Occurrence of dechloranes in fish from the Garonne and the Dordogne rivers in France.

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Introduction

Flame retardants (FRs) are chemicals added to a wide range of consumer and industrial products in order to limit fire initiation and propagation in a context of fire safety. Some halogenated FRs have been registered in the United Nations Stockholm Convention annexes, due to their persistence in the environment, long-range transport, bioaccumulation and toxicity. Although raising concerns, Dechloranes constitute a group of polychlorinated FRs that are still used [1]. In particular, Dechlorane Plus (DP) has been detected in various environmental matrices and in different aquatic and terrestrial biota, thus exhibiting bioaccumulation and biomagnification potentials [2]. However, occurrence data in biota remain scarce, particularly at the French level.

Regarding analytical methods dedicated to Dechloranes, most authors use gas chromatography (GC) coupled to mass spectrometry (MS, MS/MS or HRMS) fitted with electron impact (EI) or negative chemical ionisation [3,4], and use Pressurised Liquid Extraction (PLE) or Soxhlet for extraction, followed by acidic silica columns or Gel Permeation Chromatography for purification.

The aim of this work was (i) to develop and optimize an analytical strategy dedicated to the identification and quantification of a range of Dechloranes in fish muscle samples and (ii) to apply it to a set of samples collected in the two rivers in the South West of France, the Dordogne and the Garonne.

Materials and methods

Standards

Analytical standards of anti-DP, syn-DP, Dechlorane 601, 602, 603, 604, 604CB, Chlordene Plus (CP) (Figure 1) and the external standard $^{13}C_{12}$-PCB-194 were obtained from Wellington Laboratories. $^{13}C_{10}$-labelled internal standards of anti-DP, syn-DP and Dec-602 were purchased from Cambridge Isotope Laboratories and used for isotopic dilution method quantification.

Samples

Fish muscle samples (*Silurus sp.*) were collected from Dordogne (5 sites, n=20) and Garonne (4 sites, n=23) rivers in 2014 (Figure 2), freeze-dried and extracted by PLE with a mixture of toluene/acetone 7:3 (v/v). After reconstitution in *n*-hexane, extracts were cleaned up through a silica gel column containing H_2SO_4, further partitioned between *n*-hexane and NaOH 1 N and reconstituted in toluene. Particular attention was paid to procedural contamination.

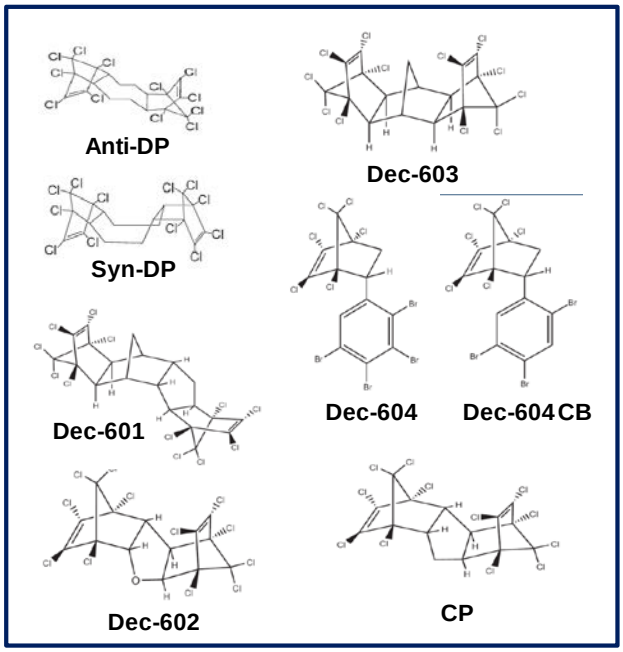

Figure 1: Chemical structures of the Dechloranes studied in this work.

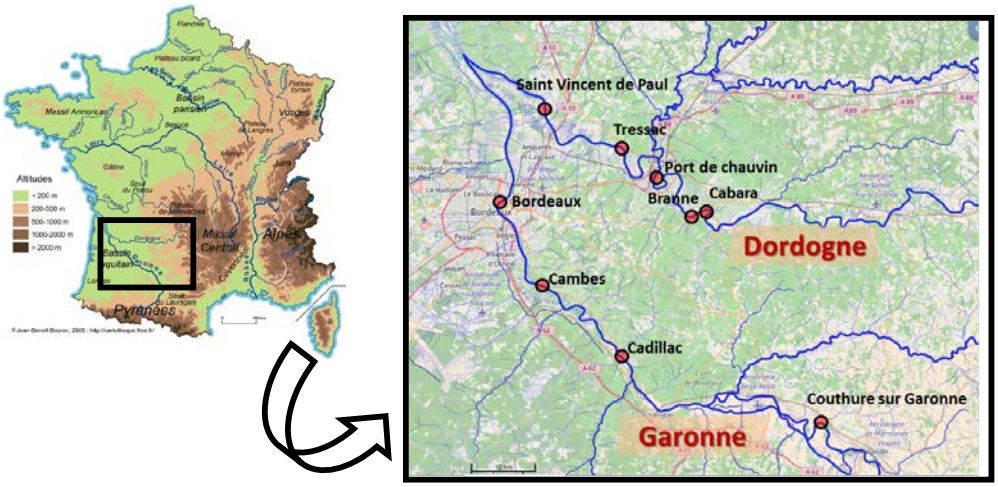

Figure 2: Sampling sites locations.

Instrumental method

Analyses were performed using a Scion-456-GC coupled to a Scion TQ-MS from Bruker (Billerica, MA, USA) operating in the EI mode. The capillary column was a HT8-PCB (30 m x 0.25 mm). Extracts were injected in the splitless mode at 250 °C. The oven temperature program started at 100 °C (2 min), rose to 280 °C at 25 °C.min^{-1}, then ramped to 325 °C at 5 °C.min^{-1} (5 min). Helium at 1 mL.min^{-1} was used as carrier gas. All targeted compounds were separated, thanks to selected column (Figure 3).
Auxiliary and source temperatures were set at 310 °C and 250 °C, respectively. The electron energy was set at 70 eV. Optimised transitions in Selected Reaction Monitoring mode are described in Table 1.

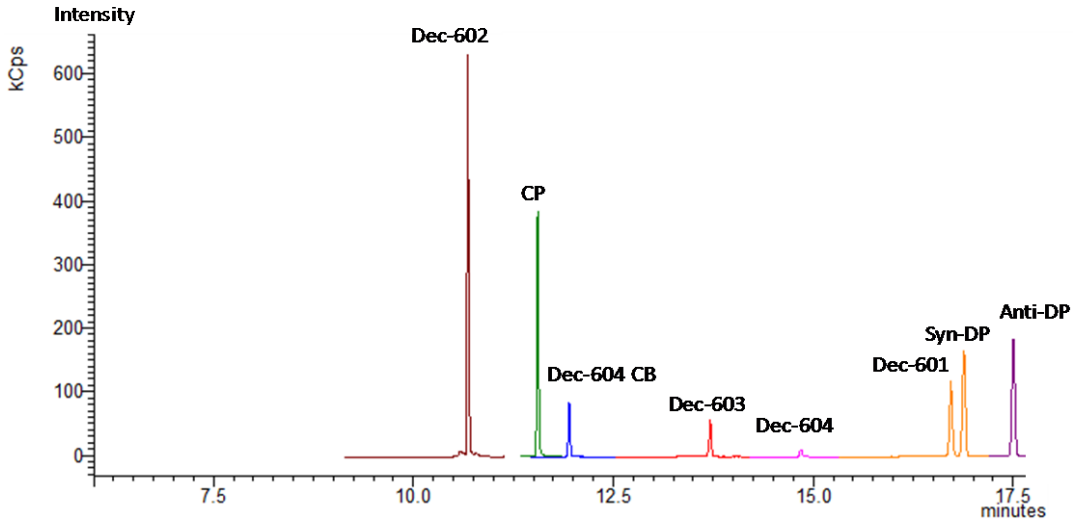

Figure 3: Chromatographic separation obtained for Dechloranes by GC-EI-MS/MS.

Table 1: Optimised SRM transitions using GC-EI-MS/MS (CE: Collision energy).

Compound	Quantifier	Qualifier	CE (eV)	Theoretical ion ratio
Anti-DP, Syn-DP, Dec-601, Dec-602, CP	271.8>236.8	273.8>238.8	15	0.81
Dec-603	262.8>227.9	264.8>229.9	20	0.65
Dec-604	440.7>280.8	438.7>280.8	40	0.60
$^{13}C_{10}$-DP, $^{13}C_{10}$- Dec-602	276.8>241.8	278.8>243.8	15	0.81
$^{13}C_{12}$-PCB-194	441.8>371.8	439.8>369.8	25	0.89

Results and discussion

Analytical parameters

Based on six calibration curves ranging from 5 to 2000 pg/µL in vial and triplicate analysis of a quality control fish sample pool, the obtained Limits of Reporting (LoR) were 8.9 (Anti-, Syn-DP), 1.7 (Dec-602, -603) and 1.5 pg/g fresh weight (fw) (CP). The limits of quantification were found to be 34, 95 and 5 pg per vial for Dec-601, -604 and -604CB, respectively.

Quantification of Dechloranes in Silurus

Dec-601, -604 and -604CB were not detected in any sample. CP was detected in only one sample, at 13.8 pg/g fw. For other compounds, detection frequencies above LoRs were 16, 19, 26, 2 and 79% for Anti-DP, Syn-DP, Dec-603, CP and Dec-602, respectively.

Dec-602 was found at concentrations ranging from n.d. to 80.3 pg/g fw, with a median value of 3.0 pg/g fw. Dec-603 was found in 11 samples only with the concentration ranging from 8.28 pg/g fw to 575 pg/g fw. Syn-DP and Anti-DP ranged from n.d. to 30.5 pg/g fw and from n.d. to 65.5 pg/g fw respectively.

The fractional abundance of the anti-DP isomer (f_{anti}) was calculated for each sample by dividing the concentration of anti-DP with the sum of syn-DP and anti-DP concentrations (Figure 4). The obtained value was equal to 0.68 ± 0.2 similar to those found in commercial mixture and literature [3].

The concentration levels of Anti-DP and Syn-DP that have been found in Dordogne samples were higher than those measured in Garonne. Dec-602 was found in the two rivers whereas Dec-603 and CP were found only in the Garonne river.

The concentrations of Dechloranes found during this study were within an order of magnitude similar than those observed in some previous study [4]. However it is importance to keep in mind that these fishes were sampled in two basins that present a relatively low anthropogenic pressure.

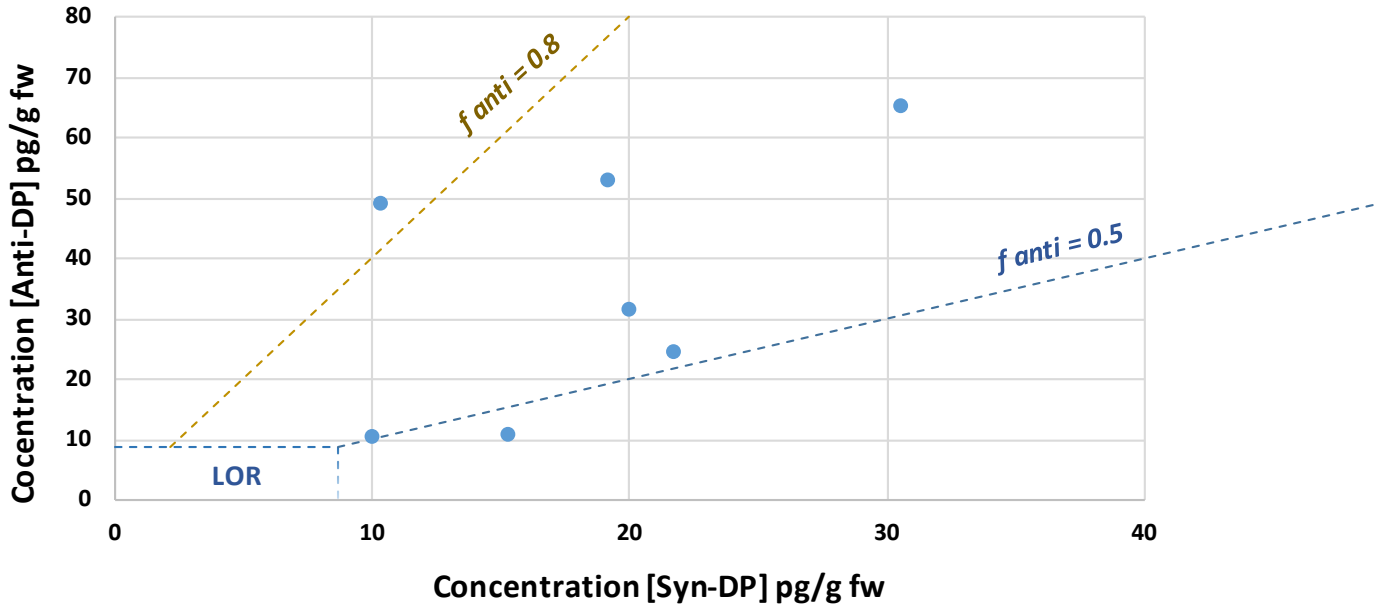

Figure 4: Concentration of Anti-DP *versus* Syn-DP for each quantified sample above LoR (pg/g fw).

Conclusion and perspectives

A GC-EI-MS/MS method has been developed for the analysis of Dechloranes using PLE for extraction and acidic silica column chromatography and LLE for sample purification. The protocol was successfully applied to a series of fish samples. As a perspective, this method will be evaluated and applied to other food samples from the French market to estimate the dietary Human exposure at the French level in a risk assessment context.

Ackowledgements

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