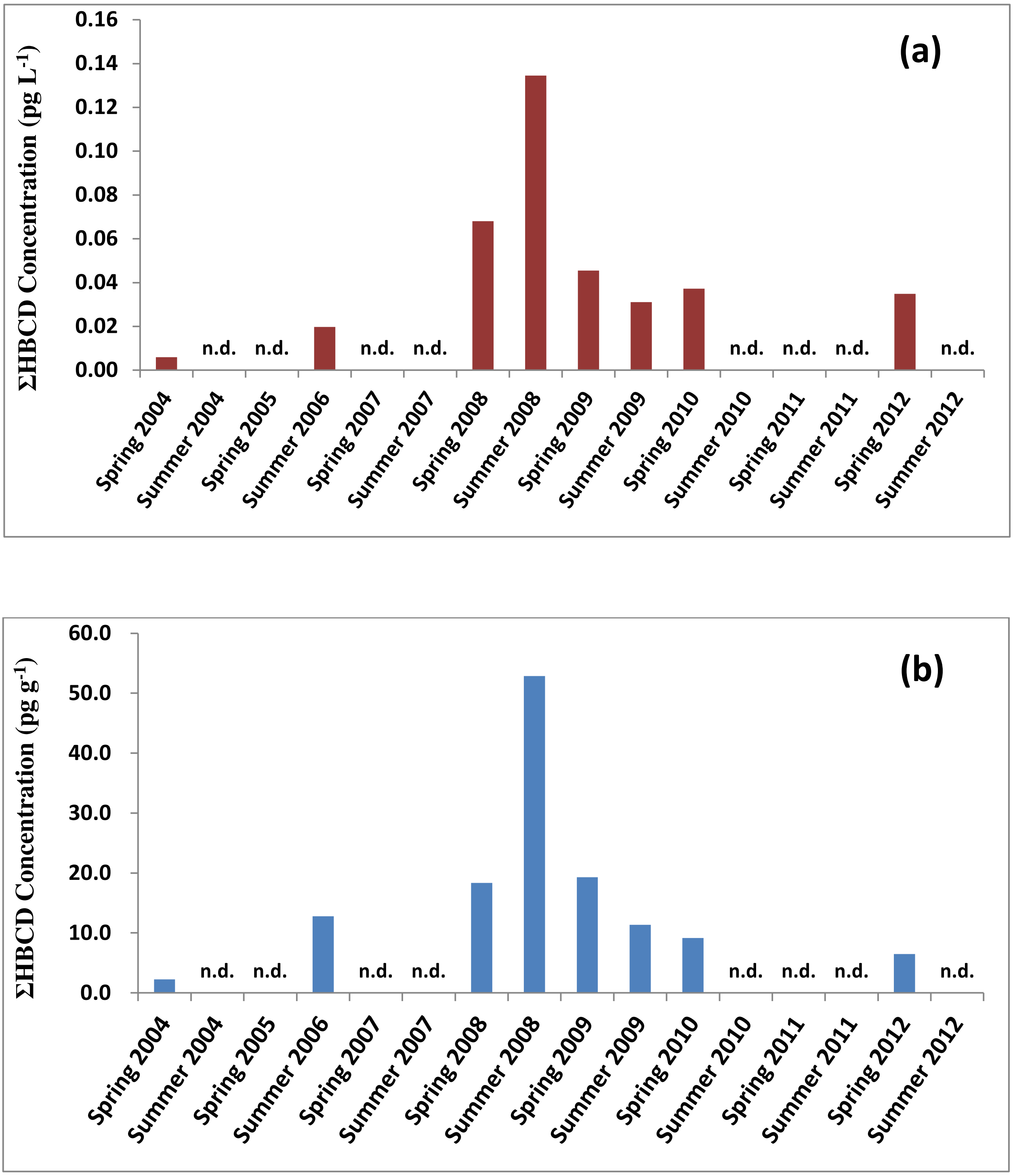

Figure 2: Seasonal trends in concentrations of ΣHBCDs in NRSS samples on both: (a) a water volume (pg L^{-1}), and (b) TSS normalised basis (pg g^{-1} dw), spring 2004 to summer 2012

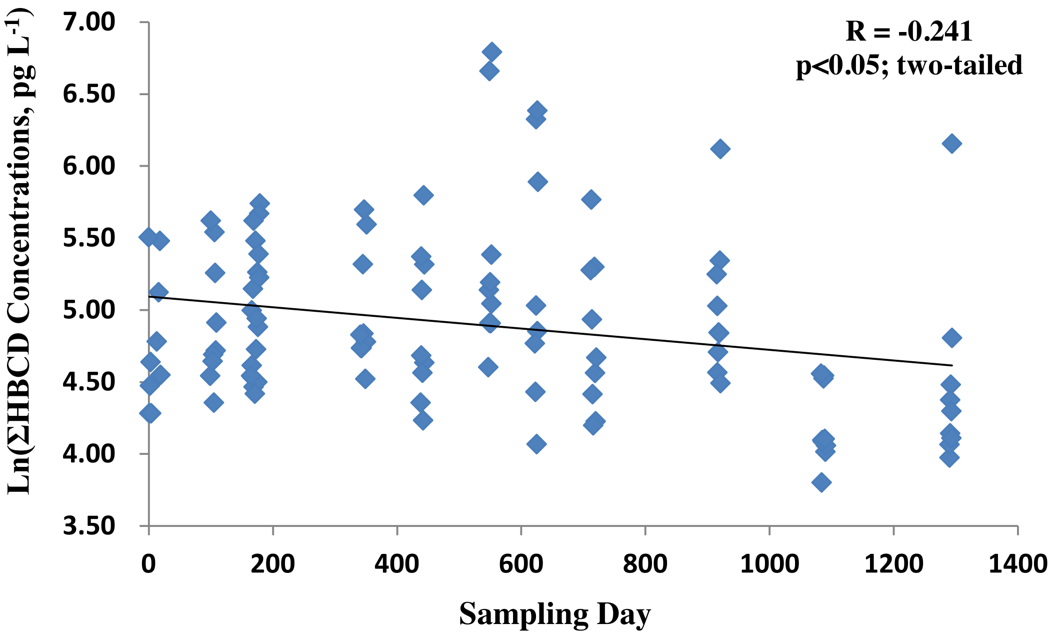

Figure 3: Temporal trends of HBCD concentrations in English lake water (July 2008-February 2012)

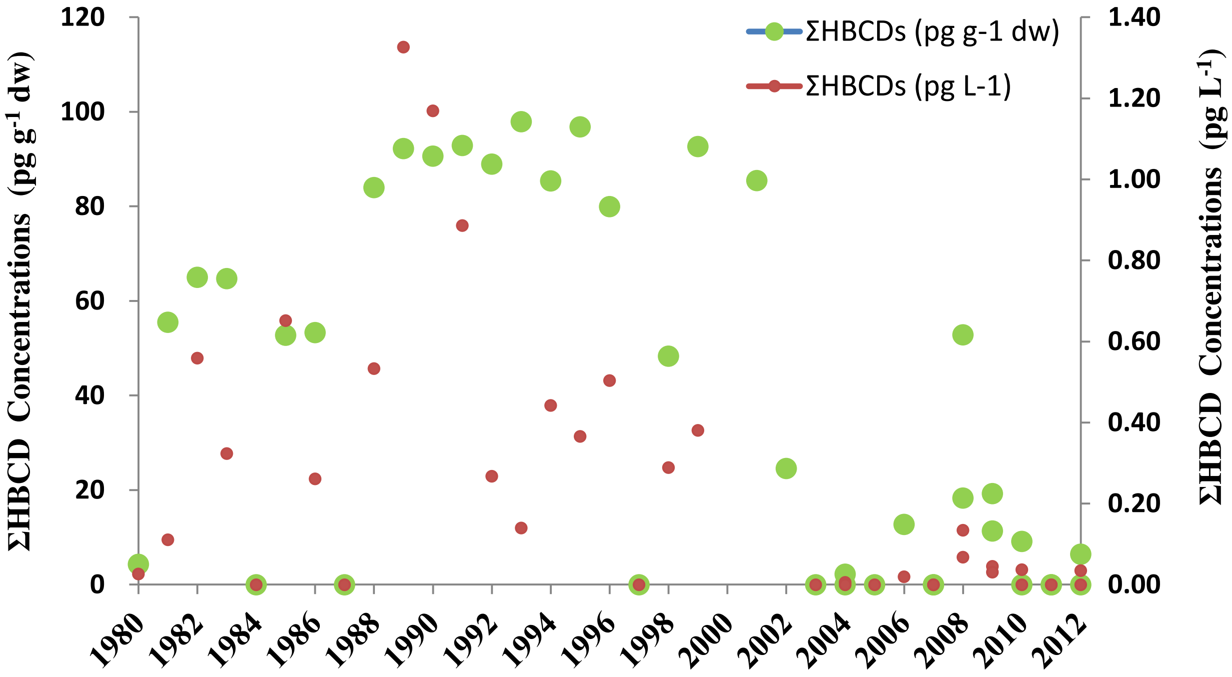

Figure 4: Temporal trends of ΣHBCDs in archived NRSS, 1980-2012

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