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1 **Abstract**

2 Legacy (i.e. polybrominated diphenyl ethers, PBDEs, and hexabromocyclododecane, HBCDD) and alternative
3 halogenated flame retardants (HFRs) were analyzed in 31 whole fish samples from Lake Geneva in 2018. Two
4 fish species, namely the burbot (*Lota lota*) and the roach (*Rutilus rutilus*) were selected, hypothetically
5 representing different habitats, feeding behaviors and different metabolic capacities. Roach ($N = 20$) and
6 burbot ($N = 11$) displayed similar size and mass, but the latter species was overall leaner than the former. The
7 sum of individual PBDE concentrations ($0.54 - 9.86 \text{ ng g}^{-1}$ wet weight - ww) was similar in both species, but the
8 respective molecular profiles suggested contrasted metabolic capacities. HBCDD sum of isomer concentrations
9 ranged from non-detected to 3.477 ng g^{-1} (ww), also similar in both species. Both PBDEs and HBCDD levels were
10 far below the threshold that indicates a risk to fish predators. Referring to previous surveys, which involved a
11 wider range of species, PBDE concentrations have declined or are stable. HBCDD concentrations remained low,
12 despite the PBDE ban, which could have fostered the consumption of other HFRs. The occurrence of alternative
13 HFRs was also low for most compounds analyzed. Only dechloranes and decabromodiphenyl ethane (DBDPE)
14 had detection rates above 50 %. Dechloranes spanned a concentration range between 5 and 10 times the
15 quantification limits (0.002 to 0.005 ng g^{-1} wet weight), lower than DBDPE (<0.005 to 2.89 ng g^{-1} wet weight).
16 Quality standards targeting biota are currently missing for these emerging chemicals.

17 **Keywords**

18 Lake Geneva; Halogenated flame retardants; PBDE; hexabromocyclododecane; dechlorane; DBDPE; roach;
19 burbot

20 **Introduction**

21 Lake Geneva is one of the largest (580 km²) and deepest (309 m) lakes in Western Europe (CIPEL 2014). It
22 provides about one million surrounding-area inhabitants with various services, including drinking water supply,
23 recreation or fisheries. The international commission for the protection of Lake Geneva waters (CIPEL) was
24 established in 1957 by a French-Swiss treaty in order to monitor water quality, coordinate water protection or
25 remediation-related environmental management, and inform the public (CIPEL 2014).

26 The analysis of mercury and other trace elements in fish meat was first introduced in CIPEL's monitoring
27 program in 1975 and has since continued uninterrupted. Legacy contaminants (polychlorinated biphenyls,
28 dichloro-diphenyl trichlorethane and its metabolites) were added to the list of contaminants monitored in the
29 1980s.

30 In 2006, Europe banned the use of PBDEs in most of its current applications (E.C. 2003; E.P. and E.C. 2013). The
31 ban was expected to bring about a decrease in the concentrations PBDEs found in freshwater fish meat.
32 However, the market then replaced PBDEs with alternative flame retardants (FRs), including
33 hexabromocyclododecane (HBCDD), a brominated flame retardant used primarily in expandable polystyrene
34 but also in other applications including electronics, textiles and upholstery (KEMI 2008). Europe has restricted
35 the use of HBCDD since 2011, under Annex XIV of the REACH regulation (E.C. 2011a). The market shares of
36 alternative FRs should therefore increase. Both PBDEs and HBCDD are included in the European Union's list of
37 priority substances, and both should be monitored in biota (E.P. and E.C. 2013). In the case of Lake Geneva,
38 polybrominated diphenyl ethers (PBDEs) have been considered since 2008 (Ortelli et al. 2009); HBCDD
39 compound was first considered in the 2012 CIPEL fish contamination survey. As alternative FRs may share some
40 properties with PBDEs, such as hydrophobicity, there is accordingly a need to determine whether these
41 chemicals are also of concern for biota in the lake or not.

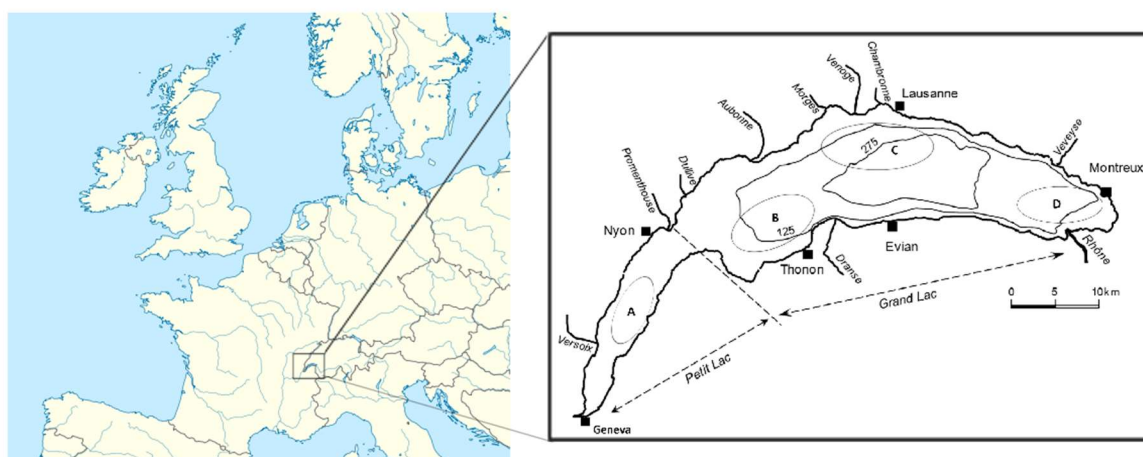
42 This study is part of the Lake Geneva fish survey campaign carried out in 2018. Its specific objectives regarding
43 flame-retardants were (i) to determine the current status of fish contamination by PBDEs and HBCDD, and (ii)
44 to assess the occurrence and contamination levels of an array of emerging HFRs. The previous fish
45 contamination surveys used regulatory thresholds for fish consumption as interpretative criteria. This kind of
46 benchmark has some advantages, in particular in terms of communication to the public, but the previous
47 surveys unfortunately failed to follow some of the sampling requirements for the use of regulatory thresholds
48 for fish consumption, as presented in (E.C. 2011b) and other sources. Moreover, the lake is bordered by France
49 on one side and Switzerland on the other, so each nation may have its own different approach to consumer
50 protection against food contaminants, whereas the CIPEL's goal is to advise both the French and Swiss
51 authorities on potential threats to the ecosystem services provided by the lake, and on the related trends.
52 These considerations prompted a move to adopt interpretative criteria focusing on ecosystem protection
53 instead of sanitary thresholds for the 2018 survey.

54 **Materials and Methods**

55 *Sampling*

56 We selected two fish species, i.e. burbot (*Lota lota*) and roach (*Rutilus rutilus*), that represent different

57 habitats, feeding behaviors and metabolic capacities. Burbot live deeper than roach, and feeds on benthic
58 invertebrates, while roach feeds on zooplankton and occasionally on algae or plants (Horppila and Peltonen
59 1997; Kamjunke et al. 2002). Specimens of both species were collected from professional fishermen in four
60 areas of the lake (Figure 1), during the summer 2018, so as to avoid the reproduction period. These four areas
61 were those surveyed in previous CIPEL monitoring campaigns, namely (A) “Petit Lac”, (B) in front of the French
62 shore, (C) in front of the Swiss shore in the Vaud canton, and (D) in the Eastern end of the lake in the Valais
63 canton. Ideally, five to seven individuals of each species were required in each zone. A total of 45 fish were
64 obtained, namely 27 roach individuals and 18 burbot; fishermen could not provide burbot in zone A and only
65 six roach specimens were collected in zone C. Note that this HFR study was part of a wider survey, targeting
66 many other contaminants, and seven specimens of each species were kept apart (not analyzed for HFRs) for
67 specific purposes, not concerned by the present study. Thus, 20 roach and 11 burbot were ultimately
68 processed for HFR analysis (Table S1 in Supplementary Material, SM). Immediately after collection, the fish
69 were measured and weighed and the samples were placed in refrigerated boxes (at approximately 4°C) until
70 they could be frozen (-20°C), and then sent to LABERCA (French Reference Laboratory for halogenated
71 pollutants in food) for analysis.



72
73 *Figure 1 - Lake Geneva and fish sampling areas*

74 *Analysis*

75 The legacy HFRs included six PBDE congeners representing a mixture of Penta- and Octa-BDE technical
76 products, namely BDE 28, 47, 99, 100, 153 and 154, three HBCDD stereo-isomers (α , β and γ). All six PBDEs are
77 listed along with HBCDD as priority substances in the European Union, which is not yet the case for other BDE
78 congeners such as BDE209. Alternative HFRs included penta- and hexabromobenzene (PBBz and HBBz
79 respectively); pentabromotoluene (PBT), three polybrominated biphenyls (PBB 52, 101 and 153), three
80 dechloranes, namely Dec-602 (DDC-DBF), Dec-603 (DDC-Ant) and Dechlorane + (DDC-CO), which corresponds
81 to the sum of Syn-DP and Anti-DP, decabromodiphenyl ethane (DBDPE) and 1,2-Bis(2,4,6-tribromophenoxy)
82 ethane (BTBPE); except PBBz and HBBz, abbreviations were taken from (Bergman et al. 2012). All these
83 compounds are hydrophobic and persistent (Table S2 in Supplementary Material - SM).

84 The method is described in details elsewhere (Abdel Malak et al. 2018; Bichon et al. 2018). Each individual fish

85 was defrosted, ground whole, then freeze-dried, and the resulting material was ground again to get a
86 homogenous powder. The lipid fraction was extracted from 1.5 g of dry matrix by pressurized liquid extraction
87 (Speed Extractor, Büchi, Rungis, France) using a toluene/acetone (70/30 v/v) mixture at high pressure (100 bar)
88 and high temperature (120 °C). The extracts were evaporated, and the dry residues dissolved in hexane for the
89 purification step. All labelled standards (¹³C) corresponding to each substance to be quantified were added
90 prior to the extraction step, except for PBT which was quantified using ¹³C PBBz, and DDC-ANT, quantified using
91 ¹³C Anti-DP. Standard solutions were purchased from Wellington Laboratories (Guelph, Ontario, Canada).

92 Purification involved two or three successive steps, depending of the analyte: first, the hexane extracts were
93 passed through a homemade multilayer acidic silica column (5 g of silica gel at bottom, 20 g of 22% acidified
94 silica in the middle, 25 g of 44 % acidified silica at top) to separate out the substances according to their affinity
95 with the phase and solvent. PBDEs, PBBs and alternative HFRs were first eluted using hexane, then
96 dichloromethane was used to eluate HBCDDs. The HBCDD fraction was further separated and purified by
97 liquid/liquid repartition with a hexane and sodium hydroxide solution, while the remaining fractions containing
98 other HFRs passed through a homemade Florisil® column (6 g) in order to separate the hexane fraction
99 containing PBDEs and some HFRs, and the toluene fraction containing other HFRs. This non-PBDE fraction was
100 then re-purified again on a carbon/celite column.

101 PBDEs and most HFRs were analyzed by gas chromatography (Agilent 7890, Palo Alto, CA) coupled with high
102 resolution mass spectrometry (Jeol JMS 800D, Tokyo, Japan), whereas HBCDD was quantified by liquid
103 chromatography (Agilent 1200 HPLC) coupled with tandem mass spectrometry (Agilent 6410, Santa Clara, USA).

104 All methods were performed according to an ISO standard 17025-accredited system. The methods used were
105 validated and ISO 17025-accredited for PBDEs and HBCDDs and characterized for other compounds.

106 In order to validate the quality of the analysis, internal standards were added to each sample and
107 complementary labeled standards were added at the end of each process in order to calculate recoveries. The
108 method met the quality assurance requirements of the European Commission Regulation (EU) N°2017/644
109 (Annex III) that deals with certain halogenated persistent organic pollutants (POPs) using quantification analysis
110 by isotopic dilution (E.C. 2017). All the calculated recoveries were between 65% and 115%. Moreover, heated
111 laboratory glassware was rinsed with dichloromethane prior to use and all the steps for preparation, freeze-
112 drying and purification steps were carried out in an over-pressurized room to avoid any contamination coming
113 from the materials and air. For each sample batch, one blank consisting of one celite sample and one QC
114 sample was added and implemented in blank and QC charts. As analytical contamination was fully under
115 control, the values found in blanks were not deducted. The laboratory participates in regular (twice-a-year)
116 proficiency tests organized by the European Reference Laboratory (EURL) for POPs, which serves to guarantee
117 the accuracy of the analytical method.

118 *Contamination assessment*

119 For PBDEs and HBCDD, the contamination magnitude was assessed by comparing the geometric means of
120 measured concentrations against the European standards for secondary poisoning ($QS_{sec-pois}$). This criterion

121 belongs to the set of quality standards (QS) determined prior to the establishment of an Environmental Quality
122 Standard under the Water Framework Directive in Europe (E.C. 2011c). The $QS_{sec-pois}$ aims to protect wildlife from
123 adverse effects resulting from the predation of contaminated fish. It was derived based on review of existing
124 toxicological data for wildlife and the use of extrapolation factors, which depend of the kind of data collected
125 (E.C. 2011c). The $QS_{sec-pois}$ may or may not be the EQS ultimately selected, depending on a comparative
126 assessment involving the QSs set for food consumption, drinking water or protection of pelagic organisms (E.C.
127 2011c): for HBCDD, the $QS_{sec-pois}$ is far below the QS for food consumption, and is thus the EQS, whereas for PBDEs
128 it the $QS_{sec-pois}$ is far above the EQS, which is based on a food consumption benchmark (E.C. 2014).

129 Targeting the protection of wildlife against secondary poisoning entails the analysis of whole fish, as secondary
130 predators are presumed to eat practically all their prey (E.C. 2014).

131 *Data processing, statistics*

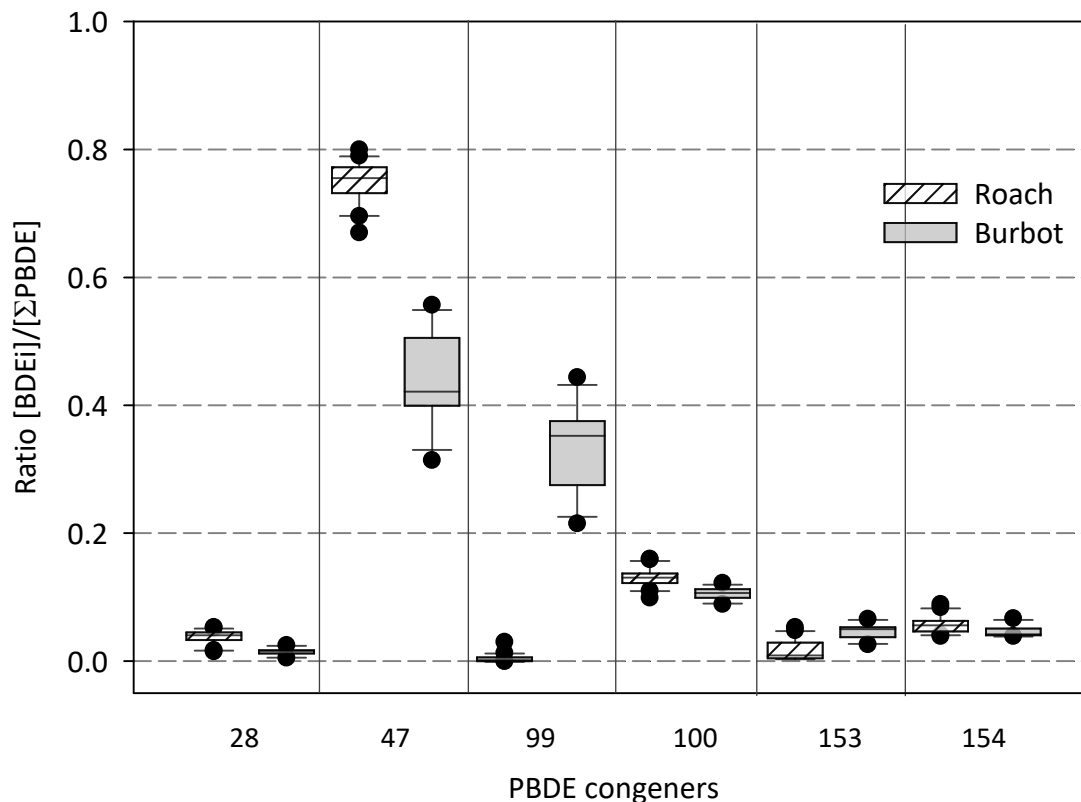
132 We used Pro-UCL 5.1 (<https://www.epa.gov/land-research/proucl-software>) for the determination of quantiles
133 of measured concentrations while accounting for non-detects. These quantiles were not estimated when
134 detection rates were below 50 %. Comparisons were performed using Mann Whitney or Kruskal-Wallis tests,
135 which were run on XLStat v.19.4 software. Potential relationships among variables were assessed either with a
136 Pearson correlation test, or by multiple linear regression. The default significance threshold was set at 0.05.

137 **Results and discussion**

138 Roach ranged in size from 15 to 34 cm (mean 22.6 ± 4.8 cm) and in mass from 40.6 to 452 g (mean 138 ± 102
139 g). Burbot displayed similar size and mass ranges, i.e. 22 to 39 cm (mean 29.6 ± 5.0 cm) and 68 to 530 g (mean
140 157 ± 137 g) respectively. The burbot specimens were leaner overall than roach, with mean lipid contents of
141 $3.71 \pm 1.81\%$ and $7.33 \pm 2.89\%$ respectively. Sex ratios were unbalanced in both species, with a majority of
142 male roach specimens and a majority of female burbot specimens. However, there were 36 % sexually
143 immature burbot individuals, and 35 % sexually immature roach.

144 *PBDE*

145 All six PBDE congeners were quantified in all samples (Table S3 in SM). The sum of concentrations of these six
146 congeners (Σ PBDE) ranged between 0.597 ng g^{-1} wet weight (ww) and 9.86 ng g^{-1} ww for roach, and between
147 0.544 ng g^{-1} ww and 2.60 ng g^{-1} ww for burbot, showing no significant between-species difference in
148 contamination (Mann-Whitney test, p -value 0.502). The respective contamination profiles were nevertheless
149 clearly distinct, especially with a higher BDE 47 proportion in roach (67 to 80 %) than in burbot (31 to 56 %).
150 Conversely, BDE 99 represented less than 3 % of Σ PBDE in roach but ranged between 21.5 and 44.4 % in burbot
151 (Figure 2). These contrasted ratios suggest that roach and burbot differ in their respective metabolic capacities
152 to debrominate the higher-brominated congeners such as BDE99, as already demonstrated for other species
153 (Stapleton et al. 2004; Tomy et al. 2004b).



154

155 *Figure 2: Distributions of PBDE congener ratios to ΣPBDE in roach (grey) and burbot (cross-hatched)*

156 Multiple linear regression analysis found that both size and lipid content contributed significantly to explaining
 157 the variability of ΣPBDE in roach (p -values 0.02 and 0.05 respectively), but overall the variance explained was
 158 low (adjusted $R^2 = 0.217$). We did not test for the influence of sex, as the sample sex ratio was too unbalanced
 159 and the sample size was too small.

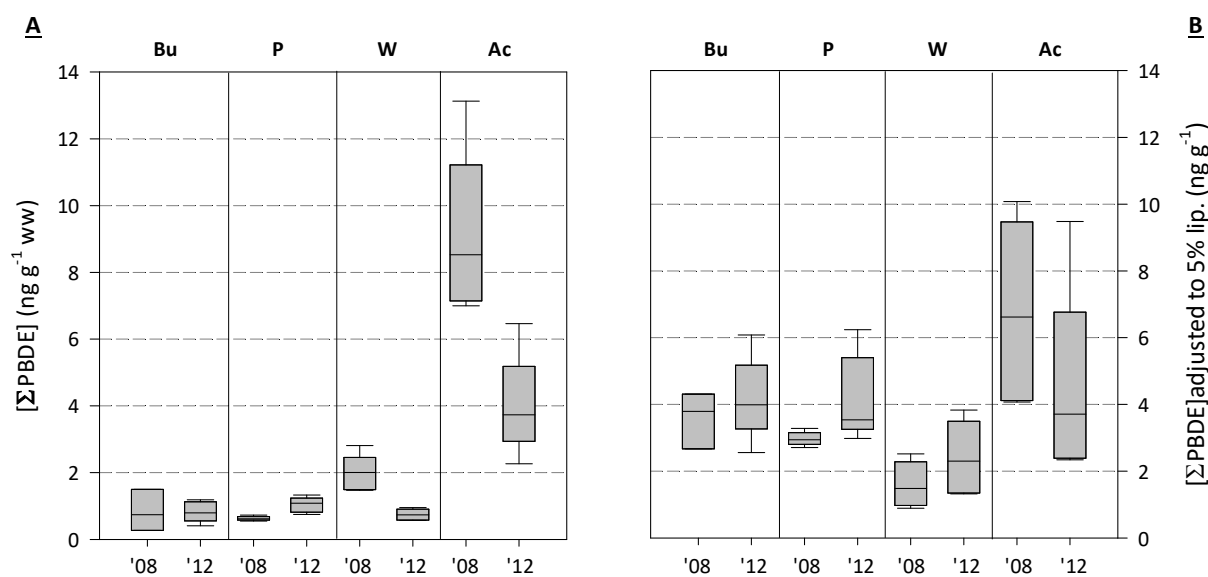
160 None of the ΣPBDE values exceeded nor was even close to the $QS_{sec-pois}$ of $44 \text{ ng g}^{-1} \text{ ww}$. Checking the
 161 compliance to the EQS_{biota} , of $0.0085 \text{ ng g}^{-1} \text{ ww}$ (E.P. and E.C. 2013) would rely on measurements in fillets, as
 162 this standard is based on human consumption (E.C. 2014). Considering whole-body to fillet concentration ratios
 163 between 1.2 and 1.8 (Fliedner et al. 2018), or even between 2.5 and 5 (Gandhi et al. 2017), it seems likely that
 164 all fish samples would exceed the EQS_{biota} . This same exceedance was also found in German rivers (Fliedner et
 165 al. 2016), as well as in Lake Maggiore (Guzzella et al. 2018), a large Alpine lake comparable to Lake Geneva in
 166 terms of climate and anthropic pressure.

167 Reported concentrations of persistent contaminants in lake fish from industrialized regions vary greatly;
 168 sources of variability include lake characteristics (Houde et al. 2008), anthropic pressures, species monitored
 169 and more. This makes it difficult, if not wholly misleading, to compare PBDE contamination levels among lakes.
 170 Several studies point to BDE 47 as dominant in ΣPBDE (e.g. Perez-Fuentetaja et al. 2015; Poma et al. 2014),
 171 even when more congeners were analyzed (Gandhi et al. 2017). The higher proportion of BDE 47 is generally
 172 attributed to debromination of more brominated congeners, including BDE 209 (Poma et al. 2014). Fish size

173 and lipid content are commonly cited as controlling Σ PBDE levels (e.g. Gandhi et al. 2017), along with fish
174 trophic position (Guzzella et al. 2018; Perez-Fuentetaja et al. 2015), but the relative influence of these factors
175 on PBDE accumulation nevertheless appear to vary between species and ecosystems (Gandhi et al. 2017).
176 Following the ban of most common commercial formulations, Σ PBDE declined in Great Lakes fish (Gandhi et al.
177 2017) as well as in fish from US water bodies downstream from textile manufacturing sites (Chen et al. 2011).
178 However, given the global PBDE stocks involved (Abbasi et al. 2019), PBDEs are set to persist in the
179 environment for decades.

180 PBDEs only screened for twice in past CIPEL fish surveys — first in 2008 (Ortelli et al. 2009) and then in 2012
181 (Edder et al. 2013). The fish species in these studies included burbot, perch (*Perca fluviatilis*), whitefish
182 (*Coregonus lavaretus*) and Arctic char (*Salvelinus alpinus*), and analyses were performed on fillets. Furthermore,
183 the set of congeners analyzed in both studies included the same six congeners as in the current study, plus
184 BDE183. Arctic char was the most contaminated species in both campaigns, followed by whitefish in 2008 (Figure
185 3-A). PBDE concentrations were found lower in 2012 than in 2008 for Arctic char and whitefish, but slightly
186 (though significantly) higher for perch. Burbot cannot be compared between campaigns due to the low number
187 of samples analyzed in 2008 and the shift from fillet to whole-body in 2012. The interspecies differences in 2008
188 and 2012 may reflect both respective lipid contents and trophic positions. Indeed, in 2008 Arctic char fillets had
189 a higher lipid content (4.1 – 11.4 %) than perch (0.9 – 1.3 %) but less than whitefish (4.6 – 8.2 %), and its trophic
190 position is estimated at 4.4 ± 0.5 , similar to perch (4.4 ± 0.0) but higher than whitefish (3.1 ± 0.0 ; (Froese and
191 Pauly 2019). Furthermore, whitefish samples were significantly leaner in 2012 than in 2008, which contributed
192 to the apparent decrease of Σ PBDE for this species: when adjusted to a standard lipid content of 5%, as
193 recommended for monitoring purposes in Europe (E.C. 2014), PBDE concentrations in Arctic char in 2008 and
194 2012 were indeed closer (Figure 3-B) but the concentrations were still lower in 2012 than in 2008, although the
195 difference was no longer significant. Following this adjustment, perch and whitefish samples displayed higher
196 Σ PBDE in 2008 than in 2012 (Figure 3-B), but the difference was only significant for perch, which is similar to the
197 recent trend observed for the bream in some German rivers (Fliedner et al. 2016).

198



199
 200 *Figure 3: Box plots of Σ PBDE (sum of BDE28, 47, 99, 100, 153, 154, 154 and 183 concentrations) in Lake Geneva burbot, perch,*
 201 *whitefish and Arctic char in 2008, 2012 (A: raw concentrations; B: concentrations adjusted to a standard lipid content of 5%;*
 202 *Bu: burbot; P: perch; W: whitefish; Ac: Arctic char)*

203 HBCDD

204 Detection rates varied among the three main isomers: α HBCDD was systematically detected and quantified,
 205 whereas β HBCDD and γ HBCDD were less frequently detected (20 % and 80 %, respectively, in roach, and 45 %
 206 and 45 %, respectively, in burbot; Table S4 in SM). Consequently, α HBCDD represented on average $94.8 \pm 5.9\%$
 207 of Σ HBCDD (sum of concentrations of α , β and γ isomers) in roach and $96.9 \pm 2.1\%$ in burbot, in line with
 208 previous observations (Du et al. 2012; Hühnerfuss 2000 ; Tomy et al. 2004a). The magnitude of contamination
 209 was similar in both species, ranging from $0.445 \text{ ng g}^{-1} \text{ ww}$ to $3.477 \text{ ng g}^{-1} \text{ ww}$ in roach and from $0.253 \text{ ng g}^{-1} \text{ ww}$
 210 to $2.689 \text{ ng g}^{-1} \text{ ww}$ in burbot. All Σ HBCDD values were far below the $QS_{\text{sec-pois}}$ for this substance ($167 \text{ ng g}^{-1} \text{ ww}$).

211 There is little data available for HBCDD in Lake Geneva prior the 2018 survey: a single pool of ten whitefish
 212 (Gerecke et al. 2003), nine male lake trout (*Salmo trutta lacustris*) individuals collected in November 2004
 213 (Cheaib et al. 2009), and 27 individuals from six species (pike – *Esox lucius*, Arctic char – *Salvelinus fontinalis*,
 214 perch – *Perca fluviatilis*, burbot, whitefish and trout) analyzed in the CIPEL 2012 survey. In all these studies,
 215 fillet was the matrix analyzed. Concentrations observed in 2012 were highest in Arctic char ($1.457 - 5.019 \text{ ng g}^{-1}$
 216 ww), followed by whitefish and perch ($0.405 - 0.727 \text{ ng g}^{-1} \text{ ww}$ and $0.427 - 0.764 \text{ ng g}^{-1} \text{ ww}$ respectively).
 217 Burbot ($0.144 - 0.380 \text{ ng g}^{-1} \text{ ww}$) and pike ($0.101 - 0.259 \text{ ng g}^{-1} \text{ ww}$) were the least contaminated.

218 Contamination levels measured in 2012 and 2018 in Lake Geneva fish were thus low, contrasting with the trend
 219 observed in some German rivers where HBCDD concentrations have been increasing since 2013 (Flidner et al.
 220 2016). A similar trend was also noticed downstream from textile manufacturing sites in the USA after the
 221 Penta-BDE ban (Chen et al. 2011).

222 Alternative HFRs

223 The frequency of occurrence of alternative HFRs was low (3.2% - 19.4 %) for most compounds, and even null
 224 for PBB 101. Four compounds, i.e. DBDPE and dechloranes (DDC-DBF, DDC-Ant, DDC-CO), were quantified rates
 225 at rates above 50 %, enabling us to estimate their respective quantiles while accounting for non-detects (Table

226 1). The maximum concentrations of the less-frequent compounds remained close to their respective limits of
 227 quantification, whereas the concentrations of dechloranes spanned a range of 5 to 10 times the respective
 228 limits of quantification (Table S5 in SM).

229 A- Burbot

Chemical	LOQ	Quantification rate (%)	Maximum concentration	1 st quartile	Median	3 rd quartile
PBB52	0.005	0.0%	<LQ			
PBB101	0.005	0.0%	<LQ			
PBB153	0.005	9.1%	0.010			
PBT	0.005	18.2%	0.019			
HBB	0.005	0.0%	<LQ			
PBBz	0.005	0.0%	<LQ			
DBDPE	0.005	90.9%	2.889	0.110	0.174	0.484
BTBPE	0.002	9.1%	0.006			
DDC-DBF	0.002	100.0%	0.028	0.011	0.011	0.018
DDC-Ant	0.002	54.5%	0.010	0.002	0.003	0.004
DDC-CO	0.005	100.0%	0.044	0.014	0.026	0.029

230 B- Roach

Chemical	LOQ	Quantification rate (%)	Maximum concentration	1 st quartile	Median	3 rd quartile
PBB52	0.005	10.0%	0.007			
PBB101	0.005	0.0%	<LQ			
PBB153	0.005	0.0%	<LQ			
PBT	0.005	15.0%	0.020			
HBB	0.005	25.0%	0.030			
PBBz	0.005	5.0%	0.005			
DBDPE	0.005	100.0%	1.539	0.157	0.270	0.431
BTBPE	0.002	25.0%	0.010			
DDC-DBF	0.002	100.0%	0.086	0.009	0.012	0.023
DDC-Ant	0.002	75.0%	0.009	0.002	0.003	0.004
DDC-CO	0.005	40.0%	0.169			

231 *Table 1: Whole-body concentration distributions (ng g⁻¹ ww) of emerging halogenated FRs detected in roach and burbot from*
 232 *Lake Geneva. Quartile and median concentrations were not determined when quantification rates were < 50 %*

233 DBDPE concentrations ranged between < LOQ (i.e. 0.005 ng g⁻¹ ww) and 2.89 ng g⁻¹ ww. Fish above the third
 234 quartile (0.552 ng g⁻¹ ww when both species are considered together) were sampled in areas B, C and D, and
 235 were partitioned evenly between the two species. These findings contrast with a recent study on Northern
 236 American Great Lake fish, where PBBs and dechloranes were predominant while DBDPE remained below the
 237 limit of detection and was considered as practically non-bioavailable (Wu et al. 2019). DBDPE was not detected
 238 in Lake Maggiore zooplankton and fish, despite concentrations as high as 30 ng g⁻¹ dry weight (dw) in sediments
 239 (Poma et al. 2014). DBDPE was also frequently measured in suspended matter from German rivers at
 240 concentrations as high as 3 ng g⁻¹ dw but not in bream (*Abramis brama*) fillets from the same sites, suggesting
 241 that this compound is less bioaccumulative than PBDEs (Dreyer et al. 2019). There is currently no standard or
 242 benchmark available for DBDPE and knowledge about its toxicity is scarce. It is therefore impossible to
 243 conclude about adverse effects of DBDPE on the species sampled or their predators.

244 **Conclusion**

245 The 2018 sampling campaign found that none of the legacy FRs were of concern in terms of risk of secondary

246 poisoning. However, the temporal trends for PBDE or HBCDD remain unclear. BDE209, which was authorized
247 for use years after the first restrictions on PBDE, has so far not been analyzed and should be accounted for in
248 future monitoring campaigns. Among the emerging halogenated FRs introduced as alternatives to PBDEs and
249 HBCDD, dechloranes were frequently detected but their concentrations remained close to the LOQ; only
250 DBDPE was found at concentrations most often above its LOQ.

251 *Outlook*

252 Demand for FRs remains high, and the latest studies posit a diversification of the FRs brought to market (Dreyer
253 et al. 2019; Gustavsson et al. 2018). Future monitoring campaigns should therefore address a larger set of FRs,
254 in particular organophosphate FRs (Castro-Jiménez et al. 2016; van der Veen and de Boer 2012) while
255 continuing to survey PBDEs (including BDE 209) for at least some time to come.

256

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357

Legacy and alternative halogenated flame retardants in Lake Geneva fish

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Supplementary Material

1 Characterization of fish samples

Zone	Species	Sample #	Fish mass (g)	Fish size (cm)	Sex	Lipid content (%)
A	roach	GEG03	116.27	21	nd	13.7
A	roach	GEG04	95.02	20	nd	9.7
A	roach	GEG05	69.55	19	male (?)	7.6
A	roach	GEG06	52.21	17	nd	7.2
A	roach	GEG07	84.61	20	male (?)	9.0
B	roach	FRG02	94.81	20	male (?)	5.2
B	roach	FRG03	92.09	20	male	4.2
B	roach	FRG04	94.27	21	male	4.1
B	roach	FRG05	128.24	22	male (?)	5.7
B	roach	FRG06	88.28	21	male (?)	3.4
B	roach	FRG07	96.94	20	male	5.9
B	burbot	FRL04	68.81	26	nd	1.2
B	burbot	FRL05	98.50	27	nd	1.7
B	burbot	FRL06	168.16	31	female	3.4
B	burbot	FRL07	67.98	25	nd	1.9
C	roach	VDG03	345.49	31	male	12.5
C	roach	VDG04	451.54	33	male	11.1
C	roach	VDG05	40.61	16	nd	5.4
C	roach	VDG06	48.27	15	male (?)	5.5
C	burbot	VDL03	102.06	23	female	5.1
C	burbot	VDL04	137.46	26	female	4.6
C	burbot	VDL05	78.35	22	female	5.2
C	burbot	VDL06	104.80	23	nd	5.2
C	burbot	VDL07	87.30	23	female	5.6
D	roach	VSG03	164.74	26	male	8.8
D	roach	VSG04	227.74	27	nd	9.1
D	roach	VSG05	172.03	24	male (?)	8.0
D	roach	VSG06	158.60	26	nd	5.9
D	roach	VSG07	153.78	25	nd	4.4
D	burbot	VSL03	278.34	39	male	1.4
D	burbot	VSL05	531.60	38	male	5.4

Table S 1 – Fish characteristics (nd: undetermined; (?): uncertain)

1 2 Chemicals

Substance	CAS#	Log K_{ow}
BDE 28	41318-75-6	5.88
BDE 47	5436-43-1	6.77
BDE 99	32534-81-9	6.84
BDE 100	189084-64-8	7.66
BDE 153	68631-49-2	8.55
BDE 154	207122-15-4	8.55
HBCDD	3194-55-6	7.74
PBBz	608-90-2	6.44
HBBz	87-82-1	6.07
PBT	87-83-2	6.99
PBB 52	40088-45-7	7.32
PBB 101	56307-79-0	7
PBB 153	59080-40-9	7.93
DDC-DBF	31107-44-5	6
DDC-Ant	13560-92-4	7.2
DDC-CO	13560-89-9	11.27
DBDPE	84852-53-9	11.1
BTBPE	37853-59-1	9.15

2 Table S 2 - Main characteristics of HFRs selected for this study (acronyms following (Bergman et al. 2012) – Log K_{ow} values
 3 were found in (Gustavsson et al. 2018) or PubChem (<https://pubchem.ncbi.nlm.nih.gov/>)

4

5 3 Results

6 3.1 FR concentrations in whole fish

7 3.1.1 Polybrominated diphenyl ethers (PBDEs)

Sample #	PBDE 28	PBDE 47	PBDE 99	PBDE 100	PBDE 153	PBDE 154	ΣPBDE
LQ	0.0002 – 0.0010	0.0005 – 0.0029	0.0001 – 0.0015	0.0001 – 0.0010	0.0004 – 0.0019	0.0007 – 0.0023	0.0027 – 0.0093
FRG02	0.053	0.929	0.002	0.171	0.007	0.073	1.236
FRG03	0.043	0.733	0.010	0.131	0.056	0.079	1.053
FRG04	0.066	1.225	0.005	0.177	0.053	0.075	1.601
FRG05	0.064	1.071	0.015	0.210	0.070	0.096	1.526
FRG06	0.076	1.379	0.003	0.298	0.009	0.102	1.868
FRG07	0.113	1.778	0.002	0.386	0.017	0.136	2.431
VDG03	0.170	2.876	0.003	0.455	0.014	0.200	3.718
VDG04	0.107	1.727	0.002	0.291	0.013	0.126	2.266
VDG05	0.040	2.089	0.081	0.268	0.121	0.104	2.703
VDG06	0.060	1.109	0.001	0.159	0.009	0.066	1.405
VSG03	0.053	0.989	0.001	0.182	0.008	0.085	1.318
VSG04	0.049	0.930	0.002	0.183	0.016	0.108	1.287
VSG05	0.041	0.812	0.008	0.137	0.006	0.064	1.068
VSG06	0.315	7.749	0.003	1.324	0.038	0.431	9.860
VSG07	0.133	6.252	0.002	1.083	0.030	0.317	7.816
GEG03	0.033	0.472	0.003	0.079	0.013	0.042	0.641
GEG04	0.041	0.580	0.003	0.096	0.013	0.045	0.777
GEG05	0.053	1.921	0.002	0.322	0.043	0.154	2.495
GEG06	0.023	0.663	0.002	0.118	0.014	0.039	0.859
GEG07	0.026	0.400	0.008	0.081	0.029	0.053	0.597
FRL04	0.011	0.692	0.978	0.240	0.135	0.149	2.205
FRL05	0.016	0.762	0.408	0.169	0.063	0.087	1.505
FRL06	0.043	1.143	0.918	0.274	0.092	0.129	2.599
FRL07	0.007	0.217	0.191	0.066	0.036	0.026	0.544
VDL03	0.025	0.592	0.520	0.150	0.062	0.058	1.406
VDL04	0.016	0.562	0.445	0.125	0.065	0.049	1.263
VDL05	0.020	0.489	0.430	0.117	0.062	0.050	1.169
VDL06	0.019	0.467	0.416	0.099	0.060	0.045	1.106
VDL07	0.019	0.476	0.462	0.127	0.061	0.051	1.196
VSL03	0.032	0.716	0.276	0.146	0.049	0.067	1.286
VSL05	0.040	0.858	0.456	0.186	0.044	0.069	1.653

8 Table S 3 –Concentrations of PBDEs in whole fish (ng g⁻¹ ww)

9

10 3.1.2 Hexabromocyclododecane (HBCDD)

Sample #	α HBCDD	β HBCDD	γ HBCDD	Σ HBCDD
LQ	0.02	0.02	0.02	0.02
FRG02	1.42	0.05	0.05	1.52
FRG03	0.42	<LQ	<LQ	0.44
FRG04	1.29	0.05	0.10	1.43
FRG05	1.53	<LQ	0.03	1.57
FRG06	1.59	<LQ	0.03	1.63
FRG07	2.66	0.04	0.08	2.78
VDG03	3.11	<LQ	0.05	3.18
VDG04	2.35	<LQ	0.04	2.40
VDG05	0.70	<LQ	0.02	0.74
VDG06	1.22	<LQ	0.06	1.30
VSG03	1.24	<LQ	0.05	1.30
VSG04	1.10	<LQ	0.03	1.13
VSG05	0.84	<LQ	0.01	0.86
VSG06	3.39	<LQ	0.07	3.48
VSG07	2.43	<LQ	0.10	2.54
GEG03	0.72	<LQ	0.02	0.74
GEG04	0.52	<LQ	<LQ	0.54
GEG05	1.97	0.05	0.74	2.76
GEG06	0.66	<LQ	<LQ	0.68
GEG07	0.59	<LQ	<LQ	0.61
FRL04	0.24	<LQ	<LQ	0.25
FRL05	1.50	<LQ	<LQ	1.51
FRL06	2.67	<LQ	<LQ	2.69
FRL07	0.31	<LQ	<LQ	0.32
VDL03	1.94	0.04	0.05	2.03
VDL04	1.87	0.03	0.03	1.93
VDL05	1.23	0.02	0.02	1.27
VDL06	1.70	0.06	0.06	1.83
VDL07	1.17	0.02	0.02	1.21
VSL03	0.68	<LQ	<LQ	0.68
VSL03	1.36	<LQ	<LQ	1.38

11 Table S 4 – Concentrations of HBCDD isomers in whole fish (ng g⁻¹ ww)

12

13 3.1.3 Alternative halogenated flame retardants

Sample #	PBB 52	PBB 101	PBB 153	PBT	HBBz	PBBz	DBDPE	BTBPE	DDC-DBF	DDC-ANT	DDC-CO
LQ	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.002	0.002	0.005
FRG02	0.005	0.005	0.005	0.005	0.005	0.005	1.539	0.005	0.019	0.003	0.055
FRG03	0.005	0.005	0.005	0.020	0.005	0.005	0.209	0.005	0.011	0.002	0.005
FRG04	0.005	0.005	0.005	0.005	0.005	0.005	0.375	0.005	0.010	0.003	0.005
FRG05	0.005	0.005	0.005	0.005	0.005	0.005	0.660	0.005	0.013	0.005	0.005
FRG06	0.005	0.005	0.005	0.005	0.005	0.005	0.186	0.006	0.021	0.004	0.005
FRG07	0.005	0.005	0.005	0.005	0.005	0.005	0.108	0.005	0.037	0.004	0.007
VDG03	0.005	0.005	0.005	0.005	0.009	0.005	1.503	0.005	0.019	0.007	0.016
VDG04	0.005	0.005	0.005	0.006	0.011	0.005	0.090	0.005	0.028	0.002	0.057
VDG05	0.005	0.005	0.005	0.005	0.005	0.005	0.008	0.005	0.009	0.002	0.008
VDG06	0.005	0.005	0.005	0.005	0.006	0.005	1.216	0.006	0.011	0.002	0.016
VSG03	0.005	0.005	0.005	0.005	0.005	0.005	0.767	0.005	0.021	0.002	0.005
VSG04	0.005	0.005	0.005	0.005	0.005	0.005	0.164	0.005	0.011	0.004	0.005
VSG05	0.005	0.005	0.005	0.012	0.030	0.005	0.418	0.005	0.007	0.003	0.169
VSG06	0.007	0.005	0.005	0.005	0.005	0.005	0.302	0.005	0.086	0.009	0.005
VSG07	0.006	0.005	0.005	0.005	0.005	0.005	0.235	0.005	0.072	0.007	0.016
GEG03	0.005	0.005	0.005	0.005	0.005	0.005	0.122	0.005	0.004	0.002	0.005
GEG04	0.005	0.005	0.005	0.005	0.005	0.005	0.239	0.010	0.007	0.002	0.005
GEG05	0.005	0.005	0.005	0.005	0.005	0.005	0.135	0.007	0.017	0.003	0.005
GEG06	0.005	0.005	0.005	0.005	0.005	0.005	0.319	0.006	0.004	0.002	0.005
GEG07	0.005	0.005	0.005	0.005	0.005	0.005	0.470	0.005	0.009	0.004	0.005
FRL04	0.005	0.005	0.010	0.005	0.005	0.005	0.116	0.005	0.021	0.007	0.011
FRL05	0.005	0.005	0.005	0.005	0.005	0.005	0.104	0.005	0.028	0.010	0.030
FRL06	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.019	0.004	0.026
FRL07	0.005	0.005	0.005	0.005	0.005	0.005	2.889	0.005	0.011	0.004	0.022
VDL03	0.005	0.005	0.005	0.005	0.005	0.005	0.238	0.005	0.010	0.002	0.044
VDL04	0.005	0.005	0.005	0.005	0.005	0.005	0.333	0.005	0.012	0.002	0.029
VDL05	0.005	0.005	0.005	0.005	0.005	0.005	0.635	0.005	0.011	0.002	0.028
VDL06	0.005	0.005	0.005	0.019	0.005	0.005	0.092	0.005	0.005	0.002	0.016
VDL07	0.005	0.005	0.005	0.011	0.005	0.005	0.174	0.006	0.008	0.002	0.011
VSL03	0.005	0.005	0.005	0.005	0.005	0.005	0.127	0.005	0.017	0.003	0.010
VSL05	0.005	0.005	0.005	0.005	0.005	0.005	1.309	0.005	0.011	0.003	0.040

14 Table S 5 - Concentrations of alternative halogenated flame-retardants in whole fish (ng g⁻¹ ww)

15 *References*

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