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

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Chemical Risk

Abstract

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

1. Introduction

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

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

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

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

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

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

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

The aim of the present study was to report occurrence levels of DRCs in *Silurus spp.* from several river basins in France. This species is largely distributed over the French territory, and known to accumulate hydrophobic chemicals such as polychlorobiphenyls (AFSSA, 2008; Alomar et al., 2016; Squadrone et al., 2016). To the best of our knowledge, this is the first time that this set of emerging 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 $^{13}\text{C}_{10}$ -labelled *syn*-DP, *anti*-DP, Dec-602 (internal standards, IS) and
130 $^{13}\text{C}_{12}$ -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 $1\text{ ng}\cdot\mu\text{L}^{-1}$ in toluene and stored at $-20\text{ }^{\circ}\text{C}$. 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 $120\text{ }^{\circ}\text{C}$ (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 $^{13}\text{C}_{10}$ -labelled *syn*-DP, *anti*-DP and Dec-602 (4 ng each).

Extracted lipids were determined gravimetrically and reconstituted in *n*-hexane. Then, a two-step clean-up procedure was applied. First, the extract was loaded on a multilayer silica gel column comprising 5 g neutral silica gel, 5 g basic silica gel (NaOH 1 N), 5 g neutral silica gel, 20 g and 25 g acidic silica gel (22% and 44% H₂SO₄, respectively) from the bottom to the top, and topped with dry Na₂SO₄. DRCs were eluted with 120 mL *n*-hexane and reconstituted in 500 µL of a mixture of ethyl acetate/cyclohexane 1:1 (v/v). Second, the extract was subjected to a Gel Permeation Chromatography column (58 cm × 24.4 mm) packed with Bio-Beads SX-3 (Bio-Rad, Philadelphia, PA) using a mixture of ethyl acetate/cyclohexane 1:1 (v/v) as mobile phase at a flow rate of 5 mL.min⁻¹, to remove remaining interferences. The collected extract (24-36 min) was concentrated to dryness under a gentle stream of nitrogen and reconstituted in 20 µL of toluene containing 800 pg of ¹³C₁₂-PCB-194, prior to the instrumental analysis.

2.4. Instrumental acquisition

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

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

2.5. QA/QC

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

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

2.6 Data processing

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

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

3. Results and discussion

3.1. Method performances

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

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

¹³C₁₀-Dec-602, respectively. Trace amounts of *syn*-DP and *anti*-DP were detected in procedural blanks with a mean concentration of approximately 1 pg.g⁻¹ ww, based on the average sample size (Table S4). Based on the approach described in section 2.5, the LOR value was equal to 3 pg.g⁻¹ ww for both. The calculated detection limits (LOD, S/N = 3) of Dec-601, -602, -603, and CP were 0.5, 0.1, 0.2 and 0.1 pg.g⁻¹ ww, respectively. The results obtained for the NCP standard mixture showed a satisfying correlation for all the target compounds within the designed value (Table S5), which validates that the standards were properly prepared. The intermediate precision of the assay was assessed by analysing a fish sample (NCF), a non-fortified (QC) and a fortified fish oil (QCF) samples, according to the ISO 11352:2012 standards and Eppe et al. (2017) guideline. Obtained values were 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, respectively (Table S6). The trueness uncertainty was estimated based on the difference between the fortified and non-fortified fish oil, and ranged between -3.0 to +3.0%, except for CP at +20.3% (Table S6). Finally, these accuracy results led to a relatively high confidence level regarding determination of DP isomers, Dec-602 and -603. CP suffered a slight trueness bias while Dec-601 was not completely evaluated due to non-detectable levels.

3.2. Sum concentration of DP isomers

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

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

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

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

3.3. Profiles of DP isomers

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

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

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

3.4. Concentration of other DRCs

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

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

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 an average at 12.5 pg.g^{-1} ww (0.56 ng.g^{-1} lw). These values were much higher than those reported

from Latvia at $0.98 \text{ pg.g}^{-1} \text{ ww}$ (Rjabova et al., 2016) but lower than those found in China at $3.80 \text{ ng.g}^{-1} \text{ lw}$ and in Spain at $2.46 \text{ ng.g}^{-1} \text{ lw}$ (Wang et al., 2012; Santín et al., 2013). 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 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 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., 2015). Quite similarly, De la Torre et al. (2012) reported relatively low mean CP concentrations ($0.13 \text{ ng.g}^{-1} \text{ lw}$) in dolphin samples off the coast of Brazil (based on half the samples that were quantified). To date, there are few references dealing with CP concentrations in other matrix types, such as sediment (Shen et al., 2011a, 2011b) and human serum (Brasseur et al., 2014; Kim et al., 2016).

3.5. Correlations between DRCs

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

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

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

3.6. Correlation between DRCs and other POPs

Polychlorobiphenyl (PCB) concentrations were available for 97 out of 102 *Silurus spp.* samples. These PCB data were obtained in the context on a national plan aiming to establish a diagnosis of freshwater fish contamination (Eaufrance). Analytes included 12 dioxin-like PCB (DL-PCB) congeners, and six non-dioxin-like/indicator congeners. It was thus possible to seek potential relationships among PCBs and dechloranes at a national scale. As DL-PCB concentrations were almost certainly correlated to the sum of PCB concentrations (Σ PCB) or to the sum of concentrations of a few indicator congeners (AFSSA, 2009; Babut et al., 2009), we explored the correlation between dechloranes and six indicator congeners (PCB-28, -52, -138, -153 and -180) individually or as a single variable (Σ_6 PCB).

Σ DRCs and Σ_6 PCB appeared correlated on a ww basis ($\rho = 0.67$, $P < 0.0001$, $n = 77$). Among DRCs, Dec-602, which is the dominant compound in Σ DRCs, was slightly more correlated to Σ_6 PCB ($\rho = 0.81$, $P < 0.0001$); it was also correlated to each congener accounted for in Σ_6 PCB (Table S7). The correlation coefficients were lower but still significant when testing correlations on a lw basis ($\rho = 0.73$ for Dec-602 vs Σ_6 PCB, or $\rho = 0.74$ for Dec-602 vs PCB-153). This suggests that although lipid contents are influencing the accumulation of both PCBs and DRCs, other influencing factors unexplored yet are also common to both contaminant groups. Urbanization, because emissions can result from past and present uses at industrial sites or in households, cars and so on, might be one of these.

4. Conclusions and perspectives

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

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- 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 (pg.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	ΣDRCs
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	≤ LOR	≤ LOR	-	0.31	≤ LOD	≤ 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 ± 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 ± 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

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

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
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}	
<i>syn</i>-DP	0.34 ^{ns} / 0.12 ^{ns}	0.75*** / 0.86***		
<i>anti</i>-DP	0.55** / 0.23 ^{ns}			

Figure 1

[Click here to download Figure: Figure 1 \(Map\).pptx](#)

Figure 2

Lyophilisation

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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](#)