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## Occurrence of Dechlorane Plus and related compounds in catfish (*Silurus* spp.) from rivers in France

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25 **Abstract**

26 Dechlorane related compounds (DRCs), including Dechlorane Plus (*syn*-DP and *anti*-DP),  
27 Dechlorane-601, -602, -603 and Chlordene Plus (CP), constitute a group of polychlorinated flame  
28 retardants (FRs) that are still of industrial use. In particular, DRCs have been detected in various  
29 environmental matrices and in different aquatic and terrestrial biota, thus exhibiting  
30 bioaccumulation and biomagnification potentials. The present study aimed at producing first  
31 occurrence data of a range of DRCs in *Silurus spp.* samples from different rivers located in France.  
32 Determination was carried out by gas chromatography high-resolution mass spectrometry after a  
33 sample clean-up based on a multilayer silica column and gel permeation chromatography. The  
34 concentration of monitored  $\Sigma$ DRCs ranged from 1.58 to 408  $\text{pg.g}^{-1}$  wet weight (54 to 11100  $\text{pg.g}^{-1}$   
35 lipid weight). The fractional abundance of *syn*- and *anti*-DP stereoisomers was similar to that  
36 reported by other studies with an average equal to 0.60. Dec-601 was not detected in any sample.  
37 Detection frequencies ranged between 34 and 100% for other DRCs. Investigated correlations  
38 between DRCs and polychlorobiphenyls (PCBs) suggest a link with lipid content but independent  
39 contamination sources.

40

41

## 42 **1. Introduction**

43 Flame retardants (FRs) are chemicals added to a wide range of consumer and industrial products (e.g.  
44 textiles, furniture, wire coatings, electronics) in order to limit fire initiation and propagation in a  
45 context of fire safety (Stapleton et al., 2014). Some FRs, such as Dechlorane (also called Mirex) and  
46 decabromodiphenyl ether have been listed in Annex A of the Stockholm Convention on Persistent  
47 Organic Pollutants (POPs) (UNEP, 2001) due to their toxicity to humans and aquatic organisms (Wang  
48 et al., 2010). Thus, Dechlorane Plus (DP), a first Dechlorane Related Compound (DRC), appeared as a  
49 workable alternative (EPA, 2014). To our knowledge, DP is manufactured by two corporations in the  
50 world: OxyChem in Buffalo, NY, USA (formerly Hooker Chemical Corporation) and Anpon  
51 Electrochemical Co., Ltd in Jiangsu province in China (Xian et al., 2011).

52 DP is produced by a Diels-Alder condensation of two equivalents of hexachlorocyclopentadiene with  
53 one equivalent of 1,5-cyclooctadiene. Classified according to particle size, the three types of DP  
54 commercial products (DP-25, DP-35 and DP-515) are primarily composed of two stereoisomers, *syn*-  
55 and *anti*-isomers (Zhu et al., 2007) (see Table S1 for structures). Although some differences in the  
56 ratio of the two stereoisomers are possible due to the variability of production processes, a ratio of  
57 1:3 (*syn*-DP:*anti*-DP) is commonly considered (Zhu et al., 2007; Jia et al., 2011). DP has been classified  
58 as a high production volume chemical in the USA but a low production volume chemical in the EU  
59 (Barón et al., 2012). Environment Canada also listed DP on Canada's Domestic Substances List  
60 (Sverko et al., 2008). The annual production was estimated to be 450– 4500 tons in the USA between  
61 1986 and 2006 and 300–1000 tons in China between 2003 and 2005 (Wang et al., 2016). Due to its  
62 high hydrophobicity ( $\log K_{ow} = 9.3$ ), DP presents a high tendency to adsorb onto organic materials and  
63 exhibits a long half-life in the aquatic environment (Hoh et al., 2006). It is also considered chemically  
64 stable in various environmental compartments (Wang et al., 2016). From the application perspective,  
65 DP is advantageous over brominated-based flame retardants owing to its thermal and photochemical  
66 stabilities, lower density and lower production cost (Feo et al., 2012).

67 Regarding its occurrence, DP was first reported in air, fish and sediment samples from the Great  
68 Lakes region in 2006 (Hoh et al., 2006). Its ubiquitous presence has been confirmed in various  
69 environmental matrices all over the world, including wildlife and human, demonstrating that DP is  
70 persistent, susceptible to long range atmospheric transport and bioaccumulative (Sverko et al., 2011;  
71 Xian et al., 2011). Previous studies have investigated its occurrence and behaviour in the atmosphere  
72 (Hoh et al., 2006; Kakimoto et al., 2015; Xian et al., 2011), sediment (Barón et al., 2012; Xian et al.,  
73 2011; Yu et al., 2015), soil (Ma et al., 2014), water (Sverko et al., 2011), biota (L'Homme et al., 2015;  
74 Rjabova et al., 2016; Wang et al., 2015; Zhang et al., 2011) as well as food products (Aznar-Alemany  
75 et al., 2016; Kakimoto et al., 2012; Kim et al., 2014). Sverko et al. (2011) even suggested, considering  
76 DP in Annex D (candidate list) of the Stockholm Convention, so that such compounds are of public  
77 safety concerns.

78 At the same time, alternative DRCs based on hexachlorocyclopentadiene as well, such as  
79 Decchlorane-601, -602, -603 (Dec-601 to Dec-603) and Chlordene Plus (CP), were also placed on the  
80 market (Table S1). Little information however is available on the production volumes for these  
81 alternative DRCs (Yang et al., 2016). We did not find any information about the use or import of Dec-  
82 601, Dec-602, Dec-603 and CP in France. Dec-602 may still be used in the marketplace while the  
83 environmental occurrence of Dec-603 was found to be due, in part, to its presence as an impurity in  
84 technical Aldrin and Dieldrin (Shen et al., 2011a). This family of compounds exhibits properties  
85 similar to those of persistent organic pollutants (POPs), such as long-range transport potential,  
86 bioaccumulation, biomagnification and low degradation rate (Wang et al., 2011; Von Eyken et al.,  
87 2016).

88 For the determination of DRCs, the majority of studies relies on gas chromatographic separation,  
89 followed either by electron ionisation or negative chemical ionisation through electronic capture  
90 mechanism, coupled to single or tandem mass spectrometry (EI-MS(/MS) or NCI-MS(/MS))  
91 determination. These methods face insufficient detection limits in some cases with, in other cases,  
92 the need of an additional injection for separating DRCs from polybrominated diphenyl ethers (PBDEs)

93 (Sales et al., 2017). Other authors implemented electron ionisation coupled to high resolution mass  
94 spectrometry for DP identification and quantification (Wang et al., 2016) to take advantage of the  
95 mass defect induced by chlorine atoms.

96 Fish have widely been used to monitor pollution in aquatic ecosystems. In addition, fish constitutes a  
97 critical link connecting the aquatic food web to the human. Further, consumption of contaminated  
98 fish is recognised as a major source of exposure to environmental pollutants for the general  
99 population (Bodin et al., 2014). In river fish samples from industrial areas in Korea, Kang et al. (2010)  
100 observed relatively high DP concentrations, ranging from 0.61 to 126 ng.g<sup>-1</sup> of lipid weight (lw) with a  
101 mean value of 24.5 ng.g<sup>-1</sup> lw. Sun et al. (2016) reported that the DP concentrations in the Pearl River  
102 Delta (South China) ranged from 0.09 to 27 ng.g<sup>-1</sup> lw. Another study reported DRC levels in various  
103 fish species collected in Spanish rivers: Dec-602, Dec-603 and DP were detected in almost all samples  
104 at concentrations up to 174, 11.8 and 4.9 ng.g<sup>-1</sup> lw, with median values of 38.2, 2.6 and 0.9 ng.g<sup>-1</sup> lw,  
105 respectively (Santín et al., 2013). Giulivo et al. (2017) investigated the presence of DRCs in three  
106 European river basins flowing into the Mediterranean Sea in fish samples collected over 2014-2015.  
107 DRCs were detected in fishes from both the Adige (Italy) and the Sava (South-East Europe) river  
108 basins, with mean values equal to 7.59 and 3.00 ng.g<sup>-1</sup> lw, respectively; they were not detected in  
109 fishes from the Evrotas (Greece) river basin. Recent studies reported mean concentrations of DRCs in  
110 fishes from two rivers from Latvia with concentrations of 14.8, 0.98 and 11.34 pg.g<sup>-1</sup> lw for Dec-602,  
111 Dec-603 and DP, respectively (Rjabova et al., 2016). Part of these results suggests that the prevalence  
112 of DRCs in fishes arising from production and industrial zones is higher than in rural places. To the  
113 best of our knowledge, the status of DRCs in river fish from France is yet unknown.

114 The aim of the present study was to report occurrence levels of DRCs in *Silurus spp.* from several  
115 river basins in France. This species is largely distributed over the French territory, and known to  
116 accumulate hydrophobic chemicals such as polychlorobiphenyls (AFSSA, 2008; Alomar et al., 2016;  
117 Squadrone et al., 2016). To the best of our knowledge, this is the first time that this set of emerging  
118 halogenated flame retardants was determined in fish samples in France.

119

## 120 **2. Materials and methods**

### 121 *2.1. Sample collection*

122 A total of 102 *Silurus spp.* samples were collected from 22 areas covering the metropolitan French  
123 territory (Figure 1) during 2008–2011 and 2014–2015. Muscles were freeze-dried, homogenized  
124 using a stainless steel blender and stored until chemical analysis was performed.

125

### 126 *2.2. Chemicals*

127 Reference solutions of native *syn*-Dechlorane Plus (DP), *anti*-DP, Dec-601, -602, -603 and  
128 Chlordene Plus (CP) were purchased from Wellington Laboratories (Guelph, Ontario, Canada).  
129 Reference solutions of <sup>13</sup>C<sub>10</sub>-labelled *syn*-DP, *anti*-DP, Dec-602 (internal standards, IS) and  
130 <sup>13</sup>C<sub>12</sub>-PCB-194 (recovery standard) were provided by Cambridge Isotope Laboratories (Andover, MA,  
131 USA) and used according to the isotopic dilution analysis. Working solutions were prepared at  
132 1 ng.μL<sup>-1</sup> in toluene and stored at -20 °C. Silica gel (70/230 mesh) was obtained from Fluka (Buchs,  
133 Switzerland), sodium sulphate from Merck (Darmstadt, Germany). Sulphuric acid (98%) was  
134 purchased from Panreac (Barcelona, Spain) and 1 N sodium hydroxide from Reagecon (Clare,  
135 Ireland). Toluene, acetone, ethyl acetate, cyclohexane and *n*-hexane were provided by LGC  
136 Promochem (Picograde®, Wesel, Germany) and dichloromethane by Biosolve (Valkenswaard, The  
137 Netherlands).

138

### 139 *2.3. Sample preparation*

140 The procedure for sample extraction was adapted from those present in the literature (Wang et al.,  
141 2016) with minor modifications (Figure 2). Four grams of lyophilised fish muscle were extracted by  
142 Pressurized Liquid Extraction (PLE) with diatomaceous earth (Büchi, SpeedExtractor, E-914) at  
143 100 bar and 120 °C (3 cycles) with approximately 120 mL of a mixture of toluene/acetone 7:3 (v/v).  
144 The extract was fortified with a mixture of <sup>13</sup>C<sub>10</sub>-labelled *syn*-DP, *anti*-DP and Dec-602 (4 ng each).

145 Extracted lipids were determined gravimetrically and reconstituted in *n*-hexane. Then, a two-step  
146 clean-up procedure was applied. First, the extract was loaded on a multilayer silica gel column  
147 comprising 5 g neutral silica gel, 5 g basic silica gel (NaOH 1 N), 5 g neutral silica gel, 20 g and 25 g  
148 acidic silica gel (22% and 44% H<sub>2</sub>SO<sub>4</sub>, respectively) from the bottom to the top, and topped with dry  
149 Na<sub>2</sub>SO<sub>4</sub>. DRCs were eluted with 120 mL *n*-hexane and reconstituted in 500 µL of a mixture of ethyl  
150 acetate/cyclohexane 1:1 (v/v). Second, the extract was subjected to a Gel Permeation  
151 Chromatography column (58 cm × 24.4 mm) packed with Bio-Beads SX-3 (Bio-Rad, Philadelphia, PA)  
152 using a mixture of ethyl acetate/cyclohexane 1:1 (v/v) as mobile phase at a flow rate of 5 mL.min<sup>-1</sup>, to  
153 remove remaining interferences. The collected extract (24-36 min) was concentrated to dryness  
154 under a gentle stream of nitrogen and reconstituted in 20 µL of toluene containing 800 pg of  
155 <sup>13</sup>C<sub>12</sub>-PCB-194, prior to the instrumental analysis.

156

#### 157 *2.4. Instrumental acquisition*

158 Purified extracts were analysed by gas chromatography coupled to high resolution mass  
159 spectrometry with electron ionisation (GC-EI-HRMS). GC separation was performed in a HP 6890  
160 instrument (HP, Palo Alto, CA, USA). Four capillary columns were evaluated: ZB-5HT Inferno (5%  
161 phenyl, 95% dimethylpolysiloxane; 15 m x 0.25 mm, 0.1 µm), Rtx<sup>®</sup>-1614 (5% diphenyl, 95%  
162 dimethylpolysiloxane; 15 m x 0.25 mm, 0.1 µm), DB-5MS (5% phenyl, 95% dimethyl arylene  
163 polysiloxane; 30 m x 0.25 mm, 0.1 µm) and HT8-PCB (8% phenyl polycarborane-siloxane; 30 m x  
164 0.25 mm, unknown film thickness), from Phenomenex (Torrance, CA, USA), Restek (Bellefonte, PA,  
165 USA), Agilent (Santa Clara, CA, USA) and SGE Analytical Science (Ringwood, Australia), respectively.  
166 The optimised chromatographic separation of DRCs was obtained using the HT8-PCB column with the  
167 conditions hereafter described. Two microliters of the extracts were injected in the splitless mode at  
168 280 °C. Helium was used as carrier gas at 1 mL.min<sup>-1</sup>. The oven temperature program started at  
169 100 °C (2 min), rose to 280 °C at 33 °C.min<sup>-1</sup>, then ramped to 325 °C at 5 °C.min<sup>-1</sup> (6 min). Auxiliary  
170 and source temperatures were set at 280 °C. The electron energy was set at 38 eV and the filament



171 current at 400  $\mu$ A. HRMS measurements were achieved on a JMS 700D electromagnetic instrument  
172 (Jeol, Tokyo, Japan), operating at a resolution of 10,000 according to 10% valley definition. The target  
173 analytes were detected in the Selected Ion Monitoring acquisition mode using the two most intense  
174 fragments from each molecular ion cluster (Table S2).

175

#### 176 2.5. QA/QC

177 The analytes were identified according to the Commission Decision 2002/657/EC requirements.  
178 Particular attention was paid to procedural contamination at any stage of the analytical process.  
179 Glassware was rinsed with dichloromethane or, whenever possible, was heated in a muffle oven at  
180 400 °C during 4 h. PLE extraction cells with diatomaceous earth were pre-washed prior to use.  
181 Procedural blanks were performed from PLE extraction in each batch of samples and treated in the  
182 same manner as routine samples ( $n = 10$ ). The distribution of concentration levels was then used to  
183 set a limit of reporting (LOR) by considering the mean value plus three times the standard deviation.  
184 When no procedural contamination was observed, a limit of detection (LOD) was defined as three  
185 times the noise background.

186 As regards to the evaluation of the method accuracy, we participated in the Northern Contaminants  
187 Program/Arctic Monitoring and Assessment Programme Phase 11 Interlaboratory Study (NCP)  
188 organised by the Ontario Ministry of the Environment and Climate Change. However, since no  
189 samples obtained  $\geq 10$  numerical reported results for DRCs, no z-scores could be attributed for fish  
190 samples and extracts. Nevertheless, design values were available for the standard solution, with 3 to  
191 8 reporting laboratories. Moreover, in order to monitor precision and trueness along the analytical  
192 campaign, (i) an in-house quality control (QC) fish oil (1 g aliquots) routinely used for ISO 17025  
193 methods dedicated to a range of POPs (PCDD/Fs, PCBs, PDBEs, HBCDDs) (Jondreville et al., 2017) was  
194 either used as a non-fortified QC ( $n = 5$ ) or a fortified QC (QCF) (4 ng of each native compound)  
195 ( $n = 5$ ) and (ii) a significantly naturally contaminated fish muscle sample (NCF) was analysed 4 times.

196

197 2.6 Data processing

198 All the results were expressed both on a wet weight (ww) and on a lipid weight (lw) basis, in order to  
199 facilitate the comparison to the results reported in other studies. The average values were expressed  
200 according to lower-bound (LB) and upper-bound (UB) approaches. The LB average underestimates  
201 the value by considering zero if the level measured in the sample is below the limits of performance  
202 (LOR or LOD). The UB average overestimates the value by considering the limits of performance (LOR  
203 or LOD) if the level measured in the sample is below.

204 The relationships between DRCs and PCBs (previously analysed using proven methods, not  
205 published) were statistically evaluated by Spearman coefficients of correlation ( $\rho$ ) using XLStat 2017  
206 (Addinsoft, Paris, France).

207

208 **3. Results and discussion**

209 *3.1. Method performances*

210 With regard to achieving optimal GC separation and considering that the same ion at  $m/z$  271.8096 is  
211 monitored for most target analytes, the efficiency of four capillary columns was tested: ZB-5HT  
212 Inferno, Rtx<sup>®</sup>-1614, DB-5MS and HT8-PCB. While the three first ones exhibited coelution of Dec-601  
213 and *syn*-DP, generating an identification issue, the HT8-PCB was the only column allowing for their  
214 separation (Figure S1). Then, the HT8-PCB column was selected for DRCs analysis.

215 The performance of the method was evaluated with regard to the relative response factor (linearity),  
216 the recovery, the limit of reporting (LOR) or detection (LOD) and the precision. Instrumental linearity  
217 was evaluated using five calibration standards covering the concentration range from 5 to 500  $\text{pg}\cdot\mu\text{L}^{-1}$   
218 for each compound, and containing the 3 labelled internal standards at 200  $\text{pg}\cdot\mu\text{L}^{-1}$  and the recovery  
219 standard at 40  $\text{pg}\cdot\mu\text{L}^{-1}$ . The obtained relative standard deviation (RSD) and the average relative factor  
220 (RRF) for each analyte is presented in the supporting information (Table S3). The values of RSD for all  
221 compounds were lower than 20%, which reflects an acceptable linearity. The average recoveries for  
222  $^{13}\text{C}_{10}$ -labeled standards were  $113 \pm 17\%$ ,  $101 \pm 14\%$  and  $74 \pm 11\%$  for  $^{13}\text{C}_{10}$ -*syn*-DP,  $^{13}\text{C}_{10}$ -*anti*-DP and

223  $^{13}\text{C}_{10}$ -Dec-602, respectively. Trace amounts of *syn*-DP and *anti*-DP were detected in procedural blanks  
224 with a mean concentration of approximately  $1 \text{ pg.g}^{-1} \text{ ww}$ , based on the average sample size  
225 (Table S4). Based on the approach described in section 2.5, the LOR value was equal to  $3 \text{ pg.g}^{-1} \text{ ww}$   
226 for both. The calculated detection limits (LOD,  $S/N = 3$ ) of Dec-601, -602, -603, and CP were 0.5, 0.1,  
227 0.2 and  $0.1 \text{ pg.g}^{-1} \text{ ww}$ , respectively. The results obtained for the NCP standard mixture showed a  
228 satisfying correlation for all the target compounds within the designed value (Table S5), which  
229 validates that the standards were properly prepared. The intermediate precision of the assay was  
230 assessed by analysing a fish sample (NCF), a non-fortified (QC) and a fortified fish oil (QCF) samples,  
231 according to the ISO 11352:2012 standards and Eppe et al. (2017) guideline. Obtained values were  
232 14.4, 19.8, 17.9, 6.9, 21.5 and 18.9% for *syn*-DP, *anti*-DP, Dec-601, Dec-602, Dec-603 and CP,  
233 respectively (Table S6). The trueness uncertainty was estimated based on the difference between the  
234 fortified and non-fortified fish oil, and ranged between -3.0 to +3.0%, except for CP at +20.3%  
235 (Table S6). Finally, these accuracy results led to a relatively high confidence level regarding  
236 determination of DP isomers, Dec-602 and -603. CP suffered a slight trueness bias while Dec-601 was  
237 not completely evaluated due to non-detectable levels.

238

### 239 3.2. Sum concentration of DP isomers

240 Table 1 summarises the results obtained for the 102 fish samples. Despite lower detection  
241 performances compared to other DRCs, at least one DP isomer could be quantified in about half of  
242 the fish samples collected in French rivers during 2008-2015. More precisely, *syn*-DP was detected in  
243 33% of the analysed samples, whereas *anti*-DP was found in 47%.

244 In our study, the concentrations levels of DP in fish ( $n = 102$ ) ranged from  $\leq \text{LOR}$  to  $73.8 \text{ pg.g}^{-1} \text{ ww}$   
245 with an average value comprised between 8.05 (LB) and 11.63 (UB)  $\text{pg.g}^{-1} \text{ ww}$ . The highest  
246 concentration of DP was detected in a *Silurus spp.* from the Jonage channel (a branch of the Rhone  
247 River, upstream from Lyon, Figure 1), close to a hydroelectric plant. Another fish sample, from the  
248 Garonne River, also exhibited a relatively high DP level at  $45.1 \text{ pg.g}^{-1} \text{ ww}$ . This relatively high level

249 was observed in the fish presenting the highest lipid content (12.2%), which is not surprising  
250 considering the lipophilic properties of these compounds. Quite similarly, concentrations of DP  
251 reported in a recent study on salmon ( $n = 25$ ) from Latvian rivers in 2012 reached a mean  
252 concentration of  $11.34 \text{ pg.g}^{-1} \text{ ww}$ , taking into account values above LOR only ( $> 50\%$  detection  
253 frequencies for *syn*- and *anti*-DP) (Rjabova et al., 2016). This value was about two times lower than  
254 the one found in our study based on the same calculation method ( $22.9 \text{ pg.g}^{-1} \text{ ww}$ ).

255 In order to compare our results with those of other studies, the concentration of DP was also  
256 expressed on a lipid weight (lw) basis, ranging from  $\leq \text{LOR}$  to  $6.01 \text{ ng.g}^{-1} \text{ lw}$  with an average value  
257 comprised between  $0.56 \text{ (LB)}$  and  $1.14 \text{ (UB)} \text{ ng.g}^{-1} \text{ lw}$ . These results were an order of magnitude  
258 lower than those observed in previous studies focusing on river fish in Asia. For instance, Kang et al.  
259 (2010), reported DP concentrations from urban-industrial rivers in South Korea ( $n = 22$ ) in 2008 at an  
260 average of  $24.5 \text{ ng.g}^{-1} \text{ lw}$ . Wang et al., reported DP in North-Eastern China ( $n = 15$ ) in 2010 with an  
261 average equal to  $29 \text{ ng.g}^{-1} \text{ lw}$  (Wang et al., 2012). However, our results were close to those reported  
262 for Spanish river basins, which ranged from non-detected to  $2.24 \text{ ng.g}^{-1} \text{ lw}$  (Barón et al., 2012) or  
263 from non-detected to  $4.86 \text{ ng.g}^{-1} \text{ lw}$  (Santín et al., 2013). These previously reported results suggest  
264 that specific industrialized and populated urban areas could be major sources of chlorinated flame  
265 retardants.

266

### 267 3.3. Profiles of DP isomers

268 The concentrations of *anti*-DP were higher than those of *syn*-DP in about 85% of the quantified  
269 samples, results exhibiting a pronounced domination of *anti*-DP. These observations are similar to  
270 those reported by other authors (Barón et al., 2012; De La Torre et al., 2012).

271 The isomer ratio of DP is commonly used to assess the fate and distribution of DP in the environment  
272 and biota. The fractional abundance of the *anti*-isomer ( $f_{anti}$ ) is calculated by dividing the  
273 concentration of *anti*-DP by the sum concentration of *syn*- and *anti*-DP. The  $f_{anti}$  value of DP  
274 commercial products varies from 0.65 to 0.80, depending on the study. The  $f_{anti}$  value in this study

275 ranged from 0.32 to 0.88 with an average equal to  $0.60 \pm 0.12$  (Figure 3), which is similar to  
276 previously reported values for river fishes of 0.67 (Kang et al., 2010),  $0.48 \pm 0.16$  (Santín et al., 2013),  
277 0.71 (Rjabova et al., 2016) and 0.56 (Giulivo et al., 2017). According to the literature, there is a  
278 tendency towards an enrichment in *syn*-DP in higher trophic levels in aquatic biota (Kakimoto et al.,  
279 2012; Xian et al., 2011). However, how can one explain the three  $f_{anti}$  values observed above 0.75? A  
280 hypothesis could be that some exposure sources were highly dominated by *anti*-DP, corroborated by  
281 the fact that the concerned collection sites were close to one another (Loir and Loire rivers). Another  
282 hypothesis could be that inter-individual variability leads to specific enrichment in *anti*-DP in some  
283 cases.

284

#### 285 3.4. Concentration of other DRCs

286 Dec-601 was not detected in any of the 102 fish samples analysed, possibly because not  
287 bioaccumulative or more likely because not used in the considered geographical area. Conversely,  
288 Dec-602, -603 and CP were detected in almost all the samples with a detection frequency (DF) of  
289 100%, 95% and 89%, respectively.

290 Dec-602 was the most frequently detected DRC, with levels ranging from 0.31 to 226  $\text{pg.g}^{-1}$  ww (up to  
291 5.30  $\text{ng.g}^{-1}$  lw) and an average at 11.8  $\text{pg.g}^{-1}$  ww (0.56  $\text{ng.g}^{-1}$  lw). The concentrations of Dec-602 were  
292 higher than those of DP. Baron et al. (2012) suggested that the differences in log  $K_{ow}$  values for  
293 Dec-602 and DP (7.1 and 9.0, respectively) could explain such a trend. The concentrations of Dec-602  
294 were similar to those found in salmon samples ( $n = 25$ ) collected from rivers in Latvia (100% DF,  
295 average at 14.8  $\text{pg.g}^{-1}$  ww) (Rjabova et al., 2016) but lower than those reported in fish samples  
296 ( $n = 15$ ) from a river in North-Eastern China in 2010 (100% DF, average at 7.8  $\text{ng.g}^{-1}$  lw) (Wang et al.,  
297 2012).

298 The concentration levels of Dec-603 ranged from  $\leq$  LOD to 250  $\text{pg.g}^{-1}$  ww (up to 3.84  $\text{ng.g}^{-1}$  lw) with  
299 an average at 12.5  $\text{pg.g}^{-1}$  ww (0.56  $\text{ng.g}^{-1}$  lw). These values were much higher than those reported

300 from Latvia at  $0.98 \text{ pg.g}^{-1} \text{ ww}$  (Rjabova et al., 2016) but lower than those found in China at  
301  $3.80 \text{ ng.g}^{-1} \text{ lw}$  and in Spain at  $2.46 \text{ ng.g}^{-1} \text{ lw}$  (Wang et al., 2012; Santín et al., 2013).  
302 Concentration levels for CP ranged from  $\leq \text{LOD}$  to  $45.1 \text{ pg.g}^{-1} \text{ ww}$  (up to  $0.94 \text{ ng.g}^{-1} \text{ lw}$ ) with an  
303 average at  $2.51 \text{ pg.g}^{-1} \text{ ww}$  ( $0.11 \text{ ng.g}^{-1} \text{ lw}$ ). These concentrations were lower than those found in  
304 seven aquatic species ( $n = 66$ ) in China in 2010 (100% DF, from 29.8 to  $128 \text{ ng.g}^{-1} \text{ lw}$ ) (Wang et al.,  
305 2015). Quite similarly, De la Torre et al. (2012) reported relatively low mean CP concentrations  
306 ( $0.13 \text{ ng.g}^{-1} \text{ lw}$ ) in dolphin samples off the coast of Brazil (based on half the samples that were  
307 quantified). To date, there are few references dealing with CP concentrations in other matrix types,  
308 such as sediment (Shen et al., 2011a, 2011b) and human serum (Brasseur et al., 2014; Kim et al.,  
309 2016).

310

### 311 3.5. Correlations between DRCs

312 Keeping in mind that concentration levels were relatively low for such a comparison, the correlation  
313 between DRCs was assessed based on wet weight concentrations, while accounting only for  
314 quantified ( $\geq \text{LOR}$ ) values. The results (Table 2) indicate that *syn*- and *anti*-DP were moderately  
315 correlated with each other ( $\rho = 0.75$ ), presumably because *syn*-DP and *anti*-DP (structural isomers)  
316 have different bioaccumulation properties. Several studies have shown on diastereoisomers,  
317 enantiomers or atropisomers, that the spatial conformation of the compounds can affect the  
318 properties of bioaccumulation (Wong et al., 2002; Dang et al., 2010; Luo et al., 2013). Other  
319 significant correlations were observed between *syn*-DP and Dec-602 ( $\rho = 0.38$ ,  $P\text{-value} = 0.026$ ) and  
320 between Dec-603 and CP ( $\rho = 0.78$ ,  $P < 0.0001$ ).

321 The sum of wet weight based concentrations of all DRCs ( $\Sigma\text{DRCs}$ ) was correlated with lipid contents  
322 (Speaman test;  $\rho = 0.69$ ,  $P < 0.0001$ ). Dec-602, which is the dominant compound in  $\Sigma\text{DRCs}$ , was also  
323 correlated with lipid contents ( $\rho = 0.69$ ,  $P < 0.0001$ ). Nevertheless, beside lipids,  $\rho$  value suggests that  
324 other factors (unexplored yet) are also influencing DRCs accumulation in European *Silurus spp.*

325 There was no correlation between DP and other DRCs based on lipid adjusted concentrations, nor  
326 between other DRCs themselves, except a moderate correlation between Dec-603 and CP ( $\rho = 0.75$ ;  
327 Table 2). This observation suggests that these DRCs originate from independent uses, therefore  
328 spatial sources.

329

### 330 *3.6. Correlation between DRCs and other POPs*

331 Polychlorobiphenyl (PCB) concentrations were available for 97 out of 102 *Silurus spp.* samples. These  
332 PCB data were obtained in the context on a national plan aiming to establish a diagnosis of  
333 freshwater fish contamination (Eaufrance). Analytes included 12 dioxin-like PCB (DL-PCB) congeners,  
334 and six non-dioxin-like/indicator congeners. It was thus possible to seek potential relationships  
335 among PCBs and dechloranes at a national scale. As DL-PCB concentrations were almost certainly  
336 correlated to the sum of PCB concentrations ( $\Sigma$ PCB) or to the sum of concentrations of a few  
337 indicator congeners (AFSSA, 2009; Babut et al., 2009), we explored the correlation between  
338 dechloranes and six indicator congeners (PCB-28, -52, -138, -153 and -180) individually or as a single  
339 variable ( $\Sigma_6$ PCB).

340  $\Sigma$ DRCs and  $\Sigma_6$ PCB appeared correlated on a ww basis ( $\rho = 0.67$ ,  $P < 0.0001$ ,  $n = 77$ ). Among DRCs,  
341 Dec-602, which is the dominant compound in  $\Sigma$ DRCs, was slightly more correlated to  $\Sigma_6$ PCB ( $\rho = 0.81$ ,  
342  $P < 0.0001$ ); it was also correlated to each congener accounted for in  $\Sigma_6$ PCB (Table S7). The  
343 correlation coefficients were lower but still significant when testing correlations on a lw basis  
344 ( $\rho = 0.73$  for Dec-602 vs  $\Sigma_6$ PCB, or  $\rho = 0.74$  for Dec-602 vs PCB-153). This suggests that although lipid  
345 contents are influencing the accumulation of both PCBs and DRCs, other influencing factors  
346 unexplored yet are also common to both contaminant groups. Urbanization, because emissions can  
347 result from past and present uses at industrial sites or in households, cars and so on, might be one of  
348 these.

349

## 350 **4. Conclusions and perspectives**

351 A robust and sensitive method has been developed and evaluated for the analysis of DRCs in fish  
352 muscle. The method showed satisfying performances as preliminarily assessed, although a full  
353 validation is still required. The protocol was successfully applied to a relatively large set of fish  
354 samples from French rivers. The median concentration of  $\Sigma$ DRCs in *Silurus spp.* was observed quite  
355 low (in the  $\text{pg}\cdot\text{g}^{-1}$  ww range) compared to reported results from Asia where maximum values reach a  
356 few dozen or hundred  $\text{pg}\cdot\text{g}^{-1}$  ww. A moderate correlation was found between DRCs and PCBs levels,  
357 suggesting relatively independent sources and/or environmental fates. This first picture at the French  
358 level should help investigating how the environmental contamination by these emerging substances  
359 will evolve, particularly in rivers. The potential impact of such contamination from an  
360 ecotoxicological point of view, as well as consequences in terms of public health are still an open  
361 question. Moreover, it would be important to evaluate the dietary exposure of the French  
362 population, considering animal products as well as sea fish or shellfish, which could also be  
363 contaminated.

364

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368



369 **References**

- 370 AFSSA (2008). Appui scientifique et technique de l'Agence Française de Sécurité Sanitaire des  
371 aliments relative au plan d'échantillonnage national des PCB dans les poissons de rivière :  
372 proposition de méthodologie. Report No. Saisine n° 2008-SA-0019, Agence Française de  
373 Sécurité Sanitaire des Aliments (AFSSA), Maisons-Alfort.
- 374 AFSSA, 2009. Avis de l'Agence Française de sécurité sanitaire des aliments relatif à la détermination  
375 de valeurs seuil en PCB-NDL comme outil d'appréciation du risque de contamination des  
376 poissons d'eau douce et de mer. AFSSA, Maisons-Alfort, p. 18.
- 377 Alomar, H., Lemarchand, C., Rosoux, R., Vey, D., Berny, P., 2016. Concentrations of organochlorine  
378 compounds (pesticides and PCBs), trace elements (Pb, Cd, Cu, and Hg), <sup>134</sup>Cs, and <sup>137</sup>Cs in the  
379 livers of the European otter (*Lutra lutra*), great cormorant (*Phalacrocorax carbo*), and European  
380 catfish (*Silurus glanis*), collected from the Loire River (France). European Journal of Wildlife  
381 Research 62, 653-661 (10.1007/s10344-016-1038-5).
- 382 Aznar-Alemany, Ò., Trabalón, L., Jacobs, S., Barbosa, V.L., Tejedor, M.F., Granby, K., Kwadijk, C.,  
383 Cunha, S.C., Ferrari, F., Vandermeersch, G., Sioen, I., Verbeke, W., Vilavert, L., Domingo, J.L.,  
384 Eljarrat, E., Barceló, D., 2016. Occurrence of halogenated flame retardants in commercial  
385 seafood species available in European markets. Food Chem. Toxicol. 1–13.  
386 doi:10.1016/j.fct.2016.12.034.
- 387 Babut, M., Miege, C., Villeneuve, B., Abarnou, A., Duchemin, J., Marchand, P., Narbonne, J.F., 2009.  
388 Correlations between dioxin-like and indicators PCBs: potential consequences for  
389 environmental studies involving fish or sediment. Environ. Pollut. 157, 3451-3456.
- 390 Barón, E., Eljarrat, E., Barceló, D., 2012. Analytical method for the determination of halogenated  
391 norbornene flame retardants in environmental and biota matrices by gas chromatography  
392 coupled to tandem mass spectrometry. J. Chromatogr. A 1248, 154–160.  
393 doi:10.1016/j.chroma.2012.05.079.
- 394 Bodin, N., Tapie, N., Le Ménach, K., Chassot, E., Elie, P., Rochard, E., Budzinski, H., 2014. PCB

395 contamination in fish community from the Gironde Estuary (France): Blast from the past.  
396 Chemosphere 98, 66–72. doi:10.1016/j.chemosphere.2013.10.003.

397 Brasseur, C., Pirard, C., Scholl, G., De Pauw, E., Viel, J.F., Shen, L., Reiner, E.J., Focant, J.F., 2014. Levels  
398 of dechloranes and polybrominated diphenyl ethers (PBDEs) in human serum from France.  
399 Environ. Int. 65, 33–40. doi:10.1016/j.envint.2013.12.014.

400 Commission Decision of 12 August 2002 (2002/657/EC) implementing Council Directive 96/23/EC  
401 concerning the performance of analytical methods and the interpretation of results.

402 Dang, V.D., Walters, D.M., Lee, C.M., 2010. Transformation of Chiral Polychlorinated Biphenyls (PCBs)  
403 in a Stream Food Web. Environ. Sci. Technol. 44, 2836-2841.

404 De La Torre, A., Alonso, M.B., Martínez, M.A., Sanz, P., Shen, L., Reiner, E.J., Lailson-Brito, J., Torres,  
405 J.P.M., Bertozzi, C., Marigo, J., Barbosa, L., Cremer, M., Secchi, E., Malm, O., Eljarrat, E., Barceló,  
406 D., 2012. Dechlorane-related compounds in franciscana dolphin (*Pontoporia blainvillei*) from  
407 southeastern and southern coast of Brazil. Environ. Sci. Technol. 46, 12364–12372.  
408 doi:10.1021/es302934p.

409 Eaufrance, <http://www.pollutions.eaufrance.fr/pcb/>, in French, accessed 21<sup>st</sup> January 2018.

410 EPA, 2014. An Alternatives Assessment for the Flame Retardant Decabromodiphenyl Ether  
411 (DecaBDE). United States Environmental Protection Agency, January 2014.

412 Eppe, G., Schaechtele, A., Haedrich, J., Fernandes, A., 2017. Guidance Document on Measurement  
413 Uncertainty for Laboratories performing PCDD/F and PCB Analysis using Isotope Dilution Mass  
414 Spectrometry. Working Group for Measurement Uncertainty in PCDD/F and PCB Analysis.

415 Feo, M.L., Barón, E., Eljarrat, E., Barceló, D., 2012. Dechlorane Plus and related compounds in aquatic  
416 and terrestrial biota: A review. Anal. Bioanal. Chem. 404, 2625–2637. doi:10.1007/s00216-012-  
417 6161-x.

418 Giulivo, M., Capri, E., Kalogianni, E., Milacic, R., Majone, B., Ferrari, F., Eljarrat, E., Barceló, D., 2017.  
419 Occurrence of halogenated and organophosphate flame retardants in sediment and fish  
420 samples from three European river basins. Sci. Total Environ. 586, 782–791.

- 421 doi:10.1016/J.SCITOTENV.2017.02.056.
- 422 Hoh, E., Zhu, Hites, R.A., 2006. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes.  
423 Environ. Sci. Technol. 40, 1184–1189. doi:10.1021/es051911h.
- 424 ISO 11352:2012. Water quality -- Estimation of measurement uncertainty based on validation and  
425 quality control data.
- 426 Jia, H., Sun, Y., Liu, X., Yang, M., Wang, D., Qi, H., Shen, L., Sverko, E., Reiner, E.J., Li, Y.-F., 2011.  
427 Concentration and bioaccumulation of Dechlorane compounds in coastal environment of  
428 Northern China. Environ. Sci. Technol. 45, 2613–2618.
- 429 Jondreville, C., Cariou, R., Travel, A., Belhomme, L.J., Dervilly-Pinel, G., Le Bizec, B., Huneau-Salaün,  
430 A., Le Bouquin-Leneveu, S., 2017. Hens can ingest extruded polystyrene in rearing buildings and  
431 lay eggs contaminated with hexabromocyclododecane. Chemosphere 186, 62–67.  
432 doi:10.1016/j.chemosphere.2017.07.117.
- 433 Kakimoto, K., Nagayoshi, H., Akutsu, K., Konishi, Y., Kajimura, K., Hayakawa, K., Toriba, A., 2015.  
434 Dechlorane Plus and decabromodiphenyl ether in atmospheric particles of northeast Asian  
435 cities. Environ. Sci. Pollut. Res. Int. 22, 14600–14605. doi:10.1007/s11356-014-2861-4.
- 436 Kakimoto, K., Nagayoshi, H., Yoshida, J., Akutsu, K., Konishi, Y., Toriba, A., Hayakawa, K., 2012.  
437 Detection of Dechlorane Plus and brominated flame retardants in marketed fish in Japan.  
438 Chemosphere 89, 416–419. doi:10.1016/j.chemosphere.2012.05.072.
- 439
- 440 Kang, J.H., Kim, J.C., Jin, G.Z., Park, H., Baek, S.Y., Chang, Y.S., 2010. Detection of Dechlorane Plus in  
441 fish from urban-industrial rivers. Chemosphere 79, 850–854.  
442 doi:10.1016/j.chemosphere.2010.02.051.
- 443 Kim, J., Son, M. hui, Kim, J., Suh, J., Kang, Y., Chang, Y.S., 2014. Assessment of Dechlorane compounds  
444 in foodstuffs obtained from retail markets and estimates of dietary intake in Korean population.  
445 J. Hazard. Mater. 275, 19–25. doi:10.1016/j.jhazmat.2014.04.032.
- 446 Kim, J., Son, M.H., Shin, E.S., Choi, S.D., Chang, Y.S., 2016. Occurrence of Dechlorane compounds and

- 447 polybrominated diphenyl ethers (PBDEs) in the Korean general population. *Environ. Pollut.* 212,  
448 330–336. doi:10.1016/j.envpol.2016.01.085.
- 449 L’Homme, B., Calaprice, C., Calvano, C.D., Zambonin, C., Leardi, R., Focant, J.F., 2015. Ultra-trace  
450 measurement of Dechloranes to investigate food as a route of human exposure. *Chemosphere*  
451 139, 525–533. doi:10.1016/j.chemosphere.2015.07.043.
- 452 Luo, X.-J., Ruan, W., Zeng, Y.-H., Liu, H.-Y., Chen, S.-J., Wu, J.-P., Mai, B.-X., 2013. Trophic dynamics of  
453 hexabromocyclododecane diastereomers and enantiomers in fish in a laboratory feeding study.  
454 *Environ. Toxicol. Chem.* 32, 2565-2570 (10.1002/etc.2337).
- 455 Ma, J., Qiu, X., Liu, D., Zhao, Y., Yang, Q., Fang, D., 2014. Dechlorane Plus in surface soil of North  
456 China: Levels, isomer profiles, and spatial distribution. *Environ. Sci. Pollut. Res.* 21, 8870–8877.  
457 doi:10.1007/s11356-014-2823-x.
- 458 Rjabova, J., Bartkevics, V., Zacs, D., 2016. The occurrence of Dechlorane Plus and related norbornene-  
459 based flame retardants in Baltic wild salmon (*Salmo salar*). *Chemosphere* 147, 210–217.  
460 doi:10.1016/j.chemosphere.2015.12.122.
- 461 Sales, C., Poma, G., Malarvannan, G., Portolés, T., Beltrán, J., Covaci, A., 2017. Simultaneous  
462 determination of dechloranes, polybrominated diphenyl ethers and novel brominated flame  
463 retardants in food and serum. *Anal. Bioanal. Chem.* 4507–4515. doi:10.1007/s00216-017-0411-  
464 x.
- 465 Santín, G., Barón, E., Eljarrat, E., Barceló, D., 2013. Emerging and historical halogenated flame  
466 retardants in fish samples from Iberian rivers. *J. Hazard. Mater.* 263, 116–121.  
467 doi:10.1016/j.jhazmat.2013.08.068.
- 468 Shen, L., Reiner, E.J., MacPherson, K.A., Kolic, T.M., Helm, P.A., Richman, L.A., Marvin, C.H.,  
469 Burniston, D.A., Hill, B., Brindle, I.D., McCrindle, R., Chittim, B.G., 2011a. Dechloranes 602, 603,  
470 604, dechlorane plus, and chlordene plus, a newly detected analogue, in tributary sediments of  
471 the Laurentian great lakes. *Environ. Sci. Technol.* 45, 693–699. doi:10.1021/es1027844.
- 472 Shen, L., Reiner, E.J., Helm, P.A., Marvin, C.H., Hill, B., Zhang, X., MacPherson, K.A., Kolic, T.M., Tomy,

- 473 G.T., Brindle, I.D., 2011b. Historic trends of Dechloranes 602, 603, 604, Dechlorane plus and  
474 other norbornene derivatives and their bioaccumulation potential in Lake Ontario. *Environ. Sci.*  
475 *Technol.* 45, 3333–3340. doi:10.1021/es104328r.
- 476 Squadrone, S., Prearo, M., Nespoli, R., Scanzio, T., Abete, M.C., 2016. PCDD/Fs, DL-PCBs and NDL-  
477 PCBs in European catfish from a northern Italian lake: the contribution of an alien species to  
478 human exposure. *Ecotoxicol. Environ. Safe.* 125, 170-175  
479 (<http://dx.doi.org/10.1016/j.ecoenv.2015.12.004>).
- 480 Stapleton, H.M., Misenheimer, J., Hoffman, K., Webster, T.F., 2014. Flame retardant associations  
481 between children's handwipes and house dust. *Chemosphere* 116, 54–60.  
482 doi:10.1016/j.chemosphere.2013.12.100.
- 483 Sun, R., Luo, X., Tang, B., Li, Z., Wang, T., Tao, L., Mai, B., 2016. Persistent halogenated compounds in  
484 fish from rivers in the Pearl River Delta, South China: Geographical pattern and implications for  
485 anthropogenic effects on the environment. *Environ. Res.* 146, 371–378.  
486 doi:10.1016/j.envres.2016.01.021.
- 487 Sverko, E., Tomy, G.T., Marvin, C.H., Zaruk, D., Reiner, E., Helm, P.E., Hill, B., McCarry, B., 2008.  
488 Dechlorane Plus Levels in Sediment of the Lower Great Lakes. *Sci. Technol.* 42, 361-366.  
489 doi:10.1021/es0710104.
- 490 Sverko, E., Tomy, G.T., Reiner, E.J., Li, Y.F., McCarry, B.E., Arnot, J.A., Law, R.J., Hites, R.A., 2011.  
491 Dechlorane plus and related compounds in the environment: A review. *Environ. Sci. Technol.*  
492 45, 5088–5098. doi:10.1021/es2003028.
- 493 UNEP, 2001. Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on  
494 Persistent Organic Pollutants. United Nations Environment Program: Geneva, Switzerland, p 44.
- 495 Von Eyken, A., Pijuan, L., Martí, R., Blanco, M.J., Díaz-Ferrero, J., 2016. Determination of Dechlorane  
496 Plus and related compounds (dechlorane 602, 603 and 604) in fish and vegetable oils.  
497 *Chemosphere* 144, 1256–1263. doi:10.1016/j.chemosphere.2015.10.001.
- 498 Wang, D.-G., Yang, M., Qi, H., Sverko, E., Ma, W.-L., Li, Y.-F., Alaei, M., Reiner, E.J., Shen, L., 2010. An

- 499 Asia-Specific Source of Dechlorane Plus: Concentration, isomer profiles, and other related  
500 compounds. *Environ. Sci. Technol.* 44, 6608–6613. doi:10.1021/es101224y.
- 501 Wang, D.-G., Alaei, M., Sverko, E., Li, Y.-F., Reiner, E.J., Shen, L., 2011. Analysis and occurrence of  
502 emerging chlorinated and brominated flame retardants in surficial sediment of the Dalian coastal  
503 area in China. *J. Environ. Monit.* 13, 3104. doi:10.1039/c1em10241a.
- 504 Wang, D.G., Guo, M.X., Pei, W., Byer, J.D., Wang, Z., 2015. Trophic magnification of chlorinated flame  
505 retardants and their dechlorinated analogs in a fresh water food web. *Chemosphere* 118, 293–  
506 300. doi:10.1016/j.chemosphere.2014.09.057.
- 507 Wang, L., Jia, H., Liu, X., Yang, M., Hong, W., Sun, Y., Su, Y., Qi, H., Song, W., Lin, J., Li, Y.F., 2012.  
508 Dechloranes in a river in northeastern China: Spatial trends in multi-matrices and  
509 bioaccumulation in fish (*Enchelyopus elongatus*). *Ecotoxicol. Environ. Saf.* 84, 262–267.  
510 doi:10.1016/j.ecoenv.2012.07.018.
- 511 Wang, P., Zhang, Q., Zhang, H., Wang, T., Sun, H., Zheng, S., Li, Y., Liang, Y., Jiang, G., 2016. Sources  
512 and environmental behaviors of Dechlorane Plus and related compounds - A review. *Environ.*  
513 *Int.* 88, 206–220. doi:10.1016/j.envint.2015.12.026.
- 514 Wong, C.S., Lau, F., Clark, M., Mabury, S.A., Muir, D.C.G., 2002. Rainbow trout (*Oncorhynchus mykiss*)  
515 can eliminate chiral organochlorine compounds enantioselectively. *Environ. Sci. Technol.* 36,  
516 1257-1262.
- 517 Xian, Q., Siddique, S., Li, T., Feng, Y. lai, Takser, L., Zhu, J., 2011. Sources and environmental behavior  
518 of dechlorane plus - A review. *Environ. Int.* 37, 1273–1284. doi:10.1016/j.envint.2011.04.016.
- 519 Yang, R., Zhang, S., Li, X., Luo, D., Jing, C., 2016. Dechloranes in lichens from the southeast Tibetan  
520 Plateau: Evidence of long-range atmospheric transport. *Chemosphere* 144, 446–451.  
521 doi:10.1016/j.chemosphere.2015.09.011.
- 522 Yu, D., Yang, J., Li, T., Feng, J., Xian, Q., Zhu, J., 2015. Levels and distribution of Dechloranes in  
523 sediments of Lake Taihu, China. *Environ. Sci. Pollut. Res.* 22, 6601–6609. doi:10.1007/s11356-  
524 014-3794-7.

- 525 Zhang, Y., Wu, J.P., Luo, X.J., Wang, J., Chen, S.J., Mai, B.X., 2011. Tissue distribution of Dechlorane  
526 Plus and its dechlorinated analogs in contaminated fish: High affinity to the brain for *anti*-DP.  
527 Environ. Pollut. 159, 3647–3652. doi:10.1016/j.envpol.2011.07.026.
- 528 Zhu, J., Feng, Y.-L., Shoeib, M., 2007. Detection of Dechlorane Plus in Residential Indoor Dust in the  
529 City of Ottawa, Canada. Environ. Sci. Technol. 41, 7694-7698. doi:10.1021/es071716y.
- 530

531 **Figure captions**

532 **Figure 1.** Locations of the 22 sampling areas in France (map background from  
533 <http://cartographie.nature33.fr>).

534 **Figure 2.** Overview of the sample preparation procedure for the analysis of DRCs in fish muscle.

535 **Figure 3.** Concentrations ( $\mu\text{g}\cdot\text{g}^{-1}$  ww) of *syn*-DP versus *anti*-DP when both values were  $\geq$  LOR ( $n = 33$ ).

536



537 **Table 1.** Concentration ( $\text{pg.g}^{-1}$  ww and lw) of DRCs obtained for *Silurus spp.* samples ( $n = 102$ ) from French rivers. LB: lower-bound; UB: upper-bound.

	<i>syn</i> -DP	<i>anti</i> -DP	Dec-601	Dec-602	Dec-603	CP	$\Sigma$ DRCs
Lower limit ( $\text{pg.g}^{-1}$ ww)	3.0 (LOR)	3.0 (LOR)	0.5 (LOD)	0.1 (LOD)	0.2 (LOD)	0.1 (LOD)	-
Detection frequency	34%	47%	0%	100%	95%	89%	100%
Minimum in $\text{pg.g}^{-1}$ ww	$\leq$ LOR	$\leq$ LOR	-	0.31	$\leq$ LOD	$\leq$ LOD	1.58
( $\text{pg.g}^{-1}$ lw)				(12.6)			(54)
Median LB in $\text{pg.g}^{-1}$ ww	-	-	-	2.65	2.02	0.48	9.26
( $\text{pg.g}^{-1}$ lw)	-	-	-	(367)	(223)	(55.0)	(999)
Mean LB $\pm$ SD in $\text{pg.g}^{-1}$ ww	$2.60 \pm 4.74$	$5.45 \pm 10.45$	-	$11.8 \pm 30.4$	$11.9 \pm 33.6$	$2.24 \pm 6.39$	$34.0 \pm 72.0$
( $\text{pg.g}^{-1}$ lw)	( $189 \pm 468$ )	( $370 \pm 722$ )		( $555 \pm 734$ )	( $499 \pm 686$ )	( $100 \pm 129$ )	( $1712 \pm 1892$ )
Mean UB $\pm$ SD in $\text{pg.g}^{-1}$ ww	$4.60 \pm 3.74$	$7.04 \pm 9.69$	-	$11.8 \pm 30.4$	$11.9 \pm 33.6$	$2.25 \pm 6.39$	$37.6 \pm 70.8$
( $\text{pg.g}^{-1}$ lw)	( $506 \pm 448$ )	( $637 \pm 651$ )		( $555 \pm 734$ )	( $501 \pm 684$ )	( $102 \pm 127$ )	( $2302 \pm 1767$ )
Maximum in $\text{pg.g}^{-1}$ ww	20.6	53.1	-	226	250	45.1	408
( $\text{pg.g}^{-1}$ lw)	(3882)	(5269)		(5294)	(3840)	(936)	(11010)

538

539 **Table 2.** Correlation coefficients (Spearman,  $\rho$ ) between DRC concentrations (ww / lw based values).

540 ns:  $P$ -value  $> 0.05$ ; \* $P > 0.01$ ; \*\* $P \leq 0.01$ ; \*\*\* $P \leq 0.0001$ .

Variable	Dec-603	<i>anti</i> -DP	<i>syn</i> -DP	CP
<b>Dec-602</b>	0.67*** / 0.48***	0.44** / 0.22 <sup>ns</sup>	0.38* / 0.09 <sup>ns</sup>	0.65*** / 0.41***
<b>CP</b>	0.78*** / 0.71***	0.58** / 0.22 <sup>ns</sup>	0.32 <sup>ns</sup> / 0.25 <sup>ns</sup>	
<b><i>syn</i>-DP</b>	0.34 <sup>ns</sup> / 0.12 <sup>ns</sup>	0.75*** / 0.86***		
<b><i>anti</i>-DP</b>	0.55** / 0.23 <sup>ns</sup>			

541

542

Figure 1

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Marne

Yonne

Loir

Loire

Cher

Allier

Vienne

Charente

Dordogne

Lot

Garonne

Adour

Author-produced version of the article published in Chemosphere, 2018, 207, 413-420  
The original publication is available at <https://www.sciencedirect.com/science/article/pii/S0045653518309500>  
doi : 10.1016/j.chemosphere.2018.05.101

Meuse

Moselle

Meurthe

Saône

Loue

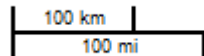
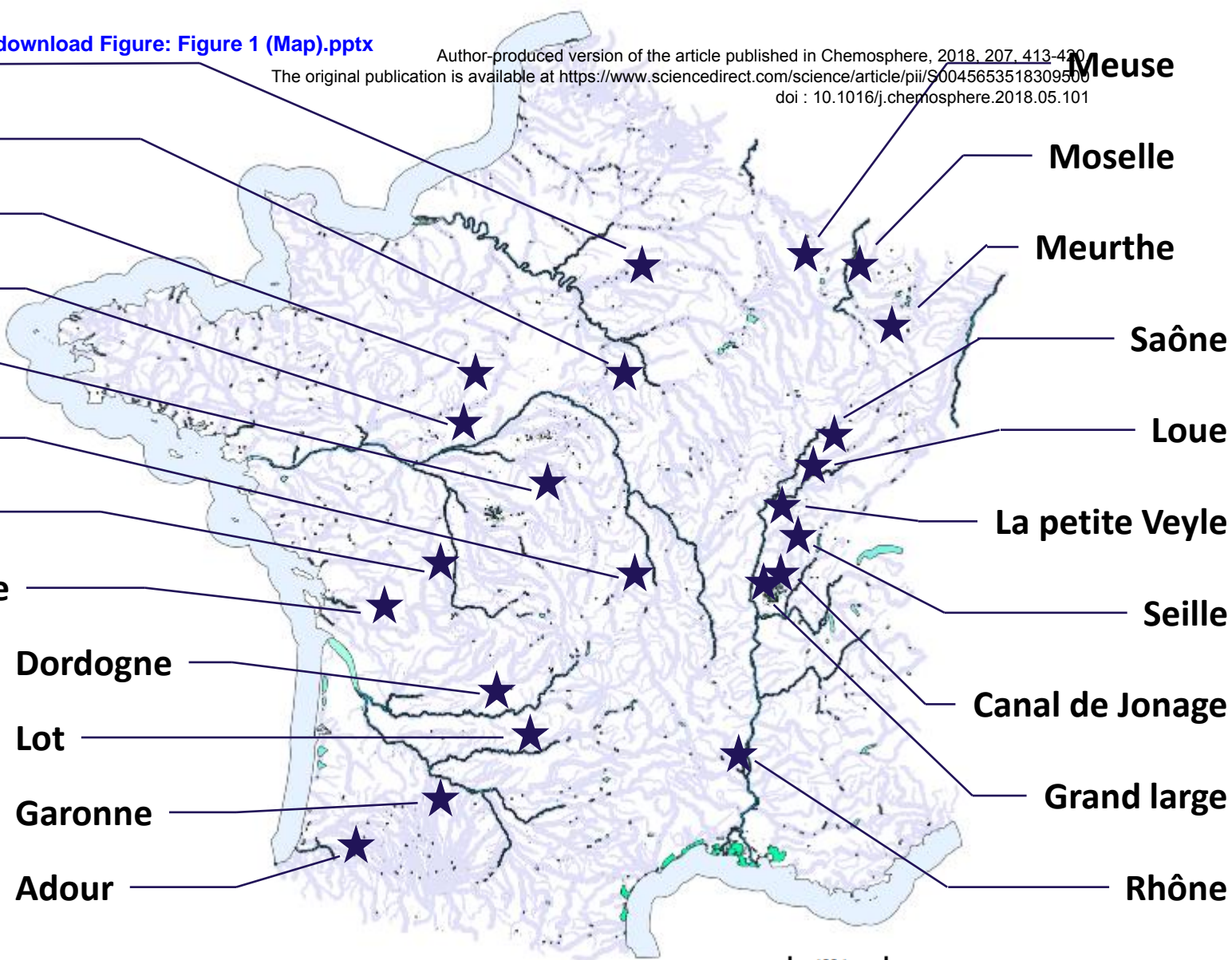
La petite Veyre

Seille

Canal de Jonage

Grand large

Rhône



## Figure 2

## Lyophilisation

[Click here to download Figure- Figure 2 \(Method\).pptx](#)  
version of the article published in Chemosphere, 2018, 207, 413-420.  
<https://www.sciencedirect.com/science/article/pii/S0045653518309500>  
doi: 10.1016/j.chemosphere.2018.05.101

## Pressurised Liquid Extraction

Toluene/acetone 7:3 (v/v)

4 ng of internal standards

## Multilayer silica gel column

Sodium sulphate, neutral (5 g), basic (5 g), neutral (5 g),  
H<sub>2</sub>SO<sub>4</sub> 22% (20 g), H<sub>2</sub>SO<sub>4</sub> 44% (25 g), sodium sulphate  
*n*-hexane (120 mL)

## Gel Permeation Chromatography

Bio-Beads SX-3

Ethyl acetate/cyclohexane 1:1 (v/v) at 5 mL.min<sup>-1</sup>  
24-36 min

0.8 ng of recovery standard

GC-EI-HRMS (R = 10,000)

Figure 3

[Click here to download Figure: Figure 3 \(f\\_anti\).pptx](#)

