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

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

Inas Abdel Malak[1,2], Ronan Cariou[1,*], Ingrid Guiffard[1], Anaïs Vénisseau[1], Gaud Dervilly-Pinel[1], Farouk Jaber[2], Bruno Le Bizec[1]

[1]LABERCA, Oniris, INRA, F-44307, Nantes, France.

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

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

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

Keywords

Chlorinated flame retardants
Environmental contaminants
Ultra-trace measurement
Food analysis
Human intake
Chemical Risk

Abstract

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

1. Introduction

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

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

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

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

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

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

2. Materials and methods

2.1. Sample collection and storage

A total of 58 food samples, considered as representative of the average consumption of fatty food groups of animal and vegetable origins for the Lebanese population (Nasreddine et al., 2006), were collected in June 2017 from supermarkets located in Beirut (Lebanon). Nutritional categories included meat (n=12), fish (n=21), egg (n=5), milk and dairy product (n=13), fat and oils added at table (n=7). More precisely, collected samples were: chicken meat (n=6), bovine meat (n=3), bovine liver (n=3), boops (n=3), gilt head bream (n=2), mackerel (n=2), whiting (n=2), anchovy (n=2), grouper (n=5), blackspot seabream (n=2), European bass (n=2), other fish (n=1), egg (n=5), milk (n=5), labne (n=4), yogurt (n=4), olive oil (n=4) and sesame oil (n=3). The food samples were weighed, homogenized, lyophilized (except for oil), homogenized again and stored at -20 °C until analysis.

2.2. Quantification of DRCs in samples

Trace analysis of targeted DRCs (*anti*-DDC-CO, *syn*-DDC-CO, DDC-ID, DDC-DBF, DDC-Ant and DDC-PDD) was performed according to previously published work (Abdel Malak et al., 2018), pending minor modifications in sample preparation. Briefly, lyophilized samples (approximately 3 g for fish or 4 g for meat, egg and dairy products) were extracted by Pressurized Liquid Extraction (Büchi, SpeedExtractor, E-914), except for oil samples (1 g). The lipid content was determined gravimetrically. Purification of the extracts involved a multilayer silica gel column (acidic, neutral and basic layers) followed by Gel Permeation Chromatography. Purified extracts were analysed by gas chromatography (6890, HP, Palo Alto, CA, USA) on a HT8-PCB column (30 m × 0.25 mm, SGE Analytical Science, Ringwood, Australia) coupled to high resolution mass spectrometry (JMS 700D, Jeol, Tokyo, Japan), operating at a resolution of 10,000 according to 10% valley definition, in the electron impact ionisation mode and in a single sequence. Identification was based on two ion traces. Determination of DDC-ID, known to be challenging, was made possible by the successful chromatographic separation from *syn*-DDC-CO monitored with the same ion ($[C_5Cl_6]^+$) in electron impact (Adbel Malak et al., 2018). Quantification was performed through isotopic dilution using $^{13}C_{10}$-*syn*-DDC-CO, $^{13}C_{10}$-*anti*-DDC-CO and $^{13}C_{10}$-DDC-DBF as internal standards, and $^{13}C_{12}$-PCB-194 as recovery standard. Diagnostic ions are described Table S2.

2.3. QA/QC and reporting

Samples were analysed through four successive series of 10 to 20 samples. Recovery rates, determined for each sample, reached averages of 74 ± 14%, 59 ± 15% and 92 ± 10% for $^{13}C_{10}$-*syn*-DDC-CO, $^{13}C_{10}$-*anti*-DDC-CO and $^{13}C_{10}$-DDC-DBF, respectively. Six procedural blanks (started from the extraction step) were introduced within the series to monitor procedural contamination. If procedural contamination was observed, a limit of reporting (LoR) was set at mean plus 3 times the standard deviation of the procedural blank. Otherwise, a limit of quantification (LOQ) was set for each sample based on a signal to noise ratio of 3:1 for the less intense signal. Trace amounts of *syn*-DDC-CO, *anti*-DDC-CO and DDC-DBF were always detected in procedural blanks, at values in the 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, respectively. For the other target compounds, LOQs were in the 1.2-14.5, 1.3-18.8 and 0.3-1.4 pg ranges per sample, respectively for DDC-ID, DDC-Ant and DDC-PDD.

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

2.4. Data processing

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

3. Results and discussion

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

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

3.1. Concentrations of ∑DDC-CO

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

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

Concerning vegetable oils, the mean concentration of ∑DDC-CO (21.1 to 52.8 pg g^{-1} lw, [LB-UB]) was in the same order of magnitude as those reported in vegetable oils (*n*=2) from Spain (average of

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} ww) (Yasutake et al., 2018).

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

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

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

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

3.2. Profiles of DDC-CO isomers

The commercial mixture of DDC-CO exhibits two stereoisomers, *anti*- and *syn*-DDC-CO, in a ratio of about 3:1 (Feo et al., 2012). The corresponding enantiomeric fraction of *anti*-DDC-CO (f_{anti}), defined as the levels ratio of *anti*-DDC-CO over ∑DDC-CO, reaches 0.75. In biota, various authors reported values of f_{anti} at 0.6 ± 0.2, depending on the origin of the sample (Kang et al., 2010; Wang et al., 2011; Von Eyken et al., 2016), due to specific enrichment in *syn*-DDC-CO in the environment. In our study, depending on the food item considered, the f_{anti} values, when quantified, ranged from 0.26 to 0.76 (Figure 1), which were close to, or lower than, the values in the technical product, and similar to those reported in the literature (Kim et al., 2014; L'Homme et al., 2015; Von Eyken et al., 2016; Wang et al., 2016). The highest value of f_{anti} (0.76) was obtained from an olive oil sample, suggesting that, in this unique case of a food item of vegetable origin, the contamination could have occurred by direct contact with the technical product, with no biological enrichment observed. Inversely, the lowest values of f_{anti}, close to 25%, were found in dairy product samples, suggesting a significant enrichment in *syn*-DDC-CO through the producing mammal organisms, possibly involving lactation, and/or fermentation. For the fish samples, the f_{anti} ranged between 0.38 and 0.62 with a mean value equal to 0.50 ± 0.08, which appeared similar to that of the commercial product and those reported in fish samples in the literature (Kakimoto et al., 2012; Wang et al., 2015; Sühring et al. (2015).

3.3. Concentration of other DRCs

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

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

Similarly, DDC-PDD was detected in 28% of all investigated foods at rather low concentrations (<2.9 pg g^{-1} ww), except for one sesame oil and an egg samples at 22.5 and 6.8 pg g^{-1} ww (UB), respectively. These concentrations were globally higher than those reported in food from Belgium and Japan, but lower compared to those reported from China, which were in the ng g^{-1} lw range (Wang et al., 2015).

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

3.4. Correlation among Dechloranes

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

3.5. Estimation of DRCs dietary intake

The Lebanese adult population (25-54 years old) was considered in the objective of proposing a first reference point for further studies in the geographical area. The occurrence levels of DRCs determined in the selected set of foodstuffs were used to perform a deterministic dietary exposure assessment, according to recognised guidelines (FAO-WHO, 2009; EFSA-FAO-WHO, 2011). The estimations of DRCs daily intake were calculated by the addition of quantities determined for each food item by multiplying the average concentration of DRCs (pg g^{-1} ww) in the considered food item (Table 1) with the daily dose of the considered food item (g day^{-1}). Based on the study of food habits described by Nasreddine et al. (2006), the average total food intake per person and per day in Lebanon is 1881.6 g, including beverages except water. The collected food samples made up 387 g per person per day in Lebanon (21% of the total food intake), covering all food from animal origin and vegetable oils, the expected major dietary intake contributors for such lipophilic environmental contaminants.

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

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

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

than for women (between 3.257 (LB) and 4.911 (UB) ng day^{-1}) (Table 3, Figure S3). The main reason is that men ingest more food than women (403.4 versus 371.9 g day^{-1}) for all considered food groups except for milk and dairy products group (227.4 versus 257.1 g day^{-1}, respectively). For similar reasons of decreasing food consumption with age, the estimated daily intake of $\sum_6$DRC has a downward trend as age increases.

4. Conclusions and perspectives

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

Acknowledgements

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

References

Abdel Malak, I., Cariou, R., Vénisseau, A., Dervilly-Pinel, G., Jaber, F., Babut, M., Le Bizec, B., 2018. Occurrence of Dechlorane Plus and related compounds in catfish (*Silurus spp.*) from rivers in France. Chemosphere 207, 413–420. doi:10.1016/j.chemosphere.2018.05.101.

Aznar-Alemany, Ò., Trabalón, L., Jacobs, S., Barbosa, V.L., Tejedor, M.F., Granby, K., Kwadijk, C., Cunha, S.C., Ferrari, F., Vandermeersch, G., Sioen, I., Verbeke, W., Vilavert, L., Domingo, J.L., Eljarrat, E., Barceló, D., 2016. Occurrence of halogenated flame retardants in commercial seafood species available in European markets. Food Chem. Toxicol. 104, 35–47. doi:10.1016/j.fct.2016.12.034.

Jondreville, C., Cariou, R., Travel, A., Belhomme, L.J., Dervilly-Pinel, G., Le Bizec, B., Huneau-Salaün, A., Le Bouquin-Leneveu, S., 2017. Hens can ingest extruded polystyrene in rearing buildings and lay eggs contaminated with hexabromocyclododecane. Chemosphere 186, 62–67. doi:10.1016/j.chemosphere.2017.07.117.

Bergman, Å., Rydén, A., Law, R.J., de Boer, J., Covaci, A., Alaee, M., Birnbaum, L., Petreas, M., Rose, M., Sakai, S., Van den Eede, N., van der Veen, I., 2012. A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. Environ. Int. 49, 57–82. doi:10.1016/j.envint.2012.08.003.

Bergman, Å., Rydén, A., 2019. Personnal communication.

Brasseur, C., Pirard, C., Scholl, G., De Pauw, E., Viel, J.F., Shen, L., Reiner, E.J., Focant, J.F., 2014. Levels of Dechloranes and polybrominated diphenyl ethers (PBDEs) in human serum from France. Environ. Int. 65, 33–40. doi:10.1016/j.envint.2013.12.014.

Cequier, E., Marcé, R.M., Becher, G., Thomsen, C., 2013. Determination of emerging halogenated flame retardants and polybrominated diphenyl ethers in serum by gas chromatography mass spectrometry. J. Chromatogr. A 1310, 126–132. doi:10.1016/j.chroma.2013.08.067.

Chen, D., Letcher, R.J., Burgess, N.M., Champoux, L., Elliott, J.E., Hebert, C.E., Martin, P., Wayland, M., Chip Weseloh, D. V., Wilson, L., 2012. Flame retardants in eggs of four gull species (*Laridae*) from breeding sites spanning Atlantic to Pacific Canada. Environ. Pollut. 168, 1–9. doi:10.1016/j.envpol.2012.03.040.

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

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

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

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

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

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

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

Giulivo, M., Capri, E., Kalogianni, E., Milacic, R., Majone, B., Ferrari, F., Eljarrat, E., Barceló, D., 2017. Occurrence of halogenated and organophosphate flame retardants in sediment and fish samples from three European river basins. Sci. Total Environ. 586, 782–791. doi:10.1016/j.scitotenv.2017.02.056.

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

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

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

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

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

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

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

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

Nasreddine, L., Hwalla, N., Sibai, A., Hamzé, M., Parent-Massin, D., 2006. Food consumption patterns in an adult urban population in Beirut, Lebanon. Public Health Nutr. 9, 194–203. doi:10.1079/phn2005855.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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. Dechlorane Plus in serum from e-waste recycling workers: Influence of gender and potential isomer-specific metabolism. Environ. Int. 49, 31–37. doi:10.1016/j.envint.2012.08.011.

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

Figure captions

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

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

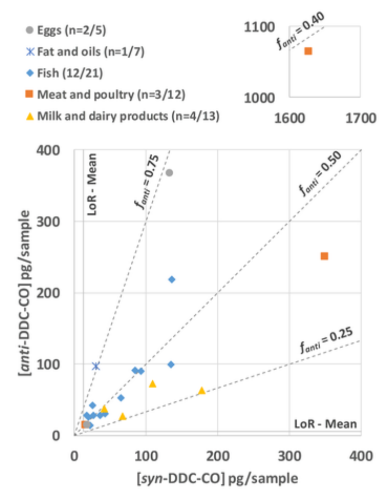
Food group		***syn*-DDC-CO**	***anti*-DDC-CO**	**DDC-ID**	**DDC-DBF**	**DDC-Ant**	**DDC-PDD**	**$\sum$DDC-CO**	**$\sum_6$DRC**
Meat and Poultry (*n*=12)	Mean [LB-UB]	[10.1 - 11.8]	[7.4 - 8.1]	[0.0 - 0.2]	[0.0 - 0.7]	[0.1 - 0.3]	[0.0 - 0.05]	[17.4 - 19.9]	[17.5 - 21.1]
	DF (%)	25	83	0	0	17	0	83	92
Fish (*n*=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 (*n*=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 (*n*=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 (*n*=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

Table 2. Estimated mean daily intakes of ∑DDC-CO and $\sum_6$DRC [LB – UB] for the adult population in Beirut, in pg day^{-1}.

Food group	**Mean of dietary intake, g day^{-1}**	**∑DDC-CO**	**$\sum_6$DRC**	**Contribution to ∑DDC-CO (%)**	**Contribution to $\sum_6$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	***syn*-DDC-CO**	***anti*-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%]

Table 3. Estimated daily intakes of $\sum_6$DRC [LB – UB] for the adult population in Beirut according to 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]



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)
f_{anti} = 0.40
1100
1000
1600
1700
400
300
200
100
0
0
100
200
300
400
LoR - Mean
f_{anti} = 0.75
f_{anti} = 0.50
f_{anti} = 0.25
LoR - Mean
[anti-DDC-CO] pg/sample
[syn-DDC-CO] pg/sample


LEBANON
Tripoli
Baalbek
Beyrouth
Mediterranean
Sea
Saïda
Marjayoun
Tyr