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Levels of dechloranes and polybrominated diphenyl ethers (PBDEs) in human serum from France

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ABSTRACT

Human exposure to dechloranes has been evaluated in Western Europe (France) with the analysis of Dechlorane Plus (DP), Dechloranes (Dec) 602, 603 and 604, Chlordene Plus (CP) and Mirex in 48 serum samples collected between 2003 and 2005. While no production source has been identified in Europe until now, detection frequencies for all investigated dechloranes were high, except for Dec 604 which was below detection limit for all samples. The mean DP concentration was 1.40 ± 1.40 ng/g lipid weight (lw), lower than levels reported in serum from Chinese population, but higher than levels reported in Canadian human milk. To the best of our knowledge, this is the first time that $\sum_5$dechlorane levels are reported for human serum. A specific pattern of contamination was found (Dec 603 > DP > Mirex > Dec 602 > CP) compared to other biota samples that have been analyzed from Europe, with Dec 603 as the most abundant dechlorane (mean level: 2.61 ± 2.63 ng/g lw). Dec 603 and CP levels were correlated with age and with levels of some bioaccumulative organochlorine pesticides (OCPs). These results indicate that bioaccumulation properties should be further investigated and taken in consideration when assessing human exposure to dechloranes. For comparison purposes, polybrominated diphenyl ether (PBDE) levels were also measured for BDE-47, -99, -100, -153 and -154 in the serum samples. As expected, BDE-47 and BDE-153 were the major congeners with mean levels of 2.06 ± 1.80 ng/g lw and 1.39 ± 0.97 ng/g lw, respectively. The mean $\sum_5$PBDE levels (4.32 ± 2.99 ng/g lw) were in the range typical of Western Europe levels, but lower than the mean $\sum_5$dechlorane levels (6.24 ± 4.16 ng/g lw). These results indicate that the attention to dechloranes should be continued if research indicates toxicological concerns.

1. Introduction

Dechlorane or Mirex ($C_{10}Cl_{12}$) was extensively used as a pesticide as well as an additive flame retardant (FR) in the USA during the 1960s and the 1970s. It was banned in the USA in 1978 because of its toxicity, persistence and high potential for bioaccumulation (Kaiser, 1978). Consequently, other related compounds such as Dechlorane Plus (DP, $C_{18}H_{12}Cl_{12}$), Dechlorane 602 (Dec 602, $C_{14}H_4Cl_{12}O$), Dechlorane 603 (Dec 603, $C_{17}H_8Cl_{12}$), Dechlorane 604 (Dec 604, $C_{13}H_4Br_4Cl_6$) and Chlordene Plus (CP, $C_{15}H_6Cl_{12}$), patented by Hooker Chemicals and Plastics Corp. (Hooker; currently OxyChem, Niagara Falls, New York), became candidates to replace Mirex. All these compounds share a bicyclo [2,2,1] heptene structure, resulting from a Diels–Alder reaction between one or two hexachlorocyclopentadiene molecules (HCCPDs) with various cyclic dienophiles. They all possess flame retardant properties similar to Mirex (International Programme on Chemical Safety, 1984). Whereas the use of DP as a flame retardant (electrical wires, cable coating, computers and polymers) is well established (Betts, 2008), listed as a high production volume chemical in the USA (US Environmental Protection Agency, 2006) and as a low production volume chemical in EU (Sverko et al., 2011), little information is available for the use of the other dechloranes. Dec 602 and Dec 604 are reported as flame retardant additives for polymeric products and they are listed on the Nondomestic Substances List published by Environment Canada (Canadian Environmental Protection Act, 1999), indicating their current use in commercial products. On the contrary, no direct applications have been reported for Dec 603 or CP to date. They were only referenced as impurities found in technical organochlorine pesticides (OCPs) (Shen et al., 2011). All these compounds are unregulated compounds and represent a possible alternative to other regulated FRs such as the polybrominated diphenyl ethers (PBDEs).

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The environmental occurrence of dechloranes was first reported in 2006 in North America when DP was detected in air, sediment and fish samples from the Laurentian Great Lakes (Hoh et al., 2006). Different studies were conducted in this particular area (Qiu and Hites, 2007; Sverko et al., 2007) potentially contaminated due to the proximity of the manufacturer Oxychem, localized on the Niagara River, the main connecting channel between Lake Ontario and Lake Erie. A relationship between environmental DP levels and the distance from the manufacturing plant was demonstrated, as well as with the local population density (Hites et al., 2010), possibly reflecting the use of DP in electrical equipment. In 2010, other dechloranes such as Dec 602, 603 and 604 were reported in sediment and fish samples from the same area (Shen et al., 2010). CP was later detected in sediments (Shen et al., 2011). Similar studies were also conducted in China. In 2010, Wang et al. collected samples from the vicinity of an important DP manufacturing plant operating since 2003 (Anpon Electrochemical Company, located in Huai'an, Northwest of Shanghai). The influence of the production plant on environmental contamination levels in this region was demonstrated. DP levels were also correlated to the proximity to e-waste recycling plants and various industrial areas (Qi et al., 2010; Wang et al., 2011; Yu et al., 2010). Additionally to DP, Dec 602 was detected in air, soil and sediment samples while Dec 603 and Dec 604 were below detection limits (Wang et al., 2010).

Even though the number of studies is still small, and measurements around other potential manufacturing plants have still to be conducted, additional data collected in Korea, Brazil, North Africa, Spain and Germany (de la Torre et al., 2011, 2012; Kang et al., 2010; Munoz-Arnanz et al., 2012; Sühring et al., 2013) indicate that DP and related compounds should be considered as possible worldwide contaminants. Furthermore, Möller et al. (2010) reported DP in air sampled in the Atlantic Ocean and suggested that this compound was possibly subject to long range atmospheric transport. The same is observed for Dec 602 as it was recently detected in Arctic Beluga whales (Shen et al., 2012). Two recent review papers described sources, occurrence and behavior of dechloranes in the environment, concluding on the need of more research dedicated to the production of data on exposure and toxicity (Sverko et al., 2011; Xian et al., 2011). Additionally to the fact of considering environmental contamination and geographical distribution, a better understanding of the behavior of DP and related compounds in terms of bioaccumulation and biomagnification is still needed. This is important since structurally similar Mirex was banned and added to the Persistent Organic Pollutant List of the Stockholm convention because, among other criteria, of its bioaccumulative potential (Stockholm Convention, 2001). A collection of limited data for aquatic and terrestrial biota was recently reported by Feo et al. (2012). It highlighted the lack of information on the toxicity of DP to aquatic and terrestrial organisms.

Even more importantly, virtually no human biomonitoring data are available for any of the dechloranes. The assessment of internal dose exposure by means of measurements of these toxicants in human tissues or fluids is currently unavailable. There have only been a couple of reports published concerning studies conducted in China and Canada. Serum and collected hair samples from workers at a Chinese e-waste recycling facility were analyzed to evaluate DP exposure. Results from these hair samples suggested that direct ingestion of dust could be considered as a major route of DP exposure of the workers (Zheng et al., 2010). In the first study to report DP levels in human serum, DP was detected at concentrations ranging from 7.8 to 465 ng/g lipid weight (lw) (Ren et al., 2009). Lower levels were later reported for a population living in an urban area of South China (2.7 to 91 ng/g lw) (Yan et al., 2012) or in a Halogenated Flame Retardant (HFR) production area of Northeastern China (1.4 to 11 ng/g lw) (He et al., 2013). DP levels were also reported in Canadian human milk, ranging from non-detected (nd) to 8 ng/g lw (Siddique et al., 2012). None of these studies however reported data for the other dechloranes which have been reported to be even more bioaccumulative than DP. Only a recent study by Cequier et al. (2013) reported DP, Dec 602 and 603 levels in human serum on a few individual serum samples (n = 10) from Norway.

The present study had two objectives. The first was to adapt an existing analytical procedure based on solid-phase extraction (SPE) and gas chromatography coupled to high resolution sector mass spectrometry (GC–HRMS) to isolate and measure levels of Mirex, DP, Dec 602, Dec 603, Dec 604, and CP in human serum samples. The second was to measure levels of these compounds in human serum samples from Western Europe (France) for which data on levels of selected persistent organic pollutants (POPs) such as OCPs were previously reported (Viel et al., 2011). Levels of selected PBDEs have also been measured in the present study to allow comparison with dechlorane levels.

2. Materials and methods

2.1. Serum samples

A total of 48 banked human serum samples of which 24 were males and 24 were females (mean age 57 ± 13 years, age range 28–86 years) were analyzed for this study. They were collected in France between 2003 and 2005, from people living in the area of a municipal solid waste incinerator in Besançon. Further details about samples and the ethical approval of the study are described in another study (Viel et al., 2011).

2.2. Lipid content determination

Enzymatic lipid determinations of unknown samples were performed by a sub-contractor clinical laboratory on a dedicated 1 mL serum sub-sample. Four types of lipids were targeted and measured: triglycerides, total cholesterol, non-esterified (free) cholesterol, and phospholipids B. Sample sizes were as follow: triglycerides (2 μL), total cholesterol (2 μL), non-esterified (free) cholesterol (50 μL), and phospholipids B (20 μL). A well documented summation method was used to estimate the total lipid concentration (Akins et al., 1989). The total lipid content was expressed in g/L. For the inter-conversion of volumetric and gravimetric data, a value of 1.026 g/mL was used for serum specific gravity.

2.3. Chemicals

Syn-DP, *anti*-DP and *syn*-DP $^{13}C_{10}$ labeled (99%) standards were supplied by Cambridge Isotope Laboratories (CIL, Andover, MS, USA). Dec 602 (95%), Dec 603 (98%) and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada) and CP was from Wellington Laboratories (Guelph, ON, Canada). Mirex was purchased from Cluzeau Info Labo (France). The EC-4058 solution of PCBs mixture containing CB-209 $^{13}C_{12}$ (99%) and the EC-1414 solution of CB-80 $^{13}C_{12}$ (99%), from CIL, were used as surrogate and instrumental (recovery) labeled standards, respectively. For BDE-47, 99, 100, 153 and 154 measurements, the BDE-CVS-F calibration solutions, the MBDE-MXFS labeled surrogate stock and the MBDE-MXFR labeled recovery stock ($^{13}C_{12}$ standards) were purchased from Wellington Laboratories. Hexane was Picograde reagent (LGC Promochem, Wesel, Germany). Nonane (analytical standard grade, Fluka) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous sodium sulfate was from Acros Organics (Geel, Belgium) and sulfuric acid of 95–97% was Baker analyzed reagent (J.T. Baker, Deventer, Holland). Silica gel 60 (0.063–0.200 mm) for column chromatography was purchased from Merck (Darmstadt, Germany).

2.4. Sample preparation

Sample sizes of 10 g were extracted using solid-phase extraction (SPE) on non-end capped isolute C18 cartridges (1 g/6 mL) (Argonaut-Sopachem, Brussels, Belgium). The C18 cartridges were eluted with 3 × 5 mL of hexane. More details on the SPE protocol can be found elsewhere (Focant et al., 2006). The 15 mL hexane extracts were then loaded on a multi-layer column made, from bottom to top, of 2 g of 22% sulfuric acid silica gel, 1 g of activated silica and 1 g of sodium sulfate. Further elution with 15 mL of hexane was performed. The evaporation of the pooled fractions was carried out using a Power Vap 6 system (Fluid Management Systems Inc., Watertown, MA, USA) equipped with specific evaporation tubes to which GC vials are screwed and can easily be disconnected once the final evaporation volume of 500 μL is reached. After adding the keeper solvent (nonane), gentle room temperature evaporation in a dust protected hood was performed to reach a final volume of 10 μL of nonane. Procedural blank samples consisting of 10 mL of Milli-Q® water (Millipore, Brussels, Belgium) followed the same procedure. A blank sample was included with each series of 8 unknown samples.

2.5. Measurement

Samples were analyzed with a GC–HRMS system (MAT95 XL, Thermo FinniganMAT, Bremen, Germany) connected by a heated transfer line (275 °C) to a CE Trace GC (ThermoQuest) equipped with an A2000S autosampler (Thermo). The GC column was a ZB-5 (15 m × 0.25 mm I.D., 0.25 μm df) (Phenomenex, Utrecht, The Netherlands). Helium was used as the carrier gas at a constant flow rate of 1 mL/min. One and two microliters of the final extract (for dechloranes and PBDEs analysis, respectively) were injected into a split/splitless injector held at 280 °C, in splitless mode. For dechlorane measurements, the GC oven temperature was maintained at 140 °C for 2 min, ramped at 30 °C/min to 280 °C then at 5 °C/min to 300 °C and held for 10 min. For PBDE measurements, the GC oven temperature was maintained at 140 °C for 1 min, ramped at 15 °C/min to 180 °C, then at 10 °C/min to 290 °C and finally at 80 °C/min to 350 °C and held for 2 min. The MS ion source temperature was 250 °C and Electron Ionization (EI) was performed with 70 eV. The HRMS instrument was operated in the selected ion monitoring (SIM) mode. Two ions were monitored for both native and labeled species at m/z 271.8102/273.8072 for dechloranes, 276.8269/278.8240 for *syn*-DP $^{13}C_{10}$, 295.9157/297.9127 for surrogate CB-209 $^{13}C_{12}$ and 301.9626/303.9597 for recovery $^{13}C_{12}$ CB-80. For PBDE measurements, the monitored ions were m/z 483.7131/485.7111 and 495.7533/497.7513 for native and labeled tetra-BDEs (47 and recovery 77), 403.8046/405.8026 and 415.8449/417.8429 for penta-BDEs (99 and 100), 481.7151/483.7131 and 493.7553/495.7533 for hexa-BDEs (153, 154, and recovery 138). Monitored ions were chosen based on signal intensity, specificity and jump between m/z values allowed during the analysis according to the magnet settling time. Samples were analyzed randomly. Calibration stability was ensured by injecting both low and high level calibration points of the curve every 20 samples. Both instrumental and procedural blanks were monitored. More details regarding the GC–HRMS procedure can be obtained in a previous report (Focant et al., 2001).

2.6. Quality assurance and quality control (QA/QC)

All samples were processed in an ISO17025 BELAC accredited laboratory. The compounds were identified based both on retention time of the corresponding standard with maximum variation of 2 s and mass spectral data. Isotope ratio between the two monitored ions was checked to ensure proper identification. The limits of quantification of the method (LOQ) were calculated based on a signal-to-noise (S/N) ratio equal to 6. For compounds detected in procedural blanks, the mean procedural blank value was subtracted from the samples and the limit of quantification was set at 3 times the standard deviation of the procedural blank. A QC serum sample was included with each series of 8 unknown samples. This internal QC was made of a pool of non-fortified human serum of 1030 adults (30–65 years old), collected between March and July 2005 in 8 different areas in France (Frery et al., 2007).

2.7. Statistical analyses

Statistical analyses were performed using XLSTAT 2013. According to the Shapiro-Wilk test, the data significantly deviated from normal distribution ($p < 0.05$). The non-parametric Spearman's rank correlation coefficients (r_s) were calculated to assess relationships between the different levels of compounds as well as with age. The Mann–Whitney *U* test was used for comparison between males and females or younger and older people. Concentrations were lipid normalized before statistical analysis and samples below LOQ were assigned with the LOQ value.

3. Results and discussion

3.1. Method performances

The sample preparation procedure was derived from our routine approach for measurement of selected polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) in human serum (Focant et al., 2006). Recovery rates were calculated using CB-80 $^{13}C_{12}$ as instrumental standard. The average surrogate standard recoveries ranged from 40% to 71% for CB-209 $^{13}C_{12}$ and from 33% to 61% for *syn*-DP $^{13}C_{10}$. Because of the comparable structures and lipophilicity of the dechloranes, similar recovery rates can be expected for the other dechloranes. These values are similar to what has previously been reported for dechlorane measurements in environmental and biological samples using similar analytical approaches (Baron et al., 2012; Shen et al., 2010, 2011). A more precise calculation would require proper ^{13}C-labeled internal standard to be used, but these compounds are not yet available. For PBDEs, recovery rates ranged from 55 to 81%, in accordance to one of our previous studies (Pirard et al., 2003).

For dechloranes, retro Diels–Alder HCCPD ion fragments were selected for quantification and isotope ratio checks. Typical chromatograms for dechloranes in standard solutions and in real serum samples are available in supplementary data (Fig. S1). The variation of the isotope ratio between the two monitored ions was within ±15% and ±30% of the theoretical value for PBDEs and dechloranes, respectively. LOQs of the methods, on a lipid weight basis, are listed in Table 1. The method allowed the measurement of all analytes, except Dec 604 for which the instrumental LOD of 0.3 pg/μL was not suited to the very low levels in serum samples. QC charts obtained for dechloranes and PBDEs, for the 6 QC samples that were analyzed during the time of unknown sample analyses are shown in Fig. 1. Values were normalized and presented in z-score units. Upper and lower control limits (UCL/LCL) corresponded to 3 σ, while warning limits were set at 2 σ. For each compound, each QC was included within 2 σ of the total average. The mean ± SD (ng/g lw) of dechlorane and PBDE levels in the non-fortified pool serum is reported in Table 2. No (certified) reference materials are available so far for dechloranes. The reproducibility of the measurements was acceptable with CV ranging from 11% to 32%, with CV for BDE-47 slightly higher (37%) due to lower control of the blank levels in our laboratory at the time of the study. Despite the fact that *syn*-DP $^{13}C_{10}$ was used, the CV for *syn*-DP was higher than for other dechloranes for which no ^{13}C-labeled internal standards were available. Furthermore, for the other dechloranes, when quantifications were tested on either *syn*-DP $^{13}C_{10}$ or CB-209 $^{13}C_{12}$, better correlation coefficients and lower CVs were always obtained with CB-209 $^{13}C_{12}$. This was verified by calibration checks over time. As reported also by

Table 1
LOQs and average levels of dechloranes and PBDEs in human serum from Western Europe population (ng/g lw) (n = 48).

	LOQ	Detection frequency (%)	Mean	Median	Min	Max	SD
Mirex	0.03	100	1.40	1.06	0.14	4.30	0.93
Syn-DP	0.08	75	0.34	0.22	nd	2.30	0.42
Anti-DP	0.16	94	1.20	0.89	nd	5.09	1.12
Total DP[a]	–	–	1.40	1.20	nd	7.04	1.40
Dec 602	0.04	100	0.64	0.44	0.15	4.21	0.63
Dec 603	0.4	90	2.61	2.01	nd	12.10	2.63
CP	0.08	92	0.20	0.16	nd	0.71	0.16
$\sum_5$dechloranes[b]			6.24	5.21	1.33	20.09	4.16
BDE-47	0.75	100[c]	2.06	1.56	< LOQ	8.72	1.80
BDE-99	0.27	100[c]	0.49	0.27	< LOQ	4.69	0.68
BDE-100	0.15	100[c]	0.34	0.26	< LOQ	1.57	0.26
BDE-153	0.05	100	1.39	1.14	0.46	5.83	0.97
BDE-154	0.02	58	0.05	0.04	nd	0.26	0.06
$\sum_5$PBDEs[d]			4.32	3.46	1.63	15.02	2.99

nd = not detected.
LOQ = Limit of quantification.
Dec 604 was not detected in any of the samples.
[a] Total DP levels were calculated with a DP calibration curve based on the sum of area of *syn*- and *anti*-DP.
[b] Sum of Mirex, Total DP, Dec 602, Dec 603 and CP.
[c] BDE-47, BDE-99 and BDE-100 were detected in procedural blanks. Values of % >LOQ for these congeners were 69, 35 and 77 respectively.
[d] Sum of BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154.

others, stability issues might be present for the *syn*-DP $^{13}C_{10}$ standard solution, but this requires further investigation to be verified.

3.2. Levels of dechloranes in human serum

DP, Dec 602, Dec 603, CP, and Mirex were detected in almost all the serum samples while Dec 604 was below detection limit for all samples. Detection frequency, mean, median, and range values are reported in Table 1. DP levels (median: 1.20, range: nd–7.04 ng/g lw) are higher but consistent with levels reported by Siddique et al. (2012) in their study on human milk from Canada (median: 0.6, range: nd–8.0 ng/g lw). Studies from China reported DP levels with median values 10 to 40 times higher for e-waste recycling plant workers (Ren et al., 2009) and 5 times higher for women living close to e-waste recycling sites (Ben et al., 2013). For both of these studies, direct occupational exposure to DP was expected according to its use and production for the electronic market in North America and China. The reason for the presence of dechloranes in human serum samples from Europe is not clear. DP, Dec 602 and Dec 603 were also detected in human serum samples from Norway (Cequier et al., 2013). Direct exposures by contact to commodities containing dechloranes and/or long range transport are possible hypothesis but no robust data are available so far to further explore them. Dec 603 surpassed all other dechloranes in terms of concentration (median value of 2.01 ng/g lw, 39% of the $\sum_5$dechloranes). Mirex, the banned product, was present at measurable levels in all samples with a median value of 1.06 ng/g lw.

No literature data are available for comparison of relative concentration pattern of Mirex, DP, Dec 602, Dec 603, Dec 604, and CP levels in serum. To our knowledge, this study is the first to report levels for these $\sum_5$dechloranes (5.21 ng/g lw) in human serum. Levels of Mirex were rarely reported in human serum studies focusing on OCPs, as Mirex concentrations are usually below LODs (Kang and Chang, 2011). The comparison within the dechlorane family showed a relative concentration pattern of Dec 603 > DP > Mirex > Dec 602 > CP (Fig. 2). Among the few studies available on dechlorane levels, this is the first time Dec 603 is reported as the most abundant dechlorane. In biota studies, Mirex usually remains the most abundant dechlorane, with levels 10 to 40 times higher than the other dechloranes in samples from Canada or Brazil, while a smaller difference is observed in samples from Spain (de la Torre et al., 2012; Guerra et al., 2011; Shen et al.,

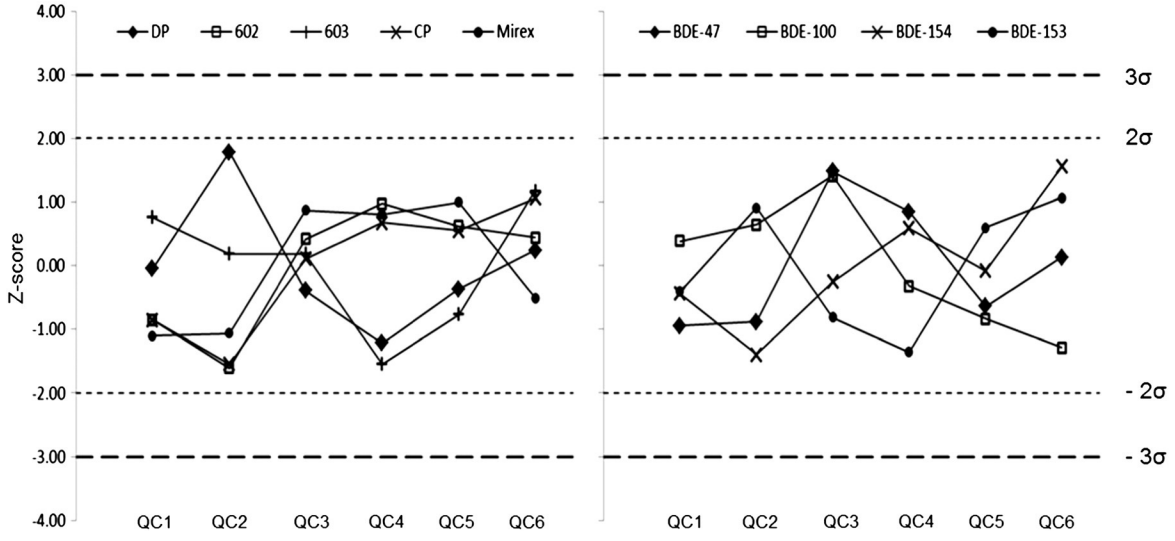

Fig. 1. Moving control chart of QC analysis. QC samples were obtained from a non-fortified pool of Western European human serum and analyzed with each series of 8 unknown samples. The mean QC levels were continuously recalculated. Dec 604 was not detected and BDE-99 level was below LOQ.

Table 2
Levels of dechloranes and PBDEs in a non-fortified pool of human serum used for quality control (n = 6).

	Mean ± SD (ng/g lw)	CV
Syn-DP	0.44 ± 0.14	31.6%
Anti-DP	1.02 ± 0.28	27.0%
Total DP[a]	1.39 ± 0.38	27.2%
Dec 602	0.40 ± 0.08	19.5%
Dec 603	1.65 ± 0.24	14.7%
Dec 604	nd	
CP	0.22 ± 0.02	11.2%
Mirex	0.67 ± 0.17	25.0%
BDE-47	1.11 ± 0.41	36.8%
BDE-99	< LOQ[b]	
BDE-100	0.21 ± 0.03	15.3%
BDE-153	0.95 ± 0.23	24.1%
BDE-154	0.05 ± 0.01	29.9%

nd = not detected.
[a] Total DP levels were calculated with a DP calibration curve based on the sum of area of *syn*- and *anti*-DP.
[b] LOQ of BDE-99 = 0.27 ng/g lw.

2010). In our study, Mirex and DP were detected at relatively similar levels, higher than Dec 602. Similar results were reported by de la Torre et al. (2012) for their study on Franciscana Dolphin from Brazil. Mirex was the most abundant dechlorane, but DP and Dec 603 were reported at higher levels than Dec 602. In the study of Cequier et al. (2013), DP levels in human serum from Norway were similar to levels reported in the present study, and around 2 times higher than levels of Dec 602 and Dec 603, the only other dechloranes reported in that study. DP was detected at lower levels than Dec 602 in bird eggs or fish samples from both Spain and Canada (Baron et al., 2012; Guerra et al., 2011). Dec 602 has already been suggested to possibly be more bioavailable or bioaccumulative than DP based on their estimated octanol-water partition coefficients (K_{ow}) and bioconcentration factors (BCF) (Shen et al., 2010). These results support the hypothesis that not only the geographical localization influences the pattern of contamination levels. The higher level of Dec 603 compared to Dec 602 could be related not only to a higher level of exposure but also to a specific biotransformation or bioaccumulation in mammals or humans. In the study of de la Torre et al. (2012) on mammals, they obtained the highest biotransformation half-life (HL; day) value for Dec 603 (138000), followed by DP (33100) > CP (12630) > Dec 602 (2752) > Dec 604 (1219) > Mirex (109).

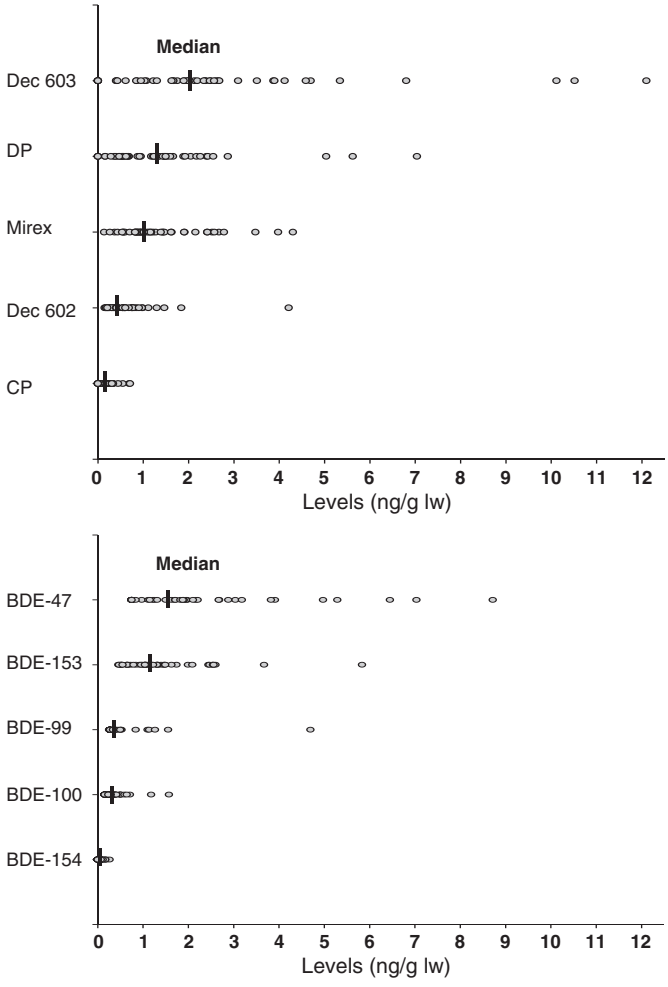

Fig. 2. Distribution of analyte levels in human serum samples and estimation of the relative concentration pattern based on median values (n = 48).

Another mammal study on Artic Beluga whales reported Dec 602 at low levels (0.08 to 0.3 ng/g lw) while DP, Dec 603, and Dec 604 were not detected (Shen et al., 2012). The exposure level certainly remains an important factor to take in consideration, like it is the case for biotransformation as dechlorinated products were also detected. Therefore, more investigations are needed to fully integrate factors such as exposure level, bioavailability, bioaccumulation, and biotransformation to better understand the relative distribution of the various dechloranes in human serum samples.

Dec 602 was detected in all human serum samples while Dec 604 was not detected at all. Such a situation was also reported in other biota studies (Baron et al., 2012; de la Torre et al., 2012; Shen et al., 2012). Although the presence of Dec 604 in samples is likely dependent on bioaccumulation parameters, it could also be a possible marker of production source proximity. The study of Shen et al. (2010) in Canada demonstrated a relationship between samples located in the Niagara area, close to the manufacturer Oxychem, and contamination of Dec 602 and Dec 604. Similar trends obtained for Dec 602 and Dec 604 possibly reflected usage patterns of these compounds in some flame retarded polymers. A production source in Europe is nevertheless possible as Dec 604 has been already reported in biota samples from Spain (Guerra et al., 2011).

Spearman's correlation coefficients were used to investigate possible relationships between the different dechlorane levels (Table 3). Correlation values with statistical significance ($p < 0.05^{*}$ or $p < 0.01^{**}$) were obtained between all the reported dechloranes, except between DP and Mirex. CP and Dec 603 showed the strongest correlation ($r_s = 0.83$ with $p < 0.01$), as well as CP and Dec 602 ($r_s = 0.71$ with $p < 0.01$). The lowest but significant value ($r_s = 0.29$ with $p < 0.05$) was obtained between DP and Dec 602. DP has been reported as a potential flame retardant in use in Europe. The reason for the lack of correlation between DP and Mirex is not clear. One can think that although DP is exclusively used as a FR, Mirex was also mainly used as a pesticide and this would therefore result in a different type of exposure. The ban of Mirex could also be impacting the correlation, but should also do for the other dechloranes such as Dec 602, Dec 603, and CP, unless the novel aspect of their use counterbalances this effect. Whether the presence of dechloranes in human serum is related to their use as FRs in Europe or from use as pesticides remains undefined. Balance between contamination from exposure and bioaccumulation must be considered. Additionally, one has to keep in mind that no production sources have been located in Europe to date, opening the discussion to possible long range transport as another source of exposure.

3.3. Comparison of dechlorane and PBDE levels in human serum

Levels of BDE-47, 99, 100, 153 and 154 are listed in Table 1. The $\sum_5$PBDE levels ranged from 1.63 to 15.02 ng/g lw, with a median

Table 3
Evaluation of potential relationships between dechlorane and PBDE levels as well as with age in human serum samples (n = 48). Correlation coefficients were obtained with the statistical Spearman correlation test.

	Syn-DP	*Anti*-DP	DP	Dec 602	Dec 603	CP	Mirex	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153
Syn-DP	1.00											
Anti-DP	**0.68****	1.00										
DP	**0.82****	**0.96****	1.00									
Dec 602	0.14	**0.39****	**0.29***	1.00								
Dec 603	**0.31***	**0.51****	**0.51****	**0.53****	1.00							
CP	**0.33***	**0.52****	**0.49****	**0.68****	**0.83****	1.00						
Mirex	−0.05	0.25	0.16	**0.58****	**0.52****	**0.57****	1.00					
BDE-47	−0.14	−0.05	−0.12	0.11	0.16	**0.29***	0.08	1.00				
BDE-100	0.01	−0.03	−0.04	0.14	0.26	**0.36***	0.05	**0.73****	1.00			
BDE-99	0.12	0.22	0.21	0.23	**0.46****	**0.47****	0.06	**0.58****	**0.63****	1.00		
BDE-154	0.27	−0.01	0.05	0.17	0.01	0.14	0.08	0.23	**0.31***	0.18	1.00	
BDE-153	0.21	**0.29***	0.24	**0.45****	**0.34***	**0.43****	0.06	**0.38****	**0.53****	**0.44****	0.08	1.00
Age	0.04	0.20	0.22	0.03	**0.53****	**0.42****	**0.32***	0.10	0.13	0.26	−0.10	0.00

Values in bold are significant with a p value <0.05* or <0.01**.

value of 3.46 ng/g lw. BDE-47 and BDE-153 were the most abundant PBDEs with a contribution of 45% and 33% to the total amount, respectively. The relative concentration pattern is BDE-47 > BDE-153 > BDE-99 ≈ BDE-100 > BDE-154 (Fig. 2). Similar results with predominant BDE-47 and BDE-153 have been reported in human serum studies from Sweden, Korea, Greece or Slovakia (Chovancova et al., 2012; Guvenius et al., 2003; Kalantzi et al., 2011; Lee et al., 2007). Several studies from both the US and Europe differently reported patterns related to the commercial PentaBDE mixture content, with a major contribution of BDE-47 and BDE-99 (Antignac et al., 2009; Frederiksen et al., 2009; Sjödin et al., 2004). Such differences may be related to possible variations in routes of exposure and use of PBDE mixtures. As for the case of the Canadian milk samples (Siddique et al., 2012), the median DP level (1.20 ng/g lw) was lower than the $\sum_5$PBDEs (3.46 ng/g lw). However, once other dechloranes are included, the mean $\sum_5$dechlorane level (5.21 ng/g lw) is higher than the mean $\sum_5$PBDE level. Dec 602, Dec 603, and CP therefore appear to be important congeners to measure if one has to estimate a global dechlorane exposure. Focusing on DP only might lead to an under estimation of the real dechlorane exposure. Such data indicate that the attention devoted to dechloranes should be continued if research indicates toxicological concerns.

PBDE levels were correlated (Table 3) except for BDE-154 that was only correlated with BDE-100 ($r_s = 0.31$, $p < 0.05$). The $\sum_5$PBDE level was slightly lower than the $\sum_5$dechlorane level (Table 1) with median values of 3.46 ng/g lw and 5.21 ng/g lw, respectively. Potential relationships between dechlorane and PBDE levels were evaluated (Table 3). The results demonstrated correlations between CP and all PBDEs, except BDE-154 (not correlated with the other PBDEs). BDE-153 was correlated with Dec 602, Dec 603 and CP. A study on PBDEs 47, 99, and 153 metabolism mediated by human liver microsomes reported that only BDE-47 and BDE-99 were metabolized. This study provided a possible explanation for the high bioaccumulation rate of BDE-153 in humans (Lupton et al., 2009). The hypothesis is that the correlation obtained could result from a similar behavior of these dechlorane compounds. Different results were obtained by de la Torre et al. (2012) when they evaluated the correlation between dechloranes and PBDEs in marine mammal samples from Brazil. They only reported correlations between DP and PBDEs. However, levels and relative concentration patterns of PBDEs were different. Siddique et al. (2012) also reported correlations between PBDEs and DP for breast milk samples from Canada but not with a consistent pattern. The PBDE pattern was similar to our study although the levels were 5 times higher.

3.4. Comparison of dechlorane and OCP levels in human serum

Individual and $\sum_5$ of dechlorane or PBDE levels did not statistically differ between males and females. Age was not correlated with PBDE levels, in accordance with previous observations (Kalantzi et al., 2011), while significant correlations were found between age and Dec 603, CP and Mirex levels (Table 3). When the samples were split in two groups ($n_1 = n_2 = 24$), with age ranges of 29–58 years for the first group and 59–86 years for the second group, levels of Dec 603 and CP statistically differed ($p < 0.05$) with higher levels for the second group.

Because OCPs are persistent and bioaccumulative compounds, it is interesting to note that only Dec 603 and CP demonstrated relationships with some OCP levels already reported for these samples (Viel et al., 2011). Significant statistical correlations ($p < 0.05$) were found between Dec 603 and beta-HCH ($r_s = 0.35$), Dec 603 and trans-nonachlor ($r_s = 0.36$), CP and beta-HCH ($r_s = 0.33$) as well as CP and trans-nonachlor ($r_s = 0.35$). Beta-HCH is considered as a byproduct (5–14%) of gamma-HCH (of Lindane), a well-used pesticide. Beta-HCH isomer correlated with Dec 603 and CP while no correlation was found with the gamma-isomer. Some studies reported greater bioaccumulation of the beta-isomer over the gamma-isomer (Kolarikova et al., 2013). A similar behavior was observed with trans-nonachlor. Although trans- and cis-nonachlor are both chlordane derivatives, correlations were found only with the trans-isomer. Some studies have already reported higher bioaccumulation of the trans-isomer over the cis-isomer (Bondy et al., 2000). Also, food web magnification factors (FWMFs) were determined for beta-HCH and trans-nonachlor (Skarphedinsdottir et al., 2010). The correlation of Dec 603 and CP with these specific OCP isomers could be related to both exposure and bioaccumulation properties. Dec 603 and CP are known to be present as impurities in technical products. In the study of Shen et al. (2011), Dec 603 was observed in technical Aldrin and Dieldrin while CP was found only in technical Chlordene and Chlordane, at levels lower than 1%. The higher levels of Dec 603 in the Lake Erie of Canada were suggested to be related to the use of Aldrin and Dieldrin. Lower levels of CP were detected compared to Dec 603 in our samples which is similar to other studies on dechlorane levels including CP. However, in terms of exposure, Aldrin, Dieldrin or Chlordane was banned in France in 1992 (INERIS, 1992). Results of monitoring studies performed in 2000 and 2005 were optimistic for the eradication of these pesticides (INERIS, 2007) and to our knowledge, no preferential use of Aldrin or Eldrin over Chlordane was reported.

3.5. Levels of DP isomers

Syn- and *anti*-DP isomers were analyzed separately. Higher levels and frequency of detection were obtained for the *anti*-isomer (Table 1). The *anti*-DP fraction (f_{anti}, amount of *anti*-DP in total DP) was calculated for 33 samples and ranged from 0.65 to 0.86, with a mean value of 0.75 ± 0.07 (RSD = 9.3%). In several studies, the f_{anti} value was compared with the reported ratio of commercial DP products, to assess potential differences between isomers behavior. According to Ben et al. (2013), the technical DP f_{anti} value should be comprised

between 0.60 and 0.80, based on variation reported from various batches or manufacturers (Hoh et al., 2006). Our results are included in this range and therefore support the hypothesis of no specific isomer bioaccumulation, although sources of exposure for Europe have not been identified yet. However, the evaluation of a potential isomer bioaccumulation based on sample measurements and technical values comparison should be done carefully. A study on rats and DP exposure reported similar f_{anti} values that ranged between 0.75 and 0.80 for muscle, liver and serum samples but it was also demonstrated that these DP f_{anti} values decreased significantly with higher levels of exposure (Li et al., 2013). A similar behavior was obtained for the study on Peregrine Falcon eggs sampled in Spain and Canada (Guerra et al., 2011). Lower DP f_{anti} values were obtained for samples from Canada, when the DP levels were 10 to 50 times higher than levels reported in Spain. Both f_{anti} value and DP level should be taken into consideration for the evaluation of a potential stereoselective bio-accumulation.

4. Conclusions

This study is the first report of $\sum_5$dechlorane levels in Western European (France) human serum. Despite the fact that no production sources have been identified in Europe to date, DP and related dechloranes were detected. A specific pattern of contamination was found, and Dec 603 was reported with high levels, compared to other biota samples that have been analyzed from Europe. Results demonstrated that bioaccumulation properties should be taken in consideration in addition to possible routes of human exposure. Dose-toxicity data are needed for these chemicals in order to initiate proper human risk assessment. The hypothesis of long range transport has also to be considered until more information on production and use is made available for Europe. Nevertheless, our study indicates that at least part of the European population might be exposed to dechloranes. This is further supported by recent levels reported from a preliminary study performed in Norway (Cequier et al., 2013). In addition, the $\sum_5$dechlorane level is higher than the $\sum_5$PBDE level. Because unregulated dechloranes are reported to present similar physico-chemical properties and cost advantages over brominated flame retardants (Oxychem, 2007), efforts should be made to better understand their behavior as they might become the next family of FR to consider for human biomonitoring.

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