

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

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9

10 Abstract:

11 Some organic pollutants including polychlorinated biphenyls (PCBs), polybrominated
12 diphenylethers (PBDEs) and hexachlorobenzene (HCB) have been banned from production
13 and use in the UK for more than 30 years but due to their toxicity and persistence are still of
14 concern. However, due to their hydrophobicity they are present at very low concentrations
15 and are difficult to measure in water, and so other matrices need to be sampled in order to
16 best assess contamination. This study measured concentrations of Σ ICES 7 PCBs (PCB
17 congeners 28, 52, 101, 118, 138, 153 and 180) and Σ 6 PBDEs (PBDE congeners 28, 47, 99,
18 100, 153, 154) and HCB in both bed-sediments and wild roach (a common pelagic fish) in the
19 Thames Basin. The highest sediment concentrations were detected in an urbanised tributary
20 of the Thames, The Cut at Bracknell (HCB: 0.03-0.40 $\mu\text{g}/\text{kg dw}$; ICES 7 PCBs: 4.83-7.42
21 $\mu\text{g}/\text{kg dw}$; 6 BDEs: 5.82-23.10 $\mu\text{g}/\text{kg dw}$). When concentrations were expressed on a dry
22 weight basis, the fish were much more contaminated than the sediments, but when sediment
23 concentrations were normalised to organic carbon concentration they were comparable to the
24 fish lipid normalised concentrations. Thus, despite the variability in the system, both
25 sediments and wild fish can be considered suitable for representing the level of POPs
26 contamination of the river system given sufficient sample numbers.

27 Keywords: POPs, Sediment, Fish, River Thames

28 1. Introduction

29 Due to their persistence, bioaccumulation potential and toxicity many Persistent Organic
30 pollutants (POPs) remain of concern and are prominent in environmental legislation
31 (Vonderheide *et al.*, 2008; Kuzyk *et al.*, 2010; Nicolaus *et al.*, 2015). These compounds of
32 concern, which include organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs)
33 and polybrominated diphenyl ethers (PBDEs), have been eliminated or severely reduced in
34 production and use due to environmental concerns. This study focuses on PCBs and
35 hexachlorobenzene (HCB), a fungicide, for which an environmental quality standard for biota
36 has been set in the first version of the EU Priority Substances Directive (European Union,
37 2008) which were both banned in the EU more than 30 years ago, as well as PBDE flame
38 retardants most of which have been banned since 2004.

39 Normally, chemical pollutants in rivers are monitored by regular sampling of the water
40 column, but here there is a problem, because in the UK in recent years, HCB, PBDEs and
41 PCBs concentrations are close to or lower than the detection limits for current methods. For
42 example, between 2000 and 2015 only six out of 4373 Environment Agency HCB
43 measurements from the non-tidal Thames and its tributaries were above the detection limit of
44 1 ng/l (<http://environment.data.gov.uk/water-quality>).

45
46 The chemicals in the current study have log K_{ow} values between 5 and 8 (Schenker *et al.*,
47 2005; Rowe, 2009) so they tend to partition much more favourably to organic matrices than
48 water. However, natural water bodies contain suspended sediments which may be partly or
49 wholly composed of organic matter which can act as an important sorbent for POPs (Katagi,
50 2002). These suspended sediments will ultimately become bed-sediments and consequently,
51 high concentrations of POPs can be found in bed-sediments of rivers (e.g. up to 4 or 5 $\mu\text{g}/\text{kg}$
52 dry weight for BDE 99 and BDE 47 respectively in River Viskan, Sweden 1995 (Sellström *et*

53 *al.*, 1998); 105-400 µg/kg dw for the sum of 27 PCBs (ICES 7 PCBs¹ contributed about half
54 of that) and up to 272 µg/kg dw for the sum of 10 tri- to hexa-BDEs (including the 6
55 commonly monitored ones) in the Scheldt river, Belgium (Covaci *et al.*, 2005; Vane *et al.*,
56 2007). In the UK, high levels organic pollutants have been observed in the Mersey, Clyde,
57 and Tyne estuaries (Vane *et al.*, 2007; Vane *et al.*, 2010; Nicolaus *et al.*, 2015). The
58 concentrations of PCBs in some sediment samples from the Thames estuary were recently
59 reported to have exceeded the Ecotoxicological Assessment Criteria (EACs) derived by the
60 Oslo and Paris Convention (OSPAR) by up to 218 fold (Nicolaus *et al.*, 2015). The difficulty
61 with bed-sediment sampling, however, is that the distribution of fine organic rich sediments
62 can be very variable across a river, even over distances of a few metres (Hedges and Keil,
63 1995; Bianchi *et al.*, 2007; Wakeham and Canuel, 2016).

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

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.

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

89 This study had the following objectives:

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

97

98 **2. Materials and methods**

99 **2.1 Sediment sampling**

100 The sediment samples were collected in 2013 using 28mm diameter copper tubes filled with
101 dry ice to freeze the sediment to the core, which was then pulled up allowing the collection of

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

120

121 **2.2 Fish Tissue Archive Project (Fish collecting)**

122 CEH Wallingford has been building up a sample base for fish from UK rivers since 2007
123 (The Fish Tissue Archive). Whole fish samples have been collected and stored frozen for
124 future use, to allow the measurement of chemical contamination levels and their spatial or
125 temporal trends. Normally ten roach (*rutilus rutilus*, approx. 15 cm long) per site and year are
126 caught by fish monitoring teams of the Environment Agency killed on site with an overdose

127 of 2-phenoxyethanol, and then shipped in a liquid nitrogen cooled dry shipper to a -80 °C
128 freezer in CEH. A subset of these fish samples were prepared for analysis by breaking the
129 whole fish into a few pieces without defrosting and grinding them into frozen fish powder
130 with a cryogrinder (SPEX SamplePrep 6850). The powder was then divided into pre-cooled
131 glass vials and kept in a -80 °C freezer until further analysis. Around 10% of the collected
132 fish samples have already been analysed and part of the results (HCB, HCBd, PBDEs in
133 fishes from River Glen, Nene, Kennet and Thames, and PCBs, DDTs, Lindane in eels from
134 the lower Thames) have been reported (Jürgens *et al.*, 2013; 2015). Details of the analysed
135 fish can be found in the supporting information, Table SI 2 and the sampling sites are marked
136 in Figure 1. More detailed fish sampling information is described in Jürgens *et al.* (2013).

137

138 **2.3 Analytical methods for organic pollutants**

139 • **Extraction and Purification**

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

143 The sediment samples were defrosted overnight and then washed through a 1 mm mesh sieve
144 using Milli-Q water to remove fine particles stuck on the sieve. The resulting samples were
145 centrifuged to reduce water content and sub-samples of 10 g wet sediment were mixed with
146 10 g anhydrous sodium sulphate to remove water. The prepared sediment samples were then
147 extracted in dichloromethane (DCM) (approximately 150 ml) at 40 °C for 16 hours in a
148 Soxhlet apparatus. The surface layer from Littlemore Upstream (LM US) was repeated in
149 triplicate to quantify methodological precision. Recovery standards containing ¹³C-labelled
150 PCBs: 28, 52, 101, 138, 153, 180 and BDEs: 51, 128, 190 were added to the samples before
151 extraction and 5 g of copper powder was added into the receiving flask to reduce the potential
152 interference of sulphides on the analyses. The resulting extracts were evaporated to about 5

153 ml on a rotary evaporator and then were further concentrated to about 0.5 ml under a gentle
154 stream of nitrogen. The extracts were purified with an acid silica column followed by a gel
155 permeation column (GPC). The eluent was collected in a vial and then concentrated to about
156 1 ml under a gentle nitrogen stream. After that, the concentrated eluent was transferred to a
157 GC vial containing a known amount of internal standards: PCB 30, ¹³C-PCB141, ¹³C-
158 PCB208, BDE69, BDE181 in 25 µl dodecane and blown down under nitrogen to 25 µl.
159 Frozen fish powder samples (around 5 g of frozen fish powder well mixed with 10 g
160 anhydrous sodium sulphate) were extracted using similar procedures to that used for the
161 sediment samples except that copper addition was not required. Procedural blanks (10 g
162 anhydrous sodium sulphate) were used in each extraction batch. A small portion of the
163 Soxhlet extract was used for gravimetric determination of the lipid content after the solvent
164 had evaporated. The remaining extract was evaporated to a small volume (about 1 ml) and
165 was then taken up for clean-up and further analysis similar to the sediment samples (more
166 details of the fish analysis are in Jürgens *et al.*, 2013; 2015).

167

168 • **GC-MS Analysis**

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

176

177 • **Quality Assurance/Quality Control**

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

190

191 **2.4 Sediment Organic Carbon content**

192 The concentrations of organic pollutants in the sediment samples should be normalised to dry
193 weight and their organic carbon content to allow comparison to assessment criteria (e.g.
194 Ecotoxicological Assessment Criteria (EACs) of OSPAR 2009). Therefore, the moisture
195 content and the organic carbon content of the sediment samples were determined. Around 10-
196 20 g wet sediment samples were oven dried at 105 °C (\pm 5 °C) overnight (24h), cooled and
197 weighed to determine the moisture content. After that, the dried sediment samples were
198 ground using a Planetary Ball Mill (PM 100, RETSCH). The sediment organic carbon
199 content was determined using an Elementar Vario EL elemental analyser (Elementar
200 Analysensysteme, Hanau, Germany). The instrument is calibrated using a working standard
201 (Acetanilide) with approximate concentrations of 71.1% total C. The standard is analysed at
202 the beginning of every run, with every 10 samples and again at the end of a run and used to

203 apply a daily correction factor. Two reference soils material are analysed with each batch of
204 samples at intervals of every 20 samples.

205

206 **3. Results and Discussion**

207 **3.1 Contamination levels in Sediment**

208 River bed-sediments can be a major sink/source of organic pollutants in river systems (Lu *et*
209 *al.*, 2015). However, few studies reported the recent contamination levels of organic
210 pollutants in sediment of the Thames. Over the period 1990-1995 a mean value of 34.4 µg/kg
211 was reported for PCB as 249 Aroclor-1248 in salt marsh sediment of Two Tree Island in the
212 Thames estuary (Scrimshaw and Lester, 2001). Twenty-five sediment samples from different
213 sites and core depth were analysed for HCB, ICES 7 PCBs (PCB 28, PCB 52, PCB 101, PCB
214 118, PCB 138, PCB 153 and PCB 180), and 6 BDEs (BDE 28, BDE 47, BDE 99, BDE 100,
215 BDE 153, BDE 154) in the current study. ICES 7 PCBs are recommended by the
216 International Council for Exploration of Sea (ICES) for marine environment monitoring.
217 They are also listed in the latest EU Commission Regulation on methods of sampling and
218 analysis for the control of PCBs (European Commission 2014), without labelling them as
219 ICES 7. The 6 BDEs were chosen as indicators for the contamination of PBDEs in the
220 Thames environment as they are the most commonly found congeners in the environment and
221 are commonly monitored and regulated (e.g. European Union, 2008; 2013).

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

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

232 The lowest concentrations of HCB, Σ ICES 7 PCBs and Σ 6 BDEs were detected in the
233 sediments from the River Ock, while the highest values were found at the sites in The Cut
234 and Littlemore Brook (Table 1, Figure 2). The sampling site in the River Ock is in a rural
235 area with little sewage input. The Cut is within an urbanised area and has particularly high
236 exposure to human activities (Putro *et al.*, 2016). It receives high sewage effluent input from
237 Bracknell (on average 43.3% of the flow is treated sewage). Littlemore Brook is an urbanised
238 tributary within an industrialised sub-catchment of the River Thames. In Littlemore Brook,
239 samples were taken from two sites close to each other (about 100m apart), either side of the
240 effluent discharge channel of the Oxford (Sandford) Sewage Treatment Work (STW). In the
241 majority of cases, the concentrations of the studied chemicals were higher in the sediment
242 samples collected from downstream of the STW than in those collected from upstream (Table
243 1, Figure 2). The sewage effluent could be an on-going source of the contaminations of the
244 studied chemicals in the sediment. However, overall no significant linear correlations (R^2
245 ranged from 0.0677 to 0.2575) were detected between sediment concentrations of HCB, Σ
246 ICES 7 PCBs and Σ 6 BDEs with the modelled sewage water fraction in the sediment
247 samples from the River Thames and its tributaries (Figure SI 2). The sewage effluent content
248 at the sediment sampling sites was estimated using the Low Flows 2000 Water Quality
249 eXtension model (LF2000 WQX, Wallingford HydroSolutions). The model calculates in a
250 Monte Carlo framework to account for the variability in river flows and per capita influent
251 load. The model randomly selects river and effluent flows from a defined distribution and
252 does 2000 mass balance calculations using different river and effluent flows for each time.

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

258

259 **3.2 Variation in sediment concentration with depth**

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

274

275 **3.3 Contamination in Thames fish**

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

278 HCB in Thames and Kennet fish (0.06-1.48 µg/kg) were similar to those in fish from other
279 UK rivers (River Glen: mean 0.21 µg/kg; River Nene: mean 0.68 µg/kg) (Jürgens *et al.*,
280 2013). The sum of the concentrations of the 6 BDEs (2.30-24.47 µg/kg with a mean value of
281 9.35 µg/kg) in all of the analysed fish samples from the River Thames were several orders of
282 magnitude higher than the EU EQS of just 0.0085 µg/kg (European Union, 2013).
283 Nevertheless, the levels of Σ 6 BDEs in Thames fish were lower than the levels reported in
284 another recent survey for the River Don (10.55-128.40 µg/kg) (Rose *et al.*, 2015). For PCBs,
285 the concentrations for Σ ICES 7 PCBs in Thames fish (ranged from 3.09-25.66 µg/kg with a
286 mean value of 11.65 µg/kg) exceed the US EPA unrestricted consumption threshold of 5.9
287 µg/kg for Σ PCBs (Lu *et al.*, 2015). The levels of Σ ICES 7 PCBs were higher than those
288 previously reported in fish from the upper Thames (<0.77-3.32 µg/kg) and the River Glen
289 (2.22-3.84 µg/kg), and were comparable to the levels in fish from the River Nene (3.57-16.39
290 µg/kg) (Yamaguchi *et al.*, 2003; Jürgens, 2015). As only a limited number of fish have been
291 analysed, it is difficult to demonstrate either temporal or spatial trends of the contaminants in
292 Thames fish, but the fish contamination was much lower in the River Kennet tributary than
293 those detected in the sites of the main river. The catchment of the River Kennet is mainly
294 rural in character and the average sewage content at the sampling site is only 3% by volume
295 (Jürgens, 2015).

296

297 **3.4 Comparison of Fish Concentrations with Sediment Values**

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

304 $\mu\text{g}/\text{kg dw}$ respectively for Σ 6 BDEs, Σ ICES 7 PCBs, and HCB, which were higher than
305 those in the sediment samples² (0.30, 2.90, and 0.03 $\mu\text{g}/\text{kg dw}$) (Figure. 3). Therefore, at first
306 it might seem that there is no relationship between fish and sediments with respect to POPs in
307 the Thames Basin. However, when the data is normalised to either lipid (for the fish) or
308 organic carbon (for the sediment) then a similar level of contamination to these matrices can
309 be seen (Figure 3). There is one site on the River Kennet where the fish samples and sediment
310 samples were from the identical location. The dry weight values in fish were about 2-10 times
311 higher than that in the sediment (Figure SI 4). Applying the normalisation for OC and lipid
312 content however didn't influence the described relationship significantly.

313 In this study, the BSAFs (biota-sediment accumulation factors) (Burkhard *et al.*, 2005) were
314 calculated for the POPs in the roach from the River Kennet to evaluate the relationship
315 between the fish and sediment contamination (Table 2). It is assumed that POPs in water, fish
316 and sediment are at equilibrium and the BSAFs do not substantially change with varying
317 environmental factors. For the 6 BDEs and the ICES 7 PCBs, the BSAF factors were a bit
318 lower than those reported for the same fish species from the Orge River (France) (Teil *et al.*,
319 2012). The BSAF factors for BDE 28 and BDE 47 were much higher than those for other
320 congeners, which is consistent with the findings of Teil *et al.* (2012) and Sellström *et al.*
321 (1998). To our knowledge, there is no BSAF data available for HCB in roach in the literature.
322 However, the BSAF values were comparable to those reported for caged carp in Dutch
323 freshwater sites field studies (0.17-1.42 $\mu\text{g}/\text{g lipid} / \mu\text{g}/\text{g OC}$) (Verweij *et al.*, 2004).

324

325 **4. Conclusion**

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

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

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

338

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346

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512 **Figure Captions List:**

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

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

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

519

520 **Table Captions List:**

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

523 **Table 2.** BSAF ($\mu\text{g}/\text{kg}_{\text{lipid}}$ / $\mu\text{g}/\text{kg}_{\text{org.carbon}}$) values for PBDEs, PCBs and HCB in the
524 River Kennet