



HAL
open science

Assessment of dechlorane plus and related compounds in foodstuffs and estimates of daily intake from lebanese population

Inas Abdel Malak, Ronan Cariou, Ingrid Guiffard, Anais Venisseau, Gaud Dervilly-Pinel, Farouk Jaber, Bruno Le Bizec

► To cite this version:

Inas Abdel Malak, Ronan Cariou, Ingrid Guiffard, Anais Venisseau, Gaud Dervilly-Pinel, et al.. Assessment of dechlorane plus and related compounds in foodstuffs and estimates of daily intake from lebanese population. *Chemosphere -Oxford- Global Change Science-*, Elsevier, 2019, 235, pp.492-497. 10.1016/j.chemosphere.2019.06.148 . hal-02735097

HAL Id: hal-02735097

<https://hal.inrae.fr/hal-02735097>

Submitted on 26 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial | 4.0 International License

1 **Assessment of Dechlorane Plus and related compounds in foodstuffs and estimates of daily intake**
2 **from Lebanese population**

3

4 Inas Abdel Malak^{1,2}, Ronan Cariou^{1,*}, Ingrid Guiffard¹, Anaïs Vénisseau¹, Gaud Dervilly-Pinel¹, Farouk
5 Jaber², Bruno Le Bizec¹

6

7 ¹LABERCA, Oniris, INRA, F-44307, Nantes, France.

8 ²Lebanese University, Faculty of Sciences I, Laboratory of Analysis of Organic Compounds (LACO), 508
9 Hadath, Beirut, Lebanon.

10

11 *Corresponding author at: Laboratoire d'Étude des Résidus et Contaminants dans les Aliments
12 (LABERCA), Route de Gachet, Nantes, F-44307, France

13 E-mail address: laberca@oniris-nantes.fr

14

15

16 **Keywords**

17 Chlorinated flame retardants

18 Environmental contaminants

19 Ultra-trace measurement

20 Food analysis

21 Human intake

22 Chemical Risk

23

24 **Abstract**

25 Dechlorane Related Compounds (DRCs), including Dechlorane Plus (*syn/anti*-DP or *syn/anti*-DDC-CO)
26 and related compounds (Dec-601 or DDC-ID, Dec-602 or DDC-DBF, Dec-603 or DDC-Ant and
27 Chlordene Plus or DDC-PDD), are a group of polychlorinated flame retardants of concern since they
28 were first reported in various environmental and biota matrices about one decade ago. In this work,
29 we investigated the dietary intake of the Lebanese population to these lipophilic environmental
30 contaminants upon the evaluation of selected foodstuff contamination. Collected food samples
31 ($n=58$) were selected to be representative of the lipid fraction of the whole diet of the Beirut
32 population. The samples were analysed using pressurized liquid extraction, silica multilayer column
33 followed by gel permeation chromatography for purification and GC-EI-HRMS for separation and
34 detection. Detection frequency of at least one compound among Dechlorane Plus (*syn*-DP and *anti*-
35 DP), Dechlorane 602, 603 and Chlordene Plus) was 91%. The mean concentrations of \sum_6 DRCs, by food
36 group, ranged from 4.7 to 29.5 pg g^{-1} wet weight in lowerbound (LB) and from 6.7 to 76.9 pg g^{-1} wet
37 weight in upperbound (UB). Based on food habits, the dietary intake of Beirut adults was estimated
38 to be between 3.71 (LB) and 5.61 (UB) ng day^{-1} . Dechlorane Plus and Dechlorane 602 were the
39 dominant compounds, contributing to 70 and 24% of the total intake (LB value), respectively. This
40 study reports for the first time the occurrence of Dechloranes in Lebanese foods and proposes
41 corresponding deterministic dietary exposure scenario.

42

43 **1. Introduction**

44 Flame retardants (FRs) are chemical substances that are incorporated in flammable products like
45 electronics, textiles and plastics, to inhibit flammability and increase fire safety. Dechlorane Plus (CAS
46 13560-89-9, $C_{18}H_{12}Cl_{12}$), or DDC-CO according to the accepted practical abbreviation (PRAB) (Bergman
47 et al., 2012) (Table S1), a highly chlorinated FR additive, has been manufactured for more than 40
48 years and used in electrical wire and cable coatings, computer connectors, and plastic roofing
49 materials (Wang et al., 2016). DDC-CO has been used as a substitute to Mirex (also known as
50 Dechlorane) (Fang et al., 2014) and has been suggested as a potential substitute to
51 decabromodiphenyl ether in some applications (Zhou et al., 2017). The United States Environmental
52 Protection Agency has classified DDC-CO as a high-production volume chemical (US EPA, 2019).
53 OxyChem (Niagara Falls, USA) and Anpo Electrochemical Co. (Jiangsu, China) are the only two known
54 DDC-CO manufacturers with an annual production of about 450–4500 tons in USA and 300–1000 tons
55 in China (Von Eyken et al., 2016; Wang et al., 2016). The commercial DDC-CO mixtures are composed
56 of two isomers, *syn*- and *anti*-DDC-CO, with an approximate ratio of 1:3 (Giulivo et al., 2017). DDC-CO
57 shares similar properties to Persistent Organic Pollutants (POPs), including high lipophilicity,
58 bioaccumulation potential, and potential for long-range transport, and has become ubiquitous in the
59 environment (Na et al., 2017; Wang et al., 2017). The environmental occurrence of DDC-CO was first
60 reported in air, fish and sediment samples from the Great Lakes area in 2006 (Hoh et al., 2006). Some
61 studies showed that DDC-CO accumulates in wildlife and human tissue (Sühring et al., 2015; Wu et
62 al., 2016). Tomy et al. (2007) demonstrated the biomagnification of DDC-CO along trophic levels via
63 food chain.

64 In the wake of DDC-CO, other alternative Dechlorane Related Compounds (DRCs), based on
65 hexachlorocyclopentadiene as well, such as Dechlorane 601 (CAS 13560-90-2, $C_{20}H_{12}Cl_{12}$, DDC-ID),
66 Dechlorane 602 (CAS 31107-44-5, $C_{14}H_4Cl_{12}O$, DDC-DBF), Dechlorane 603 (CAS 13560-92-4, $C_{17}H_8Cl_{12}$,
67 DDC-Ant), and Chlordene Plus (CAS 13560-91-3, $C_{15}H_6Cl_{12}$, DDC-PDD), with PRAB according to
68 Bergman et al. (2012) and Bergman and Rydén (2019) (Table S1), were commercialized to replace of

69 Mirex. These DRCs have subsequently been detected in various environmental and food samples as
70 they are released into air, soil and water due to manufacturing and improper handling and disposal
71 of DRC-containing products and materials (Sales et al., 2017; Abdel Malak et al., 2018).

72 Recent human biomonitoring studies reporting the presence of DRCs in plasma and human serum
73 (Yan et al., 2012; Cequier et al., 2013; Brasseur et al., 2014; Chen et al., 2015; Fromme et al., 2015,
74 Qiao et al., 2018), hair (Chen et al., 2015; Qiao et al., 2018), cord blood (Sales et al., 2017) and human
75 milk (Siddique et al., 2012). Alike other chemical contaminants, human exposure to DRCs can be
76 related to inhalation of indoor air, ingestion of dust and dietary intake (Kim et al., 2014).

77 Several studies have reported the occurrence of DRCs in various food and seafood matrices in Japan
78 (Kakimoto et al., 2012; Yasutake et al., 2018), Korea (Kim et al., 2014), Belgium (L'Homme et al.,
79 2015 ; Poma et al., 2018) and European markets (Aznar-Alemany et al., 2016). Estimated mean daily
80 intakes were reported in the order of magnitude of $\text{ng day}^{-1} \text{ person}^{-1}$ for Asian countries, considering
81 at least most fatty matrices of animal origin and oils, where POP-like substances are expected.
82 Reported exposure was much lower in Belgium, at the hundreds of $\text{pg day}^{-1} \text{ person}^{-1}$ order of
83 magnitude, but not all fatty food groups were considered. As such, dietary exposure data is missing
84 worldwide to enable proper risk assessment.

85 In the present study, we investigated food consumption as a possible route of human exposure to
86 DRCs in Lebanon. Various foods, including vegetable oil, meat, fish, egg, and dairy products, were
87 analysed in order (i) to investigate the occurrence of DRCs in Lebanese foodstuffs and (ii) to estimate
88 the dietary intake of the Lebanese adult population in a risk assessment context.

89

90 **2. Materials and methods**

91 *2.1. Sample collection and storage*

92 A total of 58 food samples, considered as representative of the average consumption of fatty food
93 groups of animal and vegetable origins for the Lebanese population (Nasreddine et al., 2006), were
94 collected in June 2017 from supermarkets located in Beirut (Lebanon). Nutritional categories

95 included meat ($n=12$), fish ($n=21$), egg ($n=5$), milk and dairy product ($n=13$), fat and oils added at
96 table ($n=7$). More precisely, collected samples were: chicken meat ($n=6$), bovine meat ($n=3$), bovine
97 liver ($n=3$), boops ($n=3$), gilt head bream ($n=2$), mackerel ($n=2$), whiting ($n=2$), anchovy ($n=2$), grouper
98 ($n=5$), blackspot seabream ($n=2$), European bass ($n=2$), other fish ($n=1$), egg ($n=5$), milk ($n=5$), labne
99 ($n=4$), yogurt ($n=4$), olive oil ($n=4$) and sesame oil ($n=3$). The food samples were weighed,
100 homogenized, lyophilized (except for oil), homogenized again and stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

101

102 2.2. Quantification of DRCs in samples

103 Trace analysis of targeted DRCs (*anti*-DDC-CO, *syn*-DDC-CO, DDC-ID, DDC-DBF, DDC-Ant and DDC-
104 PDD) was performed according to previously published work (Abdel Malak et al., 2018), pending
105 minor modifications in sample preparation. Briefly, lyophilized samples (approximately 3 g for fish or
106 4 g for meat, egg and dairy products) were extracted by Pressurized Liquid Extraction (Büchi,
107 SpeedExtractor, E-914), except for oil samples (1 g). The lipid content was determined
108 gravimetrically. Purification of the extracts involved a multilayer silica gel column (acidic, neutral and
109 basic layers) followed by Gel Permeation Chromatography. Purified extracts were analysed by gas
110 chromatography (6890, HP, Palo Alto, CA, USA) on a HT8-PCB column (30 m \times 0.25 mm, SGE
111 Analytical Science, Ringwood, Australia) coupled to high resolution mass spectrometry (JMS 700D,
112 Jeol, Tokyo, Japan), operating at a resolution of 10,000 according to 10% valley definition, in the
113 electron impact ionisation mode and in a single sequence. Identification was based on two ion traces.
114 Determination of DDC-ID, known to be challenging, was made possible by the successful
115 chromatographic separation from *syn*-DDC-CO monitored with the same ion ($[\text{C}_5\text{Cl}_6]^+$) in electron
116 impact (Abdel Malak et al., 2018). Quantification was performed through isotopic dilution using
117 $^{13}\text{C}_{10}$ -*syn*-DDC-CO, $^{13}\text{C}_{10}$ -*anti*-DDC-CO and $^{13}\text{C}_{10}$ -DDC-DBF as internal standards, and $^{13}\text{C}_{12}$ -PCB-194 as
118 recovery standard. Diagnostic ions are described Table S2.

119

120 2.3. QA/QC and reporting

121 Samples were analysed through four successive series of 10 to 20 samples. Recovery rates,
122 determined for each sample, reached averages of $74 \pm 14\%$, $59 \pm 15\%$ and $92 \pm 10\%$ for
123 $^{13}\text{C}_{10}$ -*syn*-DDC-CO, $^{13}\text{C}_{10}$ -*anti*-DDC-CO and $^{13}\text{C}_{10}$ -DDC-DBF, respectively. Six procedural blanks (started
124 from the extraction step) were introduced within the series to monitor procedural contamination. If
125 procedural contamination was observed, a limit of reporting (LoR) was set at mean plus 3 times the
126 standard deviation of the procedural blank. Otherwise, a limit of quantification (LOQ) was set for
127 each sample based on a signal to noise ratio of 3:1 for the less intense signal. Trace amounts of
128 *syn*-DDC-CO, *anti*-DDC-CO and DDC-DBF were always detected in procedural blanks, at values in the
129 4.0-15.5, 2.0-6.8 and 0.9-6.4 pg ranges, leading to LoRs of 23.2, 9.4 and 9.1 pg per sample,
130 respectively. For the other target compounds, LOQs were in the 1.2-14.5, 1.3-18.8 and 0.3-1.4 pg
131 ranges per sample, respectively for DDC-ID, DDC-Ant and DDC-PDD.

132 An in-house fish oil (1 g aliquots) routinely used as quality control for ISO 17025 methods dedicated
133 to a range of POPs (Jondreville et al., 2017) was fortified (4 ng of each native compound) and
134 analysed as well ($n=5$). Corresponding results regarding accuracy (intermediate precision and
135 trueness uncertainty) were previously published and considered as satisfying (Abdel Malak et al.,
136 2018).

137

138 **2.4. Data processing**

139 Due to rather low DRC levels observed in this study, left-censored (lowerbound, LB) and right-
140 censored (upperbound, UB) values were both calculated so that true values were under- and over-
141 estimated (WHO, 2013). LB values corresponded to zero when lower than LOQ/LoR, observed value
142 when higher than LOQ and observed value minus LoR when higher than LoR. UB values corresponded
143 to LOQ/LoR when lower and to observed values when higher (Figure S1). LoRs being higher than
144 LOQs, discrepancies between LB and UB values were more pronounced for *syn*-DDC-CO, *anti*-DDC-CO
145 and DDC-DBF. The relationship between selected DRCs was statistically evaluated by Pearson
146 coefficients of determination using Excel 2016 spreadsheets.

147

148 3. Results and discussion

149 The concentrations of *syn*-DDC-CO, *anti*-DDC-CO, DDC-ID, DDC-DBF, DDC-Ant and DDC-PDD in food
150 groups based on wet weight (ww) and according to LB and UB scenarios are shown in Table 1.
151 Detailed results, along with lipids content (lw), are also provided in Table S3 to facilitate the
152 comparison with the literature.

153 Along the discussion, the results were compared to available values reported from Korea (Kim et al.,
154 2014), Japan (Yasutake et al., 2018) and Belgium (L'Homme et al., 2015), bearing in mind that food
155 groups do not necessary include the same food items.

156

157 3.1. Concentrations of Σ DDC-CO

158 Detection frequencies of *syn*- and *anti*-DDC-CO for all investigated foodstuffs were 40% and 86%,
159 respectively. Depending on the food group considered, detection frequencies of the sum of *syn*-DDC-
160 CO and *anti*-DDC-CO (Σ DDC-CO) ranged from 57 to 100%. The highest mean concentration of Σ DDC-
161 CO was obtained in a meat sample, (161 pg g⁻¹ ww, UB), followed by an olive oil sample (136 pg g⁻¹
162 ¹ ww, UB). However, the mean concentration of Σ DDC-CO obtained in the meat group was lower
163 than in the vegetable oil group (Table 1).

164 Regarding fish, the mean concentration of Σ DDC-CO (5.0 to 8.0 pg g⁻¹ ww, [LB-UB]) was in the same
165 order of magnitude to levels reported for fish samples collected in supermarkets in Osaka, Japan in
166 June 2011 ($n=20$, average of 2.35 pg g⁻¹ ww) (Kakimoto et al., 2012) or in rivers in Latvia in October
167 2012 ($n=25$, average of 11.34 pg g⁻¹ ww) (Rjabova et al., 2016). It was also lower than those obtained
168 from fish and shellfish collected in March 2011 in Korea ($n=70$, average of 36.34 pg g⁻¹ ww) (Kim et
169 al., 2014). No significant correlation between concentrations and lipid contents was observed.

170 Concerning vegetable oils, the mean concentration of Σ DDC-CO (21.1 to 52.8 pg g⁻¹ lw, [LB-UB]) was
171 in the same order of magnitude as those reported in vegetable oils ($n=2$) from Spain (average of

172 49.15 pg g⁻¹ lw) (Von Eyken et al., 2016) and in oils and fats ($n=5$) from Japan (average of 18.5 pg g⁻¹
173 ww) (Yasutake et al., 2018).

174 In meat, the mean concentration of Σ DDC-CO (17.4 to 19.9 pg g⁻¹ ww, [LB-UB]) was lower than values
175 reported from Korea ($n=35$, average values ranging from 9.8 to 169.8 pg g⁻¹ ww, according to meat
176 type) (Kim et al., 2014) but higher than those obtained from Japan ($n=5$, average of 3.34 pg g⁻¹ ww)
177 (Yasutake et al., 2018).

178 As regards eggs, the mean concentration of Σ DDC-CO (6.9 to 8.9 pg g⁻¹ ww, [LB-UB]) was in the same
179 order of magnitude as those reported from Korea ($n=5$, average of 15.31 pg g⁻¹ ww) (Kim et al.,
180 2014), but higher than those obtained from Belgium ($n=8$, average of 26.27 pg g⁻¹ lw) (L'Homme et
181 al., 2015). Our values were also lower than those reported in herring gull eggs from North America
182 (up to 15 ng g⁻¹ ww) (Gauthier et al., 2009). Authors suggested that the presence of DDC-CO in eggs
183 could result from the accumulation of FRs in maternal specimen via their diet and be transferred
184 during ovogenesis.

185 Finally, for milk and dairy products, the mean concentration of Σ DDC-CO (1.7 to 3.1 pg g⁻¹ ww,
186 [LB-UB]) was lower than those reported from Korea (28.1 to 39.3 pg g⁻¹ ww) (Kim et al., 2014), but
187 higher than those reported from Belgium (average of 17.6 pg g⁻¹ lw) (L'Homme et al., 2015).

188 These results tend to indicate that the DDC-CO contamination of foods from Lebanon is lower than
189 those from Korea (Kim et al., 2014), in the same order of magnitude than those from Japan (Yasutake
190 et al., 2018), and higher than those from Belgium (L'Homme et al., 2015).

191

192 3.2. Profiles of DDC-CO isomers

193 The commercial mixture of DDC-CO exhibits two stereoisomers, *anti*- and *syn*-DDC-CO, in a ratio of
194 about 3:1 (Feo et al., 2012). The corresponding enantiomeric fraction of *anti*-DDC-CO (f_{anti}), defined
195 as the levels ratio of *anti*-DDC-CO over Σ DDC-CO, reaches 0.75. In biota, various authors reported
196 values of f_{anti} at 0.6 ± 0.2 , depending on the origin of the sample (Kang et al., 2010; Wang et al., 2011;
197 Von Eyken et al., 2016), due to specific enrichment in *syn*-DDC-CO in the environment. In our study,

198 depending on the food item considered, the f_{anti} values, when quantified, ranged from 0.26 to 0.76
199 (Figure 1), which were close to, or lower than, the values in the technical product, and similar to
200 those reported in the literature (Kim et al., 2014; L'Homme et al., 2015; Von Eyken et al., 2016; Wang
201 et al., 2016). The highest value of f_{anti} (0.76) was obtained from an olive oil sample, suggesting that, in
202 this unique case of a food item of vegetable origin, the contamination could have occurred by direct
203 contact with the technical product, with no biological enrichment observed. Inversely, the lowest
204 values of f_{anti} , close to 25%, were found in dairy product samples, suggesting a significant enrichment
205 in *syn*-DDC-CO through the producing mammal organisms, possibly involving lactation, and/or
206 fermentation. For the fish samples, the f_{anti} ranged between 0.38 and 0.62 with a mean value equal
207 to 0.50 ± 0.08 , which appeared similar to that of the commercial product and those reported in fish
208 samples in the literature (Kakimoto et al., 2012; Wang et al., 2015; Sühling et al. (2015)).

209

210 3.3. Concentration of other DRCs

211 DDC-DBF was detected in 41% of the sample set, at concentrations reaching up to $97 \text{ pg g}^{-1} \text{ ww}$ (UB)
212 (Table S3). Thus, DDC-DBF appeared as the second most important DRC after Σ DDC-CO, in terms of
213 concentration, average concentrations being even higher than Σ DDC-CO in fish and milk and dairy
214 products. The concentrations of DDC-DBF were in the same order of magnitude as those reported
215 from Korea, lower than those obtained from Japan but higher than those reported from Belgium
216 (Table S4).

217 DDC-Ant was detected in 28% of the sample set, at relatively low concentrations (similar to the
218 results reported in foods from Korea, Japan and Belgium, Table S4). The highest values (7.7 and
219 $8.1 \text{ pg g}^{-1} \text{ ww}$, UB) were observed in sesame and olive oil samples.

220 Similarly, DDC-PDD was detected in 28% of all investigated foods at rather low concentrations
221 ($<2.9 \text{ pg g}^{-1} \text{ ww}$), except for one sesame oil and an egg samples at 22.5 and $6.8 \text{ pg g}^{-1} \text{ ww}$ (UB),
222 respectively. These concentrations were globally higher than those reported in food from Belgium

223 and Japan, but lower compared to those reported from China, which were in the ng g^{-1} lw range
224 (Wang et al., 2015).

225 Finally, DDC-ID was not detected in any sample.

226

227 3.4. Correlation among Dechloranes

228 In order to investigate co-contaminations in contamination phenomenon, linear regression
229 correlation analysis was performed between DP isomers and DDC-DBF only, due to the low detection
230 rate of the other DRCs. Data analysis was achieved for pg g^{-1} ww (LB) concentrations, while
231 accounting only for quantified ($>\text{LoR}$) values. The correlation between *syn*-DDC-CO and *anti*-DDC-CO
232 was moderate but significant ($R^2=0.66$, $P=0.0008$) whereas no correlation was observed between
233 DDC-DBF and *syn*-DDC-CO ($R^2=0.09$, $P=0.76$) or *anti*-DDC-CO ($R^2=0.05$, $P=0.84$). Thus, although the
234 contamination sources are considered the same, differential bioaccumulation and biotransformation
235 properties of DDC-CO isomers among species and individuals appear as the main reason for
236 moderate correlation. In addition, as expected, contaminations sources of DDC-CO and DDC-DBF
237 appear to be independent.

238

239 3.5. Estimation of DRCs dietary intake

240 The Lebanese adult population (25-54 years old) was considered in the objective of proposing a first
241 reference point for further studies in the geographical area. The occurrence levels of DRCs
242 determined in the selected set of foodstuffs were used to perform a deterministic dietary exposure
243 assessment, according to recognised guidelines (FAO-WHO, 2009; EFSA-FAO-WHO, 2011). The
244 estimations of DRCs daily intake were calculated by the addition of quantities determined for each
245 food item by multiplying the average concentration of DRCs (pg g^{-1} ww) in the considered food item
246 (Table 1) with the daily dose of the considered food item (g day^{-1}). Based on the study of food habits
247 described by Nasreddine et al. (2006), the average total food intake per person and per day in
248 Lebanon is 1881.6 g, including beverages except water. The collected food samples made up 387 g

249 per person per day in Lebanon (21% of the total food intake), covering all food from animal origin
250 and vegetable oils, the expected major dietary intake contributors for such lipophilic environmental
251 contaminants.

252 The mean dietary daily intake of DRCs per adult via selected Lebanese foods was estimated between
253 3.71 and 5.62 ng day⁻¹, according to LB and UB scenarios respectively, as shown in Table 2. It
254 appeared lower than those reported by Kim et al. (2014) in Korea (11.7 ng day⁻¹) and by Yasutake et
255 al. (2018) in Japan (7.6 ng day⁻¹), both based on representative fatty food groups, but higher than
256 those reported by L'Homme et al. (2015) in Belgium (136 pg day⁻¹), based on limited fatty food group.
257 Considering substances profile (Figure S2), DDC-CO accounted for about 70% of \sum_6 DRC in both
258 scenarios. This contribution was lower than in Korea (92%, LB) and Belgium (88%, UB) but higher
259 than in Japan (23%, LB). Indeed, DDC-DBF was the main DRC in Japan (75%, LB). In Lebanon, DDC-DBF
260 accounted for about 24% of the profile in both scenarios, appearing as the second most important
261 DRC like in Korea. With less than 7.2% of cumulated contributions, other DRCs (DDC-ID, DDC-Ant and
262 DDC-PDD) were minor compounds.

263 As regards food groups (Figure S3), meat and poultry appeared as the main contributor of \sum_6 DRC (43
264 to 34%, [LB-UB]) as well as \sum DDC-CO (61 to 46%, [LB-UB]). They were followed by milk and dairy
265 products as well as fat and oils added at table, each one contributing between 16 and 31% to the
266 total, depending on the scenario. The high contribution of milk and dairy products to the exposure to
267 DRCs is rather explained by the high consumption of these products rather than the relatively low
268 occurrence levels. Conversely, relatively high occurrence levels in fat and oils added at table
269 appeared as the main factor explaining the contribution to the exposure rather than the relatively
270 low consumption level. Fish and egg represented the lowest contributors to the dietary daily intake,
271 with less than 10% cumulated contribution.

272 In their food consumption survey, Nasreddine et al. (2006) also provided stratification data according
273 to gender and age (3 groups of 25-34, 35-44 and 45-54 years old). Comparing genders, the average
274 daily intake of \sum_6 DRC in this study was higher for men (between 4.220 (LB) and 6.382 (UB) ng day⁻¹)

275 than for women (between 3.257 (LB) and 4.911 (UB) ng day⁻¹) (Table 3, Figure S3). The main reason is
276 that men ingest more food than women (403.4 versus 371.9 g day⁻¹) for all considered food groups
277 except for milk and dairy products group (227.4 versus 257.1 g day⁻¹, respectively). For similar
278 reasons of decreasing food consumption with age, the estimated daily intake of Σ_6 DRC has a
279 downward trend as age increases.

280

281 **4. Conclusions and perspectives**

282 A robust analytical method has been applied to a series of various Lebanese fatty foods of animal and
283 vegetable origins ($n=58$) in order to investigate the occurrence of DRCs and estimate associated daily
284 intake. The detection frequency of at least one DRC in food items was 91%, supporting the fact that
285 this compound family is ubiquitous. The mean concentrations of DRCs in each food item were rather
286 low, in the pg g⁻¹ ww order of magnitude. However, the daily intake reached several ng per day and
287 per person, with slight variations depending on gender and age. DDC-CO appeared as the main
288 contributor, followed by DDC-DBF. To the best of our knowledge, this study is the first to analyse and
289 detect emerging halogenated FRs in Lebanese foods and quantify the extent of human dietary
290 exposure to them. Future work should focus on (i) total basket, including non-fatty food categories
291 and on (ii) the indoor environment (dust, air) in order to be more accurate in the estimation of
292 human exposure to these compounds. Toxicological reference values are also required to make
293 conclusions as regards resulting risk to human health.

294

295 **Acknowledgements**

296 The authors express their acknowledgments to the French General Directorate for Food as well as
297 Campus France and the Lebanese Association for Scientific Research for financial support. We
298 acknowledge Åke Bergman and Andreas Rydén as well for suggesting relevant abbreviations for two
299 DRCs.

300

301 **References**

- 302 Abdel Malak, I., Cariou, R., Vénisseau, A., Dervilly-Pinel, G., Jaber, F., Babut, M., Le Bizec, B., 2018.
303 Occurrence of Dechlorane Plus and related compounds in catfish (*Silurus spp.*) from rivers in
304 France. *Chemosphere* 207, 413–420. doi:10.1016/j.chemosphere.2018.05.101.
- 305 Aznar-Aleman, Ò., Trabalón, L., Jacobs, S., Barbosa, V.L., Tejedor, M.F., Granby, K., Kwadijk, C.,
306 Cunha, S.C., Ferrari, F., Vandermeersch, G., Sioen, I., Verbeke, W., Vilavert, L., Domingo, J.L.,
307 Eljarrat, E., Barceló, D., 2016. Occurrence of halogenated flame retardants in commercial
308 seafood species available in European markets. *Food Chem. Toxicol.* 104, 35–47.
309 doi:10.1016/j.fct.2016.12.034.
- 310 Jondreville, C., Cariou, R., Travel, A., Belhomme, L.J., Dervilly-Pinel, G., Le Bizec, B., Huneau-Salaün,
311 A., Le Bouquin-Leneveu, S., 2017. Hens can ingest extruded polystyrene in rearing buildings and
312 lay eggs contaminated with hexabromocyclododecane. *Chemosphere* 186, 62–67.
313 doi:10.1016/j.chemosphere.2017.07.117.
- 314 Bergman, Å., Rydén, A., Law, R.J., de Boer, J., Covaci, A., Alaei, M., Birnbaum, L., Petreas, M., Rose,
315 M., Sakai, S., Van den Eede, N., van der Veen, I., 2012. A novel abbreviation standard for
316 organobromine, organochlorine and organophosphorus flame retardants and some
317 characteristics of the chemicals. *Environ. Int.* 49, 57–82. doi:10.1016/j.envint.2012.08.003.
- 318 Bergman, Å., Rydén, A., 2019. Personal communication.
- 319 Brasseur, C., Pirard, C., Scholl, G., De Pauw, E., Viel, J.F., Shen, L., Reiner, E.J., Focant, J.F., 2014. Levels
320 of Dechloranes and polybrominated diphenyl ethers (PBDEs) in human serum from France.
321 *Environ. Int.* 65, 33–40. doi:10.1016/j.envint.2013.12.014.
- 322 Cequier, E., Marcé, R.M., Becher, G., Thomsen, C., 2013. Determination of emerging halogenated
323 flame retardants and polybrominated diphenyl ethers in serum by gas chromatography mass
324 spectrometry. *J. Chromatogr. A* 1310, 126–132. doi:10.1016/j.chroma.2013.08.067.
- 325 Chen, D., Letcher, R.J., Burgess, N.M., Champoux, L., Elliott, J.E., Hebert, C.E., Martin, P., Wayland, M.,
326 Chip Weseloh, D. V., Wilson, L., 2012. Flame retardants in eggs of four gull species (*Laridae*)

327 from breeding sites spanning Atlantic to Pacific Canada. *Environ. Pollut.* 168, 1–9.
328 doi:10.1016/j.envpol.2012.03.040.

329 Chen, K., Zheng, J., Yan, X., Yu, L., Luo, X., Peng, X., Yu, Y., Yang, Z., Mai, B., 2015. Dechlorane Plus in
330 paired hair and serum samples from e-waste workers: Correlation and differences.
331 *Chemosphere* 123, 43–47. doi:10.1016/j.chemosphere.2014.11.058.

332 EFSA-FAO-WHO, 2011. European Food Safety Authority, Food and Agriculture Organization of the
333 United Nations, World Health Organization, 2011. Towards a harmonised total diet study
334 approach: a guidance document. *EFSA Journal*, 9, 2450.

335 FAO-WHO, 2009. Food and Agriculture Organization of the United Nations, World Health
336 Organization, 2009. International Programme on Chemical Safety (IPCS). Principles and methods
337 for the risk assessment of chemicals in food. *Environmental Health Criteria* 240. WHO, Geneva.

338 Fang, M., Kim, J.C., Chang, Y.S., 2014. Investigating Dechlorane Plus (DP) distribution and isomer
339 specific adsorption behavior in size fractionated marine sediments. *Sci. Total Environ.* 481, 114–
340 120. doi:10.1016/j.scitotenv.2014.01.082.

341 Feo, M.L., Barón, E., Eljarrat, E., Barceló, D., 2012. Dechlorane Plus and related compounds in aquatic
342 and terrestrial biota: A review. *Anal. Bioanal. Chem.* 404, 2625–2637. doi:10.1007/s00216-012-
343 6161-x.

344 Fromme, H., Cequier, E., Kim, J.T., Hanssen, L., Hilger, B., Thomsen, C., Chang, Y.S., Völkel, W., 2015.
345 Persistent and emerging pollutants in the blood of German adults: Occurrence of Dechloranes,
346 polychlorinated naphthalenes, and siloxanes. *Environ. Int.* 85, 292–298.
347 doi:10.1016/j.envint.2015.09.002.

348 Gauthier, L.T., Letcher, R.J., 2009. Isomers of Dechlorane Plus flame retardant in the eggs of herring
349 gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America: Temporal changes
350 and spatial distribution. *Chemosphere* 75, 115–120. doi:10.1016/j.chemosphere.2008.11.030.

351 Giulivo, M., Capri, E., Kalogianni, E., Milacic, R., Majone, B., Ferrari, F., Eljarrat, E., Barceló, D., 2017.
352 Occurrence of halogenated and organophosphate flame retardants in sediment and fish

353 samples from three European river basins. *Sci. Total Environ.* 586, 782–791.
354 doi:10.1016/j.scitotenv.2017.02.056.

355 Hoh, E., Zhu, Hites, R.A., 2006. Dechlorane Plus, a chlorinated Flame Retardant, in the Great Lakes.
356 *Environ. Sci. Technol.* 40, 1184–1189. doi:10.1021/es051911h.

357 Kakimoto, K., Nagayoshi, H., Yoshida, J., Akutsu, K., Konishi, Y., Toriba, A., Hayakawa, K., 2012.
358 Detection of Dechlorane Plus and brominated flame retardants in marketed fish in Japan.
359 *Chemosphere* 89, 416–419. doi:10.1016/j.chemosphere.2012.05.072.

360 Kakimoto K, Nagayoshi H, Yoshida J, Akutsu K, Konishi Y, Toriba A, H.K., 2012. Detection of
361 Dechlorane Plus and brominated flame retardants in marketed fish in Japan. *Chemosphere* 89,
362 416–419. doi:10.1016/j.chemosphere.2012.05.072.

363 Kang, J.H., Kim, J.C., Jin, G.Z., Park, H., Baek, S.Y., Chang, Y.S., 2010. Detection of Dechlorane Plus in
364 fish from urban-industrial rivers. *Chemosphere* 79, 850–854.
365 doi:10.1016/j.chemosphere.2010.02.051.

366 Kim, J., Son, M. hui, Kim, J., Suh, J., Kang, Y., Chang, Y.S., 2014. Assessment of Dechlorane compounds
367 in foodstuffs obtained from retail markets and estimates of dietary intake in Korean population.
368 *J. Hazard. Mater.* 275, 19–25. doi:10.1016/j.jhazmat.2014.04.032.

369 Kolic, T.M., Shen, L., Macpherson, K., Fayez, L., Gobran, T., Helm, P.A., Marvin, C.H., Arsenault, G.,
370 Reiner, E.J., 2009. The analysis of halogenated flame retardants by GC-HRMS in environmental
371 samples. *J. Chromatogr. Sci.* 47, 83–91. doi:10.1093/chromsci/47.1.83.

372 L’Homme, B., Calaprice, C., Calvano, C.D., Zambonin, C., Leardi, R., Focant, J.F., 2015. Ultra-trace
373 measurement of Dechloranes to investigate food as a route of human exposure. *Chemosphere*
374 139, 525–533. doi:10.1016/j.chemosphere.2015.07.043.

375 Na, G., Yao, Y., Gao, H., Li, R., Ge, L., Titaley, I.A., Santiago-Delgado, L., Massey Simonich, S.L., 2017.
376 Trophic magnification of Dechlorane Plus in the marine food webs of Fildes Peninsula in
377 Antarctica. *Mar. Pollut. Bull.* 117, 456–461. doi:10.1016/j.marpolbul.2017.01.049.

378 Nasreddine, L., Hwalla, N., Sibai, A., Hamzé, M., Parent-Massin, D., 2006. Food consumption patterns

379 in an adult urban population in Beirut, Lebanon. *Public Health Nutr.* 9, 194–203.
380 doi:10.1079/phn2005855.

381 Poma, G., Malysheva, S. V., Gosciny, S., Malarvannan, G., Voorspoels, S., Covaci, A., Van Loco, J.,
382 2018. Occurrence of selected halogenated flame retardants in Belgian foodstuff. *Chemosphere*
383 194, 256–265. doi:10.1016/j.chemosphere.2017.11.179.

384 Qiao, L., Zheng, X.-B., Yan, X., Wang, M.-H., Zheng, J., Chen, S.-J., Yang, Z.-Y., Mai, B.-X., 2018.
385 Brominated flame retardant (BFRs) and Dechlorane Plus (DP) in paired human serum and
386 segmented hair. *Ecotoxicol. Environ. Saf.* 147, 803–808. doi:10.1016/j.ecoenv.2017.09.047.

387 Rjabova, J., Bartkevics, V., Zacs, D., 2016. The occurrence of Dechlorane Plus and related norbornene-
388 based flame retardants in Baltic wild salmon (*Salmo salar*). *Chemosphere* 147, 210–217.
389 doi:10.1016/j.chemosphere.2015.12.122.

390 Sales, C., Poma, G., Malarvannan, G., Portolés, T., Beltrán, J., Covaci, A., 2017. Simultaneous
391 determination of dechloranes, polybrominated diphenyl ethers and novel brominated flame
392 retardants in food and serum. *Anal. Bioanal. Chem.* 4507–4515. doi:10.1007/s00216-017-0411-
393 x.

394 Siddique, S., Xian, Q., Abdelouahab, N., Takser, L., Phillips, S.P., Feng, Y.L., Wang, B., Zhu, J., 2012.
395 Levels of Dechlorane Plus and polybrominated diphenylethers in human milk in two Canadian
396 cities. *Environment International* 39, 50–55. doi: 10.1016/j.envint.2011.09.010.

397 Sühling, R., Freese, M., Schneider, M., Schubert, S., Pohlmann, J.-D., Alaei, M., Wolschke, H., Hanel,
398 R., Ebinghaus, R., Marohn, L., 2015. Maternal transfer of emerging brominated and chlorinated
399 flame retardants in European eels. *Sci. Total Environ.* 530–531, 209–218.
400 doi:10.1016/j.scitotenv.2015.05.094.

401 Sun, Y., Luo, X., Wu, J., Mo, L., Chen, S., Zhang, Q., Zou, F., Mai, B., 2012. Species- and tissue-specific
402 accumulation of Dechlorane Plus in three terrestrial passerine bird species from the Pearl River
403 Delta, South China. *Chemosphere* 89, 445–451. doi:10.1016/j.chemosphere.2012.05.089.

404 Sverko, E., Tomy, G.T., Reiner, E.J., Li, Y.F., McCarry, B.E., Arnot, J.A., Law, R.J., Hites, R.A., 2011.

405 Dechlorane Plus and related compounds in the environment: A review. *Environ. Sci. Technol.*
406 45, 5088–5098. doi:10.1021/es2003028.

407 Tomy, G.T., Pleskach, K., Ismail, N., Whittle, D.M., Helm, P.A., Sverko, E.D., Zaruk, D., Marvin, C.H.,
408 2007. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci.*
409 *Technol.* 41, 2249–2254. doi:10.1021/es062781v.

410 US EPA, 2004. High Production Volume (HPV) Challenge Program.
411 <[https://iaspub.epa.gov/opthpv/public_search.publiclist?wChemicalName=13560-89-](https://iaspub.epa.gov/opthpv/public_search.publiclist?wChemicalName=13560-89-9&programFlags=>)
412 [9&programFlags=>](https://iaspub.epa.gov/opthpv/public_search.publiclist?wChemicalName=13560-89-9&programFlags=>), accessed on January 23rd, 2019.

413 Von Eyken, A., Pijuan, L., Martí, R., Blanco, M.J., Díaz-Ferrero, J., 2016. Determination of Dechlorane
414 Plus and related compounds (Dechlorane 602, 603 and 604) in fish and vegetable oils.
415 *Chemosphere* 144, 1256–1263. doi:10.1016/j.chemosphere.2015.10.001.

416 Wang, D.-G., Alaei, M., Sverko, E., Li, Y.-F., Reiner, E.J., Shen, L., 2011. Analysis and occurrence of
417 emerging chlorinated and brominated flame retardants in surficial sediment of the Dalian costal
418 area in China. *J. Environ. Monit.* 13, 3104. doi:10.1039/c1em10241a.

419 Wang, D.G., Guo, M.X., Pei, W., Byer, J.D., Wang, Z., 2015. Trophic magnification of chlorinated flame
420 retardants and their dechlorinated analogs in a fresh water food web. *Chemosphere* 118, 293–
421 300. doi:10.1016/j.chemosphere.2014.09.057.

422 Wang, P., Zhang, Q., Zhang, H., Wang, T., Sun, H., Zheng, S., Li, Y., Liang, Y., Jiang, G., 2016. Sources
423 and environmental behaviors of Dechlorane Plus and related compounds - A review. *Environ.*
424 *Int.* 88, 206–220. doi:10.1016/j.envint.2015.12.026.

425 Wang, G., Peng, J., Hao, T., Feng, L., Liu, Q., Li, X., 2017. Effects of terrestrial and marine organic
426 matters on deposition of Dechlorane Plus (DP) in marine sediments from the Southern Yellow
427 Sea, China: Evidence from multiple biomarkers. *Environ. Pollut.* 230, 153–162.
428 doi:10.1016/j.envpol.2017.06.061.

429 WHO, 2013. Reliable Evaluation of Low-level Contamination of Food - Addendum of the Report on
430 GEMS/Food-euro Second Workshop of the 26-27th May 1995.

431 Wu, P.F., Yu, L.L., Li, L., Zhang, Y., Li, X.H., 2016. Maternal transfer of Dechloranes and their
432 distribution among tissues in contaminated ducks. *Chemosphere* 150, 514–519.
433 doi:10.1016/j.chemosphere.2015.11.008.

434 Xian, Q., Siddique, S., Li, T., Feng, Y. lai, Takser, L., Zhu, J., 2011. Sources and environmental behavior
435 of Dechlorane Plus - A review. *Environ. Int.* 37, 1273–1284. doi:10.1016/j.envint.2011.04.016.

436 Yan, X., Zheng, J., Chen, K.H., Yang, J., Luo, X.J., Yu, L.H., Chen, S.J., Mai, B.X., Yang, Z.Y., 2012.
437 Dechlorane Plus in serum from e-waste recycling workers: Influence of gender and potential
438 isomer-specific metabolism. *Environ. Int.* 49, 31–37. doi:10.1016/j.envint.2012.08.011.

439 Zhou S, Fu J, He H, Fu J, Tang Q, Dong M, Pan Y, Li A, Liu W, Z.L., 2017. Spatial distribution and
440 implications to sources of halogenated flame retardants in riverine sediments of Taizhou, an
441 intense e-waste recycling area in eastern China. *Chemosphere* 184, 1202–1208.
442 doi:10.1016/j.chemosphere.2017.06.104.

443

444 **Figure captions**

445 **Figure 1.** Quantity (raw data minus mean blank, pg per sample) of *anti*-DDC-CO versus *syn*-DDC-CO
446 when both values were above LoR, for all food categories. Brackets: number of plots out of
447 number of assayed samples.

448

449 **Table 1.** Concentration of DRCs obtained for various food groups from Lebanese market, reported according to lowerbound (LB) and upperbound (UB)
 450 approaches, in pg g^{-1} ww. DF: detection frequency.

Food group		<i>syn</i> -DDC-CO	<i>anti</i> -DDC-CO	DDC-ID	DDC-DBF	DDC-Ant	DDC-PDD	Σ DDC-CO	Σ_6 DRC
Meat and Poultry (<i>n</i> =12)	Mean [LB-UB]	[10.1 - 11.8]	[7.4 - 8.1]	[0.0 - 0.2]	[0.0 - 0.7]	[0.1 - 0.3]	[0.0 - 0.05]	[17.4 - 19.9]	[17.5 - 21.1]
	DF (%)	25	83	0	0	17	0	83	92
Fish (<i>n</i> =21)	Mean [LB-UB]	[2.0 - 4.2]	[3.0 - 3.9]	[0.0 - 0.3]	[7.0 - 7.8]	[0.2 - 0.3]	[0.4 - 0.5]	[5.0 - 8.0]	[12.6 - 16.8]
	DF (%)	57	95	0	62	33	62	100	100
Egg (<i>n</i> =5)	Mean [LB-UB]	[1.7 - 3.1]	[5.2 - 5.8]	[0.0 - 0.3]	[1.2 - 1.7]	[0.2 - 0.4]	[1.36 - 1.41]	[6.9 - 8.9]	[9.6 - 12.7]
	DF (%)	40	80	0	20	20	20	100	100
Milk and Dairy Products (<i>n</i> =13)	Mean [LB-UB]	[1.0 - 2.0]	[0.7 - 1.1]	[0.0 - 0.1]	[2.9 - 3.3]	[0.05 - 0.1]	[0.01 - 0.03]	[1.7 - 3.1]	[4.7 - 6.7]
	DF (%)	31	69	0	54	31	8	77	92
Fat and oils added at table (<i>n</i> =7)	Mean [LB-UB]	[2.4 - 25.0]	[18.7 - 27.9]	[0.0 - 4.6]	[3.0 - 11.8]	[2.3 - 3.9]	[3.2 - 3.7]	[21.1 - 52.8]	[29.5 - 76.9]
	DF (%)	14	57	0	29	29	14	57	57

451

452

453 **Table 2.** Estimated mean daily intakes of Σ DDC-CO and Σ_6 DRC [LB – UB] for the adult population in Beirut, in $\mu\text{g day}^{-1}$.

Food group	Mean of dietary intake, g day^{-1}	Σ DDC-CO	Σ_6 DRC	Contribution to Σ DDC-CO (%)	Contribution to Σ_6 DRC (%)	
Meat and Poultry (n=12)	91.7	[1597 - 1818]	[1607 - 1933]	[61% - 46%]	[43% - 34%]	
Fish (n=21)	19.7	[99.5 - 158]	[248 - 332]	[4% - 4%]	[7% - 6%]	
Egg (n=5)	12.1	[84 - 108]	[117 - 154]	[3% - 3%]	[3% - 3%]	
Milk and Dairy Products (n=13)	243.1	[418 - 760]	[1140 - 1622]	[16% - 19%]	[31% - 29%]	
Fat and oils added at table (n=7)	20.4	[430 - 1078]	[602 - 1569]	[16% - 27%]	[16% - 28%]	
Total	387.0	[2629 - 3922]	[3713 - 5609]	100%	100%	
Contribution (%)		[71% - 70%]	100%	100%	100%	
Food group	<i>syn</i> -DDC-CO	<i>anti</i> -DDC-CO	DDC-ID	DDC-DBF	DDC-Ant	DDC-PDD
Meat and Poultry (n=12)	[922 - 1079]	[675 - 739]	[0 - 22.7]	[0 - 61.4]	[9.6 - 26.3]	[0 - 3.9]
Fish (n=21)	[40.3 - 81.9]	[59.2 - 76.1]	[0 - 5.1]	[137 - 154]	[3.2 - 6.6]	[7.9 - 8.3]
Egg (n=5)	[20.9 - 38]	[63.1 - 70.0]	[0 - 3.4]	[14.2 - 20.9]	[1.9 - 4.4]	[16.5 - 17]
Milk and Dairy Products (n=13)	[253 - 496]	[165 - 264]	[0 - 27.9]	[709 - 804]	[11.1 - 23.8]	[1.6 - 6.7]
Fat and oils added at table (n=7)	[48.2 - 509]	[382 - 569]	[0 - 94.3]	[60.9 - 241]	[46 - 79.8]	[65.7 - 76]
Total	[1285 - 2204]	[1344 - 1718]	[0 - 153]	[921 - 1281]	[71.8 - 141]	[91.7 - 112]
Contribution (%)	[34% - 39%]	[36% - 31%]	[0% - 3%]	[25% - 23%]	[2% - 3%]	[2% - 2%]

454

455

456 **Table 3.** Estimated daily intakes of $\Sigma_6\text{DRC}$ [LB – UB] for the adult population in Beirut according to
457 gender and age, in pg day^{-1} .

Gender	Age (year)			
	25-34	35-44	45-54	25-54
Men	[4511 – 6749]	[4221 – 6420]	[3813 – 5829]	[4220 – 6382]
Women	[3381 – 5048]	[3278 – 4928]	[3066 – 4710]	[3257 – 4911]

458

- Eggs (n=2/5)
- × Fat and oils (n=1/7)
- ◆ Fish (12/21)
- Meat and poultry (n=3/12)
- ▲ Milk and dairy products (n=4/13)



