CONCENTRATIONS OF PBDEs, HBCDs, TBBP-A, PAH, AND PCBs IN ENGLISH LAKE WATER: FIRST REPORT FROM THE OPAL PROJECT

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Abstract
Introduction: As part of a recently-commenced 5 year project studying the contamination of English freshwater lakes by persistent organic chemicals, this paper reports the concentrations of PBDEs, HBCDs, TBBP-A, PAH, and PCBs in water from 9 English lakes. *Methods and Materials:* Each lake was sampled on 3 occasions at quarterly intervals between July 2008 and January 2009 providing a summer, autumn, and winter sample for each site. *Results and Discussion:* For PBDEs, PAH, and PCBs, concentrations are in line broadly with those reported previously for the UK and elsewhere. To our knowledge, these are the first such data for HBCDs and TBBP-A. Very little seasonal variation in concentrations is evident. Concentrations of TBBP-A exceed those of PBDEs and HBCDs at every site, suggesting that despite its principal use as a reactive flame retardant, TBBP-A is migrating into the environment. Concentrations at each site of ΣHBCDs and TBBP-A are significantly positively correlated, indicating a common source or sources. Averaged across all sites the average$\pm\sigma_n$ proportion of ΣHBCDs, TBBP-A, BDE-47, and BDE-99 associated with the "freely-dissolved" phase was 47$\pm$4.7%, 61$\pm$2.9%, 36$\pm$8.3%, and 29$\pm$7.3% respectively.

Introduction
Contamination of the UK freshwater environment with polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAH) is documented[1,2]. Likewise there is increasing evidence of environmental contamination with brominated flame retardants (BFRs) like polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol-A (TBBP-A)[1,3,4]. However, knowledge of the concentrations of PCBs and PAH in English lake waters is scarce, and to our knowledge there is little known worldwide about the concentrations of PBDEs, HBCDs, and TBBP-A in freshwater. As part of the Open Air Laboratories (OPAL) project, concentrations of these and other pollutants are being monitored in 9 English freshwater lakes for 5 years between 2008 and 2012. Matrices monitored are: water, bottom sediment, and fish. In addition to facilitating the study of the behaviour of the target compounds in a range of lacustrine environments; the project will provide an invaluable base-line against which concentrations at other sites may be evaluated, as well as temporal trends in response to changes in production and usage. This paper reports concentrations of PCBs, PAH, PBDEs (tri- through hexa-BDEs), HBCDs, and TBBP-A in water samples taken during three quarters of the 1st year of the project.

Materials and Methods
Sampling Sites and Methodology
Water was sampled from 9 freshwater lakes throughout England. Figure 1 illustrates their locations. At each location, a grab sample of 40 L of water was collected in 2 x 20 L precleaned HDPE containers. Sampling was conducted every 3 months at each location. For logistical reasons, the exact sampling dates varied for each site; however, the 1st sample batch reported here was taken between 31st July and 17th August 2008 (summer); the 2nd batch between 6th November and 16th November 2008 (autumn); and the 3rd batch between 19th January and 25th January 2009 (winter). After sampling, samples were kept cool and delivered as soon as possible to the University of Birmingham, where the samples were stored cool until analysis.

Sample processing
Samples were filtered via gravity through (water side first): a glass fibre filter to collect particulate matter (GFF,

12.5 cm diameter, 1 μm pore size, Whatman, UK) followed by 2 PUF plugs (8 cm diameter, 4 cm length, 0.03 g cm^{-3} each) housed in a glass cylinder. All the filters and PUF plugs were extracted before use with CH_2Cl_2 for 8 hours in a soxhlet apparatus. Following filtration, the filter paper and PUF plug were combined for analysis for all samples, except for those taken in the summer quarter. For these samples, the filter paper and PUF plug for each sample were analysed separately to provide information on the operationally-defined "particulate phase" and "dissolved phase". Each sample was spiked prior to extraction with appropriate quantities of internal standards, specifically: ^{13}C- labelled PBDEs 28, 47, 99, 153, α, β, γ-HBCDs and TBBP-A, PCBs 34, 62, 119, 131 and 173 plus deuterated acenaphthylene, phenanthrene, anthracene, chrysene, benzo[*a*]pyrene and indeno[1,2,3-cd]pyrene. Extraction was conducted using PLE (ASE 300, Dionex) with hexane:dichloromethane (1:9, *v/v*) at 90 ˚C and 1500 psi. The heating time was 5 minutes, static time 4 min, purge time 90 s, flush volume 50%, with three static cycles.

The crude extracts were concentrated using a Zymark Turbovap® II. Half of the concentrated extract was purified by adding to a florisil column topped with sodium sulfate and eluting with 15 mL hexane followed by 15 mL CH_2Cl_2. The eluate was then concentrated and further purified by DMSO back extraction to remove interfering aliphatic compounds. The purified extract was evaporated under a gentle stream of N_2 followed by reconstitution in 50 μL of nonane (containing *p*-terphenyl and PCBs 19 and 129 used as recovery determination standards) and analysed for PBDEs, PCBs and PAHs using GC-EI/LRMS on an HP6850/5975 MSD. GC-MS conditions were as reported previously by our group[1].

The remaining half of the crude extract was purified by loading onto SPE cartridges filled with 8 g of pre-cleaned acidified silica (44% concentrated sulfuric acid, *w/w*). The analytes were eluted with 25 mL of hexane:dichloromethane (1:1, *v/v*). The eluate was evaporated to dryness under a gentle stream of N_2, then reconstituted in 200 μL methanol (containing d_{18}-γ-HBCD as a recovery determination standard). This was then analysed for HBCDs and TBBP-A using LC-ESI-MS/MS as described previously[5].

Results and Discussion
Seasonal and Spatial Variability in Concentrations and Comparison with Other Studies
Table 1 summarises the concentrations of ΣPAH, ΣPCBs, ΣPBDEs, TBBP-A, and ΣHBCDs in the analysed samples. To our knowledge this is the first report worldwide of concentrations of HBCDs or TBBP-A in freshwater; hence the data here represent a valuable benchmark for future studies. We are also aware of only a very few previous reports of concentrations of PAH and PCBs in UK lake water; the principal focus for these compounds and PBDEs previously being on contamination of bottom sediments and aquatic biota. Table 1 also reports selected data available either for non-UK locations or (in the case of PCBs and PAH) for one UK lake and suggests that the concentrations reported here are consistent largely with those reported elsewhere.

Very striking is the intra-site consistency as evidenced by the low standard deviations, indicating no obvious seasonal variability in contamination. With respect to inter-site spatial variability, this appears low for PCBs, HBCDs and PBDEs (Table 1). Greater variability is observed for PAH. However, the two sites at which the highest concentrations of PAH were observed, also displayed much higher total suspended sediment concentrations. Normalising concentrations to suspended sediment levels reduced the inter-site variability in concentrations of PAH substantially with the ratio of maximum to minimum average concentration falling to 13. Such variations in suspended sediment loadings do not reduce the substantial inter-site variations in concentrations of TBBP-A, for which the same maximum:minimum ratio is 23. We hypothesise that the greater inter-site variability displayed by TBBP-A is indicative of a shorter environmental half-life. This would result in a steeper gradient of concentration on passing from locations closer to emission sources to those further away, than for more persistent chemicals.

Source Attribution
Examination of relationships between concentrations of each contaminant group at each site reveals no significant correlations except for a significant ($p<0.05$) positive correlation between ΣHBCDs and TBBP-A. While this relationship requires continued monitoring to be confirmed; it indicates the existence of a common source or sources of these two BFRs, and may reflect the fact that unlike PAH for which the source is a range of

combustion activities, and the PCBs and the Penta-BDE formulation that is the principal source of the PBDEs monitored in OPAL; HBCDs and TBBP-A are currently manufactured. We also examined the possibility of correlation between concentrations of the target pollutants 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 correlations were found, suggesting that the sources to our sampling sites are not simply attributable to diffuse urban emissions.

Concentrations of "Additive" versus "Reactive" BFRs
Previously, we have observed that despite the far greater production and use of TBBP-A compared to HBCD and the Penta-BDE formulation; the concentrations of TBBP-A in both indoor air and dust as well as outdoor air are lower than those of either HBCDs or tri-through hexa-BDEs[5]. We attributed this to the widespread use of TBBP-A as a reactive flame retardant which makes its release from treated goods less facile than for an additive flame retardant like HBCD. In contrast, the concentrations of TBBP-A exceed those of the other BFRs monitored at every location in this study, in some cases by an order of magnitude. We suggest therefore that TBBP-A does indeed have the potential to migrate into the environment despite its primary use as a reactive flame retardant.

Table 1: Average (σ_n) HBCD Diastereomer Pattern and Concentrations of PAH (ng L^{-1}), PCBs, PBDEs, HBCDs, and TBBP-A (pg L^{-1}) in English Lake Water

Location/Compound	ΣPAH[a]	ΣPCB[b]	ΣPBDEs[c]	TBBP-A	ΣHBCDs[d]	γ-HBCD as %ΣHBCDs
Wake Valley Pond	16 (0.0)	100 (13)	44 (1.9)	140 (9.0)	100 (10)	63 (1.3)
Holt Hall Lake	10 (0.5)	95 (7.5)	62 (4.7)	170 (5.6)	120 (16)	51 (0.3)
Chapman's Pond	76 (12)	110 (7.7)	73 (1.2)	1100 (150)	150 (32)	45 (1.6)
Crag Lough	8.8 (0.2)	77 (5.2)	75 (5.5)	170 (13)	110 (15)	69 (5.4)
Marton Mere	12 (0.2)	180 (8.8)	48 (6.4)	450 (26)	190 (21)	62 (4.0)
Slapton Ley	17 (0.6)	240 (15)	60 (3.6)	3200 (200)	270 (18)	78 (1.8)
Fleet Pond	800 (33)	140 (11)	74 (11)	310 (16)	120 (49)	75 (0.7)
Edgbaston Pool	21 (0.5)	110 (11)	64 (6.5)	1900 (33)	270 (31)	65 (1.1)
Thoresby Lake	15 (0.2)	350 (23)	50 (5.2)	1200 (81)	80 (7.3)	55 (1.8)
Esthwaite Water, UK	-	680[e]	-	-	-	-
San Francisco Estuary, USA	7-120[f]	-	<DL-310[g]	-	-	-

Where concentrations of a specific congener/diastereomer were below detection limits, they were counted as zero for the purposes of calculating descriptive statistics
[a]Sum of acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*j+k*]fluoranthene, benzo[*a*]pyrene, indeno[*1,2,3-cd*]pyrene, benzo[*g,h,i*]perylene, and dibenz[*ah+ac*]anthracene
[b]Sum of PCBs 28/31, 52, 101, 118, 138, 153, and 180
[c] Sum of BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153, and 154
[d] Sum of α-, β-, and γ-HBCDs
[e]Average for "dissolved phase" only samples taken 1996-1997[2]
[f]Range for sum of both phases for samples taken 1993-2001. ΣPAH is sum of 25 PAH including all those monitored in OPAL[6]
[g]Range for sum of both phases for samples taken 2002. ΣPBDE is sum of same congeners as monitored in OPAL[7]

Congener/Diastereomer patterns
Table 1 shows the percentage of ΣHBCDs that is γ-HBCD. The intra-site variability is very low. While further monitoring may prove otherwise; it appears at this stage that there is little seasonal photolytically-mediated

variation in the HBCD diastereomer profile. Inter-site spatial variability in this parameter is evident however. The reasons for these are not obvious at present, but the shift away from the greater predominance of the γ-HBCD in the commercial HBCD formulation is – while variable - clear and is consistent with the hypothesis that the observed predominance of the α-HBCD in biota may not be due exclusively to preferential metabolism of β- and γ-HBCD by cytochrome P450[8].

With respect to PBDEs, the major congeners are BDE 99 and BDE 47. In most samples, BDE 99>BDE47, with average 47:99 ratios across all sites during the three sampling periods of 0.82 (summer – range 0.39-1.19), 0.75 (autumn – range 0.42-0.98) and 0.75 (winter – range 0.47-0.93). This general slight predominance of BDE 99 is in line with the pattern observed in UK soil for which average 47:99 ratios at 10 locations range from 0.51 to 0.88[9], as opposed to those detected in UK outdoor air at the same 10 locations for which 47:99 ratios vary between and 2.95-3.62[9]. We hypothesise that the higher K_{OA} of BDE 99[10] leads both to its greater atmospheric deposition, and greater retention by suspended sediment post deposition relative to BDE 47, with consequent lower 47:99 ratios in lacustrine environments. This is supported by the lower average 47:99 ratios in the colder autumn and winter samples. The 47:99 ratios reported here are generally lower but within the range reported for the San Francisco estuary in 2002[7]. This may be due to: differences in PBDE environmental fate and behaviour between estuarine/marine waters and freshwater; international differences in the congener profile of the Penta-BDE formulation used; or/and greater environmental persistence of BDE-99 relative to BDE-47 following recent restrictions on the manufacture and use of Penta-BDE.

Partitioning of BFRs between "Dissolved phase" and Suspended Sediment
There is currently little or no information regarding the partitioning between the "freely-dissolved" and suspended sediment phases of freshwater for PBDEs, HBCDs and TBBP-A. In this study, the GFF and PUF plugs were analysed separately for the summer samples. This provided a separate measurement for each site of the concentration associated with: (a) suspended sediment; and (b) the "freely-dissolved" phase – defined operationally here as that passing through a 1 μm pore size GFF. Across all 9 sites, the average$\pm\sigma_n$ proportion associated with the "freely-dissolved" phase was: 47±4.7% (ΣHBCDs), 61±2.9% (TBBP-A), 36±8.3% (BDE-47); and 29±7.3% (BDE-99). While there are no previous data for HBCDs and TBBP-A against which we can compare our results, those for PBDEs may be evaluated against reports of such phase partitioning for samples from the San Francisco estuary[7]. While the US data (from 3 sites) included higher brominated PBDEs as well as those monitored in OPAL (which would likely decrease the proportion of ΣBDE associated with the dissolved phase), our data are consistent with the San Francisco estuary where the percentage of ΣBDE in the dissolved phase ranged between 7 and 22%.

Conclusions
The data presented here from the early stages of the 5 year OPAL monitoring project represents a valuable baseline against which contamination of similar locations elsewhere may be evaluated, as well as temporal trends in response to changes in emissions. This is especially relevant for the current-use BFRs HBCDs and TBBP-A, for which there are very few data relating to their presence in freshwater aquatic environments. Little seasonal variation was observed for all target compounds, with concentrations remarkably consistent throughout the three seasons reported here. More substantial spatial variation is evident. Significant positive correlation between concentrations of the currently manufactured HBCDs and TBBP-A suggests a common source or sources of these BFRs. Future work in OPAL will continue to monitor concentrations in water, but will also include measurements of the target compounds in bottom sediments and fish.

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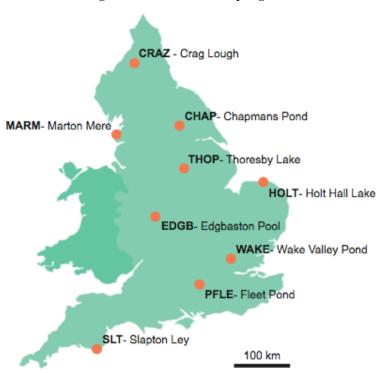10. Harner, T., and Shoeib, M. *J. Chem. Eng. Data* 2002;47:228-232.

Figure 1: Location of Sampling Sites