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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 Σ DRCs ranged from 1.58 to 408 $\text{pg}\cdot\text{g}^{-1}$ wet weight (54 to 11100 $\text{pg}\cdot\text{g}^{-1}$
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⁻¹ of lipid weight (lw) with a
101 mean value of 24.5 ng.g⁻¹ 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⁻¹ 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⁻¹ lw, with median values of 38.2, 2.6 and 0.9 ng.g⁻¹ 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⁻¹ 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⁻¹ 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 ¹³C₁₀-labelled *syn*-DP, *anti*-DP, Dec-602 (internal standards, IS) and
130 ¹³C₁₂-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⁻¹ 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 ¹³C₁₀-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% H₂SO₄, respectively) from the bottom to the top, and topped with dry
149 Na₂SO₄. 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⁻¹, 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 ¹³C₁₂-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[®]-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⁻¹. The oven temperature program started at
169 100 °C (2 min), rose to 280 °C at 33 °C.min⁻¹, then ramped to 325 °C at 5 °C.min⁻¹ (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 μ 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 ≥ 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 (ρ) 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[®]-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 ¹³C₁₀-labeled standards were 113 ± 17%, 101 ± 14% and 74 ± 11% for ¹³C₁₀-*syn*-DP, ¹³C₁₀-*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 (LB) and 1.14 (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 ± 0.12 (Figure 3), which is similar to
276 previously reported values for river fishes of 0.67 (Kang et al., 2010), 0.48 ± 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 pg.g^{-1} ww (up to
291 5.30 ng.g^{-1} lw) and an average at 11.8 pg.g^{-1} ww (0.56 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 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 ng.g^{-1} lw) (Wang et al.,
297 2012).

298 The concentration levels of Dec-603 ranged from \leq LOD to 250 pg.g^{-1} ww (up to 3.84 ng.g^{-1} lw) with
299 an average at 12.5 pg.g^{-1} ww (0.56 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 (ΣDRCs) was correlated with lipid contents
322 (Speaman test; $\rho = 0.69$, $P < 0.0001$). Dec-602, which is the dominant compound in ΣDRCs , was also
323 correlated with lipid contents ($\rho = 0.69$, $P < 0.0001$). Nevertheless, beside lipids, ρ 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 (Σ 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 (Σ_6 PCB).

340 Σ DRCs and Σ_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 Σ DRCs, was slightly more correlated to Σ_6 PCB ($\rho = 0.81$,
342 $P < 0.0001$); it was also correlated to each congener accounted for in Σ_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 Σ_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 Σ 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), ¹³⁴Cs, and ¹³⁷Cs 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 21st 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 (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	Σ DRCs
Lower limit (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 pg.g^{-1} ww	\leq LOR	\leq LOR	-	0.31	\leq LOD	\leq LOD	1.58
(pg.g^{-1} lw)				(12.6)			(54)
Median LB in pg.g^{-1} ww	-	-	-	2.65	2.02	0.48	9.26
(pg.g^{-1} lw)	-	-	-	(367)	(223)	(55.0)	(999)
Mean LB \pm SD in pg.g^{-1} ww	2.60 ± 4.74	5.45 ± 10.45	-	11.8 ± 30.4	11.9 ± 33.6	2.24 ± 6.39	34.0 ± 72.0
(pg.g^{-1} lw)	(189 ± 468)	(370 ± 722)		(555 ± 734)	(499 ± 686)	(100 ± 129)	(1712 ± 1892)
Mean UB \pm SD in pg.g^{-1} ww	4.60 ± 3.74	7.04 ± 9.69	-	11.8 ± 30.4	11.9 ± 33.6	2.25 ± 6.39	37.6 ± 70.8
(pg.g^{-1} lw)	(506 ± 448)	(637 ± 651)		(555 ± 734)	(501 ± 684)	(102 ± 127)	(2302 ± 1767)
Maximum in pg.g^{-1} ww	20.6	53.1	-	226	250	45.1	408
(pg.g^{-1} lw)	(3882)	(5269)		(5294)	(3840)	(936)	(11010)

538

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

540 ns: P -value > 0.05; * P > 0.01; ** P ≤ 0.01; *** P ≤ 0.0001.

Variable	Dec-603	anti-DP	syn-DP	CP
Dec-602	0.67*** / 0.48***	0.44** / 0.22 ^{ns}	0.38* / 0.09 ^{ns}	0.65*** / 0.41***
CP	0.78*** / 0.71***	0.58** / 0.22 ^{ns}	0.32 ^{ns} / 0.25 ^{ns}	
syn-DP	0.34 ^{ns} / 0.12 ^{ns}	0.75*** / 0.86***		
anti-DP	0.55** / 0.23 ^{ns}			

541

542

Figure 1

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Marne

Yonne

Loir

Loire

Cher

Allier

Vienne

Charente

Dordogne

Lot

Garonne

Adour

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doi : 10.1016/j.chemosphere.2018.05.101

Meuse

Moselle

Meurthe

Saône

Loue

La petite Veyle

Seille

Canal de Jonage

Grand large

Rhône

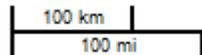
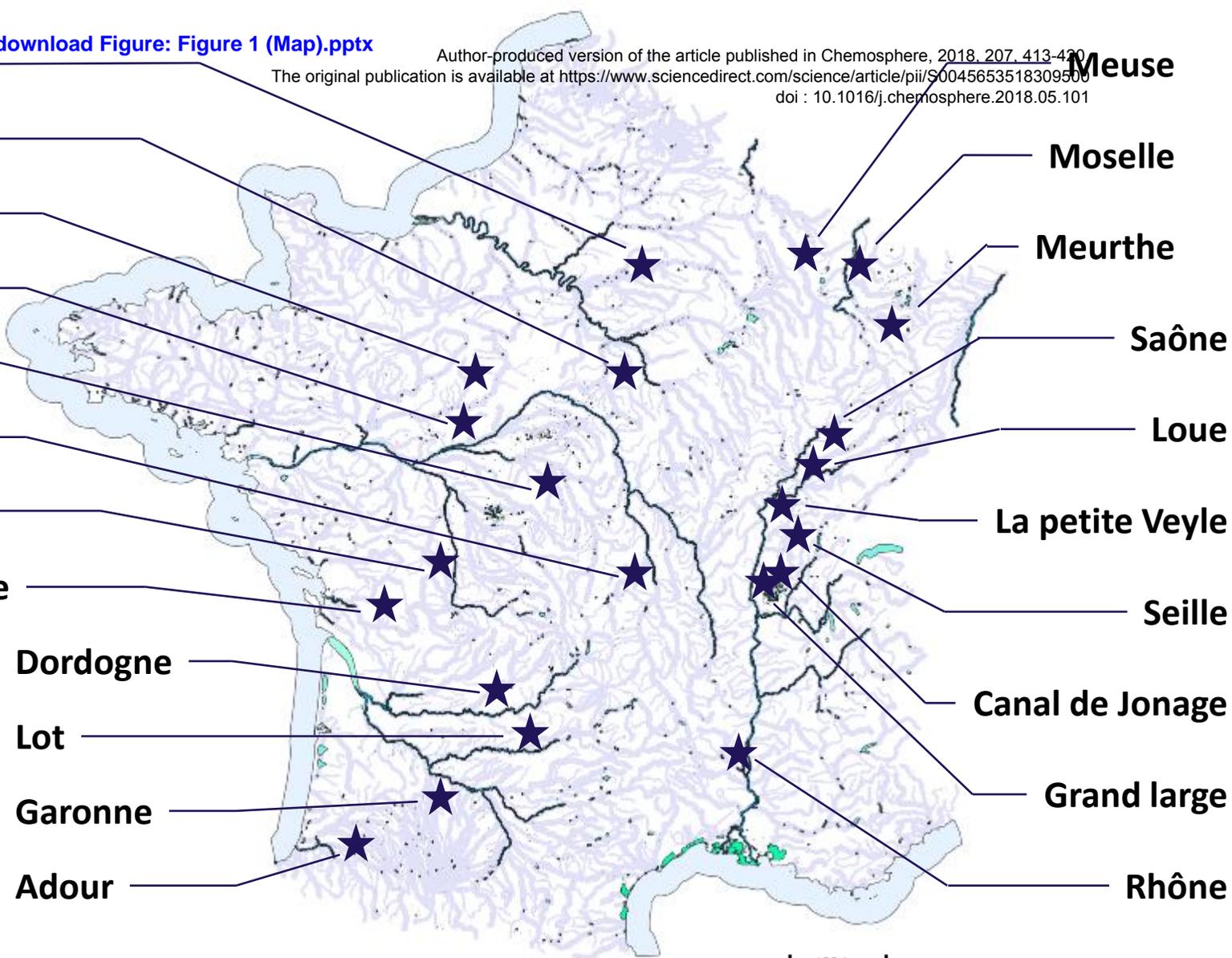


Figure 2

Lyophilisation

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<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),
H₂SO₄ 22% (20 g), H₂SO₄ 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⁻¹
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](#)

