Persistent Organic Pollutants in sediment and fish in the River Thames Catchment (UK)

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Abstract:

Some organic pollutants including polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs) and hexachlorobenzene (HCB) have been banned from production and use in the UK for more than 30 years but due to their toxicity and persistence are still of concern. However, due to their hydrophobicity they are present at very low concentrations and are difficult to measure in water, and so other matrices need to be sampled in order to best assess contamination. This study measured concentrations of ΣICES 7 PCBs (PCB congeners 28, 52, 101, 118, 138, 153 and 180) and Σ 6 PBDEs (PBDE congeners 28, 47, 99, 100, 153, 154) and HCB in both bed-sediments and wild roach (a common pelagic fish) in the Thames Basin. The highest sediment concentrations were detected in an urbanised tributary of the Thames, The Cut at Bracknell (HCB: 0.03-0.40 µg/kg dw; ICES 7 PCBs: 4.83-7.42 µg/kg dw; 6 BDEs: 5.82-23.10 µg/kg dw). When concentrations were expressed on a dry weight basis, the fish were much more contaminated than the sediments, but when sediment concentrations were normalised to organic carbon concentration they were comparable to the fish lipid normalised concentrations. Thus, despite the variability in the system, both sediments and wild fish can be considered suitable for representing the level of POPs contamination of the river system given sufficient sample numbers.

Keywords: POPs, Sediment, Fish, River Thames

1. Introduction

Due to their persistence, bioaccumulation potential and toxicity many Persistent Organic pollutants (POPs) remain of concern and are prominent in environmental legislation (Vonderheide *et al.*, 2008; Kuzyk *et al.*, 2010; Nicolaus *et al.*, 2015). These compounds of concern, which include organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), have been eliminated or severely reduced in production and use due to environmental concerns. This study focuses on PCBs and hexachlorobenzene (HCB), a fungicide, for which an environmental quality standard for biota has been set in the first version of the EU Priority Substances Directive (European Union, 2008) which were both banned in the EU more than 30 years ago, as well as PBDE flame retardants most of which have been banned since 2004.

Normally, chemical pollutants in rivers are monitored by regular sampling of the water column, but here there is a problem, because in the UK in recent years, HCB, PBDEs and PCBs concentrations are close to or lower than the detection limits for current methods. For example, between 2000 and 2015 only six out of 4373 Environment Agency HCB measurements from the non-tidal Thames and its tributaries were above the detection limit of 1 ng/l (http://environment.data.gov.uk/water-quality).

The chemicals in the current study have log K_{ow} values between 5 and 8 (Schenker *et al.*, 2005; Rowe, 2009) so they tend to partition much more favourably to organic matrices than water. However, natural water bodies contain suspended sediments which may be partly or wholly composed of organic matter which can act as an important sorbent for POPs (Katagi, 2002). These suspended sediments will ultimately become bed-sediments and consequently, high concentrations of POPs can be found in bed-sediments of rivers (e.g. up to 4 or 5 µg/kg dry weight for BDE 99 and BDE 47 respectively in River Viskan, Sweden 1995 (Sellström *et* *al.*, 1998); 105-400 µg/kg dw for the sum of 27 PCBs (ICES 7 PCBs[1] contributed about half of that) and up to 272 µg/kg dw for the sum of 10 tri- to hexa-BDEs (including the 6 commonly monitored ones) in the Scheldt river, Belgium (Covaci *et al.*, 2005; Vane *et al.*, 2007). In the UK, high levels organic pollutants have been observed in the Mersey, Clyde, and Tyne estuaries (Vane *et al.*, 2007; Vane *et al.*, 2010; Nicolaus *et al.*, 2015). The concentrations of PCBs in some sediment samples from the Thames estuary were recently reported to have exceeded the Ecotoxicological Assessment Criteria (EACs) derived by the Oslo and Paris Convention (OSPAR) by up to 218 fold (Nicolaus *et al.*, 2015). The difficulty with bed-sediment sampling, however, is that the distribution of fine organic rich sediments can be very variable across a river, even over distances of a few metres (Hedges and Keil, 1995; Bianchi *et al.*, 2007; Wakeham and Canuel, 2016).

An alternative is examining the presence of POPs in wildlife, known as biomonitoring. Monitoring aquatic wildlife for the presence of POPs is attractive for two reasons, firstly they are another potential organic sorbent and secondly they represent what we want to protect in the first place. There has been some use of macroinvertebrates, such as Gammarus species, but this has been most used in connection with metals (Lebrun *et al.*, 2015). However, Short-lived species low down the food web such as these are not ideal for monitoring low levels of POPs. Molluscs have been used for biomonitoring but there are some indications that their accumulation does not correlate well with sediments for some POPs (Bervoets *et al.*, 2005). This may be related to their low position in the food web (grazer). Fish are higher in the food web and so are more connected to their whole environment through their diet. High concentrations of POPs can be found in fish through long-term exposure to a contaminated water environment (MacKay and Fraser, 2000; Fujii *et al.*, 2007; Deribe *et al.*, 2011). Assessing the degree of contamination of priority organic pollutants in fish is now becoming

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[1] ICES 7 PCBs are recommended by International Council for Exploration of Sea (ICES) for marine environment monitoring, includes PCB congeners 28, 52, 101, 118, 138, 153 and 180.

a component of national and international efforts to monitor the distribution of organic pollutants and their adverse effects in river ecosystems (European Union, 2008; 2013). In the UK, a fish archive has been established by CEH (Centre for Ecology and Hydrology, Wallingford) (http://www.ceh.ac.uk/our-science/projects/national-fish-tissue-archive) to investigate the occurrence of pollutants in fish (mainly roach, *Rutilis rutilis*) from English rivers. Since 2007, about 200-300 fish have been caught per year from different river sites in England and stored at -80°C as a resource for monitoring chemical pollution or other aspects of fish and environmental health (Jürgens *et al.*, 2013). Roach offer a number of advantages for biomonitoring in lowland rivers as they are abundant, do not roam far, typically no more than 300 m (Baade and Fredrich, 1998; Penczak, 2006; Bolland *et al.*, 2009) and they have a broad diet. Their food sources include invertebrates, such as the larvae of many insects, molluscs, algae and plant remains (Mann, 1973).

This study had the following objectives:

- To examine if, and to what extent, the freshwater River Thames bed-sediments are contaminated with HCB, 7 PCBs and 6 PBDEs;
- To assess whether this contamination can be linked to local sewage effluent discharge;
- To examine whether POPs contamination can be correlated to the depth of the sediment sample;
- To examine if and to what extent the roach fish of the River Thames are contaminated;
- To assess whether bed-sediment and fish POPs concentrations can be correlated.

2. Materials and methods

2.1 Sediment sampling

The sediment samples were collected in 2013 using 28mm diameter copper tubes filled with dry ice to freeze the sediment to the core, which was then pulled up allowing the collection of undisturbed sediment layers (Jürgens *et al.*, 2014 and Supporting Information Figure. SI 1). The sediment samples were collected from seven sites in the River Thames and its tributaries (Littlemore Brook, a very small tributary impacted by a large sewage treatment works, both upstream and downstream of the sewage discharge, the river Thames at Wallingford Bridge and Winterbrook, The Cut, an urbanised river downstream of the town of Bracknell, and two rivers with relatively little urban impact, the river Kennet in Newbury, and the river Ock upstream of Abingdon) (Figure 1). One or two sediment cores from each site were used for determining the sediment contamination of organic pollutants in this study. The samples were removed from the tubes by filling hot water into the cores until the frozen cores slipped off. These sediment samples were left to defrost overnight and then sliced into 5-8 layers. Generally divisions were made where the appearance (e.g. colour, grain size etc.) changed, with the exception of the Ock sample which appeared uniform throughout and was therefore cut at 5 cm intervals (Supporting Information, Table SI 1). Large pieces of wood and stones were removed during the segmentation process. The divided sediment samples were added to small plastic vessels for storage and were kept frozen at -20°C. All 5 layers of one sediment core collected from the Littlemore Brook upstream site were analysed. However, for the other sediment cores, only the surface and second layers were examined for POPs contamination in this study (Table SI 1).

2.2 Fish Tissue Archive Project (Fish collecting)

CEH Wallingford has been building up a sample base for fish from UK rivers since 2007 (The Fish Tissue Archive). Whole fish samples have been collected and stored frozen for future use, to allow the measurement of chemical contamination levels and their spatial or temporal trends. Normally ten roach (*rutilus rutilus*, approx. 15 cm long) per site and year are caught by fish monitoring teams of the Environment Agency killed on site with an overdose of 2-phenoxyethanol, and then shipped in a liquid nitrogen cooled dry shipper to a -80 ºC freezer in CEH. A subset of these fish samples were prepared for analysis by breaking the whole fish into a few pieces without defrosting and grinding them into frozen fish powder with a cryogrinder (SPEX SamplePrep 6850). The powder was then divided into pre-cooled glass vials and kept in a -80 ºC freezer until further analysis. Around 10% of the collected fish samples have already been analysed and part of the results (HCB, HCBD, PBDEs in fishes from River Glen, Nene, Kennet and Thames, and PCBs, DDTs, Lindane in eels from the lower Thames) have been reported (Jürgens *et al.*, 2013; 2015). Details of the analysed fish can be found in the supporting information, Table SI 2 and the sampling sites are marked in Figure 1. More detailed fish sampling information is described in Jürgens *et al.* (2013).

2.3 Analytical methods for organic pollutants

- **Extraction and Purification**

The analytical methods for determining organic pollutants including PCBs, BDEs and HCB in sediment and biota samples from the River Thames were based on previously established and approved procedures (Jürgens *et al.*, 2013; Ma *et al.*, 2015).

The sediment samples were defrosted overnight and then washed through a 1 mm mesh sieve using Milli-Q water to remove fine particles stuck on the sieve. The resulting samples were centrifuged to reduce water content and sub-samples of 10 g wet sediment were mixed with 10 g anhydrous sodium sulphate to remove water. The prepared sediment samples were then extracted in dichloromethane (DCM) (approximately 150 ml) at 40 °C for 16 hours in a Soxhlet apparatus. The surface layer from Littlemore Upstream (LM US) was repeated in triplicate to quantify methodological precision. Recovery standards containing ^{13}C-labelled PCBs: 28, 52, 101, 138, 153, 180 and BDEs: 51, 128, 190 were added to the samples before extraction and 5 g of copper powder was added into the receiving flask to reduce the potential interference of sulphides on the analyses. The resulting extracts were evaporated to about 5 ml on a rotary evaporator and then were further concentrated to about 0.5 ml under a gentle stream of nitrogen. The extracts were purified with an acid silica column followed by a gel permeation column (GPC). The eluent was collected in a vial and then concentrated to about 1 ml under a gentle nitrogen stream. After that, the concentrated eluent was transferred to a GC vial containing a known amount of internal standards: PCB 30, ^{13}C-PCB141, ^{13}C-PCB208, BDE69, BDE181 in 25 µl dodecane and blown down under nitrogen to 25 µl.

Frozen fish powder samples (around 5 g of frozen fish powder well mixed with 10 g anhydrous sodium sulphate) were extracted using similar procedures to that used for the sediment samples except that copper addition was not required. Procedural blanks (10 g anhydrous sodium sulphate) were used in each extraction batch. A small portion of the Soxhlet extract was used for gravimetric determination of the lipid content after the solvent had evaporated. The remaining extract was evaporated to a small volume (about 1 ml) and was then taken up for clean-up and further analysis similar to the sediment samples (more details of the fish analysis are in Jürgens *et al.*, 2013; 2015).

- **GC-MS Analysis**

The purified sample extracts were analysed on a Thermo Trace GC Ultra gas chromatrograph (GC), equipped with a 50 m x 0.25 mm, 0.25 µm Agilent CP-Sil 8 CB capillary column, and coupled with a Thermo DSQ mass spectrometer (MS). The instrument was run in EI (electron impact) and SIM (single ion monitoring) mode at a source temperature of 250 °C. The target compounds were the 7 PCBs, 6 BDEs and HCB. The ^{13}C-labeled PCB standards and PBDE standards were purchased from Cambridge Isotope Laboratories, Andover, Massachusetts, while the others were purchased from Wellington Laboratories Inc., Guelph Ontario.

- **Quality Assurance/Quality Control**

For quality control, a blank sample of 10 g sodium sulphate was run with each batch of six samples. To minimise any inherent experimental bias, samples with a mixture of sites were selected for each batch. Method detection limits (MDLs) were derived based on the presence of the analyses in the method blanks. The Method Detection Limit (MDL) is defined as 3 × standard deviation + mean concentration of blanks. The MDLs ranged between 0 and 0.05 ng/g for fish, and 0 and 0.19 ng/g for sediments. For analyte concentrations that are lower than three times of the respective blank value, the MDL was simply the instrumental detection limit (the lowest observable standard on the instrument, equivalent to 1-6.25 pg/µl for the analysed compounds). Recovery standards were used to reduce the potential interference of sulphides on the analyses. The mean recoveries for the fish samples ranged between 92-106 % for PCBs and 80-90 % for PBDEs, while the mean recoveries for the sediment samples were 59%-93% for PCBs and 85%-110% for PBDEs.

2.4 Sediment Organic Carbon content

The concentrations of organic pollutants in the sediment samples should be normalised to dry weight and their organic carbon content to allow comparison to assessment criteria (e.g. Ecotoxicological Assessment Criteria (EACs) of OSPAR 2009). Therefore, the moisture content and the organic carbon content of the sediment samples were determined. Around 10-20 g wet sediment samples were oven dried at 105 °C (± 5 °C) overnight (24h), cooled and weighed to determine the moisture content. After that, the dried sediment samples were ground using a Planetary Ball Mill (PM 100, RETSCH). The sediment organic carbon content was determined using an Elementar Vario EL elemental analyser (Elementar Analysensysteme, Hanau, Germany). The instrument is calibrated using a working standard (Acetanilide) with approximate concentrations of 71.1% total C. The standard is analysed at the beginning of every run, with every 10 samples and again at the end of a run and used to apply a daily correction factor. Two reference soils material are analysed with each batch of samples at intervals of every 20 samples.

3. Results and Discussion

3.1 Contamination levels in Sediment

River bed-sediments can be a major sink/source of organic pollutants in river systems (Lu *et al.*, 2015). However, few studies reported the recent contamination levels of organic pollutants in sediment of the Thames. Over the period 1990-1995 a mean value of 34.4 µg/kg was reported for PCB as 249 Aroclor-1248 in salt marsh sediment of Two Tree Island in the Thames estuary (Scrimshaw and Lester, 2001). Twenty-five sediment samples from different sites and core depth were analysed for HCB, ICES 7 PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180), and 6 BDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154) in the current study. ICES 7 PCBs are recommended by the International Council for Exploration of Sea (ICES) for marine environment monitoring. They are also listed in the latest EU Commission Regulation on methods of sampling and analysis for the control of PCBs (European Commission 2014), without labelling them as ICES 7. The 6 BDEs were chosen as indicators for the contamination of PBDEs in the Thames environment as they are the most commonly found congeners in the environment and are commonly monitored and regulated (e.g. European Union, 2008; 2013).

Comparison of the average results for sediment samples at the seven sites in the River Thames and its tributaries showed a wide range of concentrations (<MDL - 0.34 µg/kg dw for HCB, 0.12 - 27.4 µg/kg dw for Σ ICES 7 PCBs, and <MDL - 14.4 µg/kg dw for Σ 6 BDEs) (Table 1). The contamination levels of Σ ICES 7 PCBs were similar to those reported for the Mersey Estuary, UK (11.7 - 14.4 µg/kg dw) (Vane *et al.*, 2007), but the values for HCB and Σ 6 BDEs were lower than those reported for the Mersey Estuary and the inner Clyde Estuary

(Vane *et al.*, 2007; Vane *et al.*, 2010). There are no environmental quality guidelines available for PCBs, BDEs and HCB in fresh water sediment. However, the levels of Σ ICES 7 PCBs were below the current Ecotoxicological Assessment Criteria (EACs) set up for the use in marine sediment (OSPAR, 2009).

The lowest concentrations of HCB, Σ ICES 7 PCBs and Σ 6 BDEs were detected in the sediments from the River Ock, while the highest values were found at the sites in The Cut and Littlemore Brook (Table 1, Figure 2). The sampling site in the River Ock is in a rural area with little sewage input. The Cut is within an urbanised area and has particularly high exposure to human activities (Putro *et al.*, 2016). It receives high sewage effluent input from Bracknell (on average 43.3% of the flow is treated sewage). Littlemore Brook is an urbanised tributary within an industrialised sub-catchment of the River Thames. In Littlemore Brook, samples were taken from two sites close to each other (about 100m apart), either side of the effluent discharge channel of the Oxford (Sandford) Sewage Treatment Work (STW). In the majority of cases, the concentrations of the studied chemicals were higher in the sediment samples collected from downstream of the STW than in those collected from upstream (Table 1, Figure 2). The sewage effluent could be an on-going source of the contaminations of the studied chemicals in the sediment. However, overall no significant linear correlations (R^2 ranged from 0.0677 to 0.2575) were detected between sediment concentrations of HCB, Σ ICES 7 PCBs and Σ 6 BDEs with the modelled sewage water fraction in the sediment samples from the River Thames and its tributaries (Figure SI 2). The sewage effluent content at the sediment sampling sites was estimated using the Low Flows 2000 Water Quality eXtension model (LF2000 WQX, Wallingford HydroSolutions). The model calculates in a Monte Carlo framework to account for the variability in river flows and per capita influent load. The model randomly selects river and effluent flows from a defined distribution and does 2000 mass balance calculations using different river and effluent flows for each time.

The river flow data used to estimate dilution were taken from the databases within the model (LF2000-WQX). In the modelling, the river flow was defined as log-normally distributed, while the effluent flow was defined as normally distributed. The modelling provides the mean and 90th percentile data for sewage effluent content. Here, the mean percentile effluent content data of the 2000 mass balance calculations was used.

3.2 Variation in sediment concentration with depth

A wide variation in the concentrations of PCBs, BDEs and HCB with depth was observed for the sediment sample from the site at Littlemore Brook Upstream (Figure SI 3). The concentrations of the chemicals were higher in the second layer of the sediment core than in other layers. The sediment layers were divided according to the visual structure of the sediment core, and have varying amounts of sediment organic carbon (SOC) (Top: 0.99%, second: 1.31%, third: 2.04%, fourth: 1.72%, fifth: 1.24%). However, no significant correlation between the sediment concentrations and the sediment organic carbon content was detected (Figure SI 3). Therefore, the variability cannot explained by stronger adsorption to SOC only. It could be a reflection of the trend of usage of the organic chemicals in the study area, but, unlike lake sediments, river bed-sediments are subject to disturbance due to flood events, so depth may not always correspond to time. The penta-mix BDEs, which consists mainly of BDE 99 and BDE 47, has been banned in 2004 (European Union, 2003). The concentrations of BDE 99 and BDE 47 remain high in the surface layer of the sediment sample.

3.3 Contamination in Thames fish

HCB was detected in all fish samples, but none exceeded the EU EQS (Environmental Quality Standards) of 10 µg/kg ww (Table 1) (European Union, 2013). The concentrations of

HCB in Thames and Kennet fish (0.06-1.48 µg/kg) were similar to those in fish from other UK rivers (River Glen: mean 0.21 µg/kg; River Nene: mean 0.68 µg/kg) (Jürgens *et al.*, 2013). The sum of the concentrations of the 6 BDEs (2.30-24.47 µg/kg with a mean value of 9.35 µg/kg) in all of the analysed fish samples from the River Thames were several orders of magnitude higher than the EU EQS of just 0.0085 µg/kg (European Union, 2013). Nevertheless, the levels of Σ 6 BDEs in Thames fish were lower than the levels reported in another recent survey for the River Don (10.55-128.40 µg/kg) (Rose *et al.*, 2015). For PCBs, the concentrations for Σ ICES 7 PCBs in Thames fish (ranged from 3.09-25.66 µg/kg with a mean value of 11.65 µg/kg) exceed the US EPA unrestricted consumption threshold of 5.9 µ/kg for Σ PCBs (Lu *et al.*, 2015). The levels of Σ ICES 7 PCBs were higher than those previously reported in fish from the upper Thames (<0.77-3.32 µg/kg) and the River Glen (2.22-3.84 µg/kg), and were comparable to the levels in fish from the River Nene (3.57-16.39 µg/kg) (Yamaguchi *et al.*, 2003; Jürgens, 2015). As only a limited number of fish have been analysed, it is difficult to demonstrate either temporal or spatial trends of the contaminants in Thames fish, but the fish contamination was much lower in the River Kennet tributary than those detected in the sites of the main river. The catchment of the River Kennet is mainly rural in character and the average sewage content at the sampling site is only 3% by volume (Jürgens, 2015).

3.4 Comparison of Fish Concentrations with Sediment Values

It should be noted that the fish and sediment sampling sites were not in identical locations within the Thames Basin, nor was sampling carried out at the same time. So it might have been assumed that contamination levels in the fish and sediment would bear no relation to one another. Indeed, when comparing the fish and sediment concentrations on a weight for weight basis it is clear that there is higher contamination in the fish (Figure. 3). The median values in fish samples from the River Thames and its tributaries were 30.5, 44.4, and 1.12

µg/kg dw respectively for Σ 6 BDEs, Σ ICES 7 PCBs, and HCB, which were higher than those in the sediment samples[2] (0.30, 2.90, and 0.03 µg/kg dw) (Figure. 3). Therefore, at first it might seem that there is no relationship between fish and sediments with respect to POPs in the Thames Basin. However, when the data is normalised to either lipid (for the fish) or organic carbon (for the sediment) then a similar level of contamination to these matrices can be seen (Figure 3). There is one site on the River Kennet where the fish samples and sediment samples were from the identical location. The dry weight values in fish were about 2-10 times higher than that in the sediment (Figure SI 4). Applying the normalisation for OC and lipid content however didn't influence the described relationship significantly.

In this study, the BSAFs (biota-sediment accumulation factors) (Burkhard *et al.*, 2005) were calculated for the POPs in the roach from the River Kennet to evaluate the relationship between the fish and sediment contamination (Table 2). It is assumed that POPs in water, fish and sediment are at equilibrium and the BSAFs do not substantially change with varying environmental factors. For the 6 BDEs and the ICES 7 PCBs, the BSAF factors were a bit lower than those reported for the same fish species from the Orge River (France) (Teil *et al.*, 2012). The BSAF factors for BDE 28 and BDE 47 were much higher than those for other congeners, which is consistent with the findings of Teil *et al.* (2012) and Sellström *et al.* (1998). To our knowledge, there is no BSAF data available for HCB in roach in the literature. However, the BSAF values were comparable to those reported for caged carp in Dutch freshwater sites field studies (0.17-1.42 µg/g lipid / µg/g OC) (Verweij *et al.*, 2004).

4. Conclusion

There is a continuing need to find the best approach to assess levels of POPs contamination in aquatic environments, which correctly reflect the state of the pollution problem. It is clear

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[2] Sediment samples include all surface and second layer sediments, with a total number of 25 samples.

that water measurements alone are inefficient and misleading. Passive samplers, whilst a better option, also have their problems since they are not linked to the food web. Bed-sediments and biota with a measurable lipid content are sinks for POPs and thus are good options, but at first sight their results may appear quite variable. This study suggests that OC/lipid normalised results in sediment and fish are at a similar level of contamination, which suggests that the two are connected and can provide reassuring corroboration. Thus, even pelagic fish that don't spend all their time in the sediments appear to reflect their level of contamination, presumably through food web connections. The higher concentrations found in fish compared to sediments or water make them suitable markers of POPs contamination in aquatic environments.

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Figure Captions List:

Figure1. Fish and sediment sampling sites of the River Thames Catchment (for site names, see Table 1)

Figure 2. Concentrations of HCB, Σ ICES 7 PCBs and Σ 6 BDEs in sediment samples from seven sites in the River Thames and its tributaries

Figure 3. Comparison between measured chemical concentrations in all River Thames Basin fish and sediments, showing 10, 25, 50, 75, 90%iles as well as outliers

Table Captions List:

Table 1. Concentrations of HCB, PCBs and PBDEs in fish (roach) and sediment samples from the River Thames and its tributaries

Table 2. BSAF (µg/kg_lipid / µg/kg_org.carbon) values for PBDEs, PCBs and HCB in the River Kennet