Dechlorane Related Compounds dietary exposure in the Lebanese population

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Introduction

Although raising concerns regarding their Persistent Organic Pollutant-like properties, Dechlorane Related Compound (DRCs) constitute a group of polychlorinated flame retardants that are still used [1]. In particular, Dechlorane Plus (DP) has been detected in various environmental matrices, aquatic, terrestrial biota and in human [2], thus exhibiting bioaccumulation and biomagnification potentials [3]. The commercial DP product primarily contains two stereoisomers, *syn*-DP and *anti*-DP, with a ratio of approximately 1:3 [3]. Little information regarding other DRCs such as Dechlorane 601 (Dec 601, $C_{20}H_{12}Cl_{12}$), Dechlorane 602 (Dec 602, $C_{14}H_4Cl_{12}O$), Dechlorane 603 (Dec 603, $C_{17}H_8Cl_{12}$), and Chlordene Plus (CP, $C_{15}H_6Cl_{12}$) is available in the literature. The human can be exposed to DRCs by food consumption, dust inhalation and indoor air and dermal routes [4]. Hence the human exposure pathway to DRCs has recently received growing attention. However, until now, there is little information and data on DRCs dietary exposure.

In the present work, an analytical method has been developed for the analysis of DRCs in food items by GC-EI-HRMS using multilayer silica and gel permeation columns for sample purification [5]. This method was applied to the investigation of DRCs in Lebanese food and subsequent evaluation of dietary exposure.

Materials and methods

Chemicals

Analytical standards of *syn*-DP, *anti*-DP, Dec-601, -602, -603, CP and the external standard $^{13}C_{12}$-PCB-194 were obtained from Wellington Laboratories. $^{13}C_{10}$-labelled internal standards of *anti*-DP, *syn*-DP and Dec-602 were purchased from Cambridge Isotope Laboratories.

Samples

In June 2017, a total of 58 Lebanese food samples were collected from retail stores located in Beirut, Lebanon. Various commonly consumed food groups were included: olive oil (n=4), sesame oil (n=3), chicken muscle (n=6), beef muscle (n=3), bovine liver (n=3), fish filet (n=21), egg (n=5), milk (n=5) and dairy product (*labné* (n=4) and yogurt (n=4)). After homogenization and lyophilisation, the samples were extracted with a mixture of toluene/acetone (7:3, *v/v*) using a Pressurized Liquid Extraction. The extract was cleaned up on a multilayer (neutral/basic/neutral/acidic 22%/acidic 44%) silica gel column using *n*-hexane as mobile phase, followed by gel permeation chromatography (mobile phase: mixture of ethyl acetate/cyclohexane 1:1, *v/v*). The purified solution was evaporated to dryness under a gentle stream of N_2 and reconstituted in 20 µL of toluene.

Instruments

Extracts were analysed by gas chromatograph coupled to a high resolution double sector mass spectrometer Electron ionization was set at 38 eV (GC-EI-HRMS). GC separation was performed using a HP 6890 instrument (HP, Palo Alto, CA, USA). The capillary column was a HT8-PCB (30 m x 0.25 mm). Extracts were injected in the splitless mode at 280 °C. The oven temperature program started at 100 °C (2 min), rose to 280 °C at 25 °C.min^{-1}, then ramped to 325 °C at 5 °C.min^{-1} (5 min). Helium at 1 mL.min^{-1} was used as carrier gas. Auxiliary and source temperatures were set at 280 °C. HRMS measurements were achieved on a JMS 700D electromagnetic instrument (Jeol, Tokyo, Japan), operating at a resolution of 10,000 at 10% valley. The target analytes were detected in the Selected Ion Monitoring acquisition mode.

QA/QC
Five fish oil samples fortified at 4 ng were analysed as a quality controls. Trace amounts of Dec-602, *anti*-DP and *syn*-DP were detected in the procedurals blanks. The obtained Limits of Reporting (LoR = mean value detected in the blanks plus three times the standard deviation) were 9.07, 9.42 and 23.2 pg for Dec-602, *anti*-DP and *syn*-DP, respectively. The limit of detection (LOD) of the method was calculated for each sample at signal to noise (S/N) ratio better or equal to 3.

Reporting of the results
Considering that rather low DRC levels were observed in this study, the results were reported as both lower-bound (LB) and upper-bound (UB) values. LB underestimating approach consisted in reporting zero for the target analyte whenever the level measured in the sample was below LOD (for Dec-601, Dec-603 and CP) or LoR (for Dec-602, *anti*-DP and *syn*-DP), or subtracting the limit (LoR, LOD) whenever the level measured in the sample was above. The UB overestimating approach consisted in reporting LOD or LoR values whenever the measured level was below such limits.

Results and discussion
Quantification of DRCs
DP was detected in 38% of samples, up to 159 pg/g wet weight (ww) with an average comprised between 8.96 (LB) and 14.86 (UB) pg/g ww. The highest concentration of DP was detected in a meet sample. Detection frequencies of Dec-602 was 40% in all foodstuffs. The concentrations of Dec-602 were ranging from ≤ LoR to 96 pg/g ww with an average comprised between 3.64 (LB) and 5.27 (UB) pg/g ww. The highest concentration of Dec 602 was found in a fish sample. For others compounds, detection frequencies were 28%, 2% and 28% respectively for CP, Dec-601 and Dec-603 in all foodstuffs. CP were ranged from ≤ LOD to 22.54 pg/g ww with a mean value comprised between 0.65 (LB) and 0.74 (UB) pg/g ww. Dec-603 were ranged from ≤ LOD to 8.07 pg/g ww with a mean value between 0.38 (LB) and 0.71 (UB) pg/g ww. Dec-601 was detected in only one sample (sesame oil), at 12 pg/g ww. The highest concentration of Dec 603 and CP was detected in a sesame oil sample. The obtained concentrations for each targeted DRC in each food group are summarized in **Table 1**. DP was the most contributor compounds in all food group. The highest mean concentration of DP was detected in vegetable oil group.

Table 1: Obtained detection frequencies (DF) and concentrations (mean ± std in pg/g ww) of DRCs in foodstuff samples from Lebanon market.

Food group		anti-DP	syn-DP	Dec-601	Dec-602	Dec-603	CP
Meat and	DF	83%	25%	0%	0%	17%	0%
Poultry (n=12)	LB	7.36 ± 18.3	10.1 ± 28.0	0	0	0.10 ± 0.25	0
	UB	8.06 ± 18.2	11.8 ± 27.9	0.25 ± 0.21	0.67 ± 0.46	0.29 ±0.31	0.04 ± 0.03
Fish (n=21)	DF	95%	57%	0%	62%	33%	62%
	LB	3.00 ± 4.13	2.05 ± 3.29	0	6.97 ± 20.9	0.16 ± 0.39	0.4 ± 0.73
	UB	3.86 ± 4.23	4.16 ± 3.88	0.26 ± 0.18	7.79 ± 20.8	0.33 ± 0.35	0.42 ± 0.72
Egg (n=5)	DF	80%	40%	0%	20%	20%	20%
	LB	5.22 ± 11.1	1.73 ± 3.68	0	1.17 ± 2.63	0.16 ± 0.36	1.36 ± 3.05
	UB	5.79 ± 11.1	3.14 ± 3.79	0.28 ± 0.09	1.73 ± 2.67	0.36 ± 0.25	1.41 ± 3.02
Milk and Dairy	DF	69%	31%	0%	54%	31%	8%
product (n=13)	LB	0.68 ± 1.00	1.04 ± 1.89	0	2.92 ±5.79	0.05 ± 0.08	0.01 ± 0.02
	UB	1.09 ± 1.03	2.04 ± 1.89	0.11 ± 0.06	3.31 ± 5.85	0.10 ± 0.06	0.03 ± 0.02
Vegetable oil	DF	57%	14%	14%	29%	29%	14%
(n=7)	LB	18.7 ± 32	2.36 ± 6.25	1.7 ± 4.5	2.98 ± 6.29	2.25 ± 3.85	3.22 ± 8.52
	UB	27.9 ± 32.1	25 ± 6.24	4.62 ± 3.33	11.8 ± 6.39	3.91 ± 2.72	3.72 ± 8.3

Daily intake

The estimation of daily intake was performed according to previously published food habits for the Lebanese adult population [6], by multiplying the average concentration (pg/g ww) of DRCs with the food group daily dose (g/day). Only food groups of animal origin and vegetable oils were considered. Among these food groups, milk and dairy products represent the highest mean consumption habits (243.1 g/day) and egg represent the least (12.1 g/day). **Figure 1** presents the obtained results. The dietary daily intake of Sum DRCs was estimated to be between 3.75 (LB) and 5.61 ng/day (UB). The highest level of dietary daily intake was found in meat and poultry food groups while the least was obtained in egg.

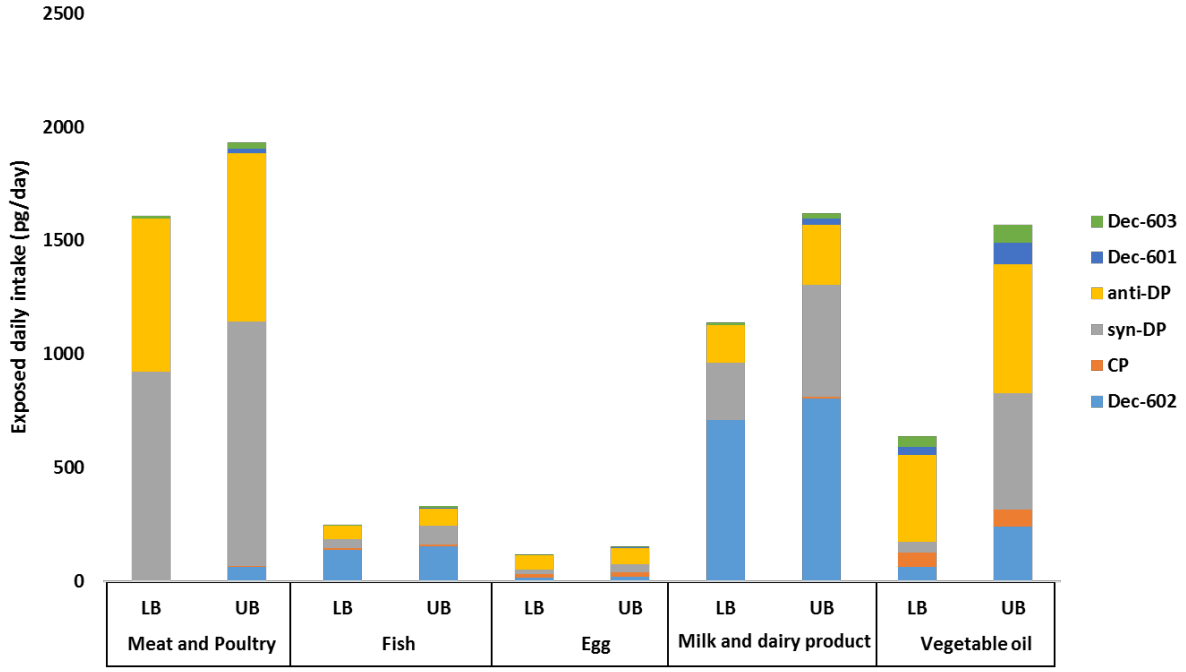

Figure 1. Mean daily intakes (pg/day, LB and UB) of DRCs for selected food groups.

Conclusion and perspectives

A robust analytical method has been developed and applied to a series of foodstuff samples from Lebanon in order to estimate the daily intake of DRCs. The observed levels were rather low in order of pg/g ww. Recent studies have investigated the contamination status and dietary intake of DRCs in various food and seafood matrices in Japan (DP = 134 pg/day) [7], Korea (DP, Dec 602 and Dec 603 = 11,7 ng/day) [4] and Belgium (Mirex, Dec 602, Dec 603, CP and DP = 136 pg/day) [8]. However, toxicological reference values are expected to initiate assessment full risk characterization regarding Lebanese consumer's exposure to DCs.

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