CHLORINATED PARAFFIN EXPOSURE THROUGH FOOD: A RAW FOOD AND MEAL STUDY IN SOUTHERN GERMANY

Krätschmer K[1,2], Schächtele A[1], Malisch R[1], Vetter W[2]

[1] European Union Reference Laboratory (EURL) for Halogenated POPs in Feed and Food, Freiburg, Germany, 79114, kerstin.kraetschmer@cvuafr.bwl.de; [2]University of Hohenheim, Institute of Food Chemistry (170b), Stuttgart, Germany, 70599

Introduction

Chlorinated paraffins (CPs) are highly complex mixtures of different carbon chain lengths and chlorination degrees produced by radical chlorination of alkane feedstock. They are classified by their range of carbon chain lengths into short chain (SCCPs, C_{10-13}), medium chain (MCCPs, C_{14-17}) and long chain CPs (LCCPs, $C_{>17}$). Based on publicly available data, annual production of CPs has been estimated at more than one million tons[1], which almost equals the total production volume of PCBs estimated at 1.3 million tons between 1929 and 1993[2]. CPs are mainly used as plasticizers and flame retardants in a wide variety of products. When released into the environment, CPs accumulate through the food chain in lipid tissue of fish or other animals, leading to human exposure by means of both food intake and environmental influences. Past market basket studies have analysed a variety of raw foods as basis for exposure estimations[3,4,5]. However, these estimation did not take into account that CPs have also been found in a variety of kitchen appliances and utensils[6,7,8] and that food preparation has been shown to influence CP contamination in a cooking study[9]. The study presented here included besides raw foods also full meals to account for the true exposure including possible influences of packaging or preparation.

Materials and methods

Raw food samples. The raw food samples were collected from supermarkets and vendors as part of the official food control in Baden-Württemberg, Germany, between September 2018 and April 2019.

Full meal samples. Full meal samples were collected from gastronomy and caterers in Baden-Württemberg, Germany as part of official food control in the food containers provided to consumers immediately before consumption. Additionally, total diet samples including breakfast, lunch and dinner provided to patients were obtained from a hospital in Freiburg, Germany along with a detailed meal plan.

Preparation and analysis. All samples were homogenised and prepared as described elsewhere[10]. CPs were determined using a GC-ECNI-Orbitrap-HRMS system and single chain standards for SCCPs and MCCPs provided by University of Hohenheim, Stuttgart, Germany. The detailed method has already been described elsewhere[10]. In brief, the single chain standards were used to determine relative response factors for each CP homologue, then assigning concentrations to homologues in individually designed standard mixtures used for calibration.

QAQC. All measurements were carried out in duplicate, if possible. Ions were considered positively identified when retention time, accurate mass and ion ratios of at least two isotopes matched the compound database. Fluctuations due to injection or different tuning were corrected by using ε-HCH as injection standard. Every batch contained also a QC standard whose SCCP and MCCP concentration could not differ more than 20% from the assigned value. If possible, all measurements were carried out using a freshly cleaned ion source and a new tune and mass calibration to ensure the system working at optimal conditions.

Results and discussion

Raw food samples

The comparison of homologue patterns throughout the food groups revealed some common characteristics for eggs, pork/poultry, beef and dairy products. However, differences in farming and processing obviously resulted in strong differences in the patterns, hinting at a variety of contamination sources in the production process in addition to in the raw food material itself.

Especially noteworthy were also minced beef and poultry samples which contained S-, M- and LCCPs, whereas different vegetable oils (especially after processing) showed homologue patterns very similar to known technical mixtures of SCCPs (Figure 1). Both findings support the hypothesis of strong procedural contamination during food production.

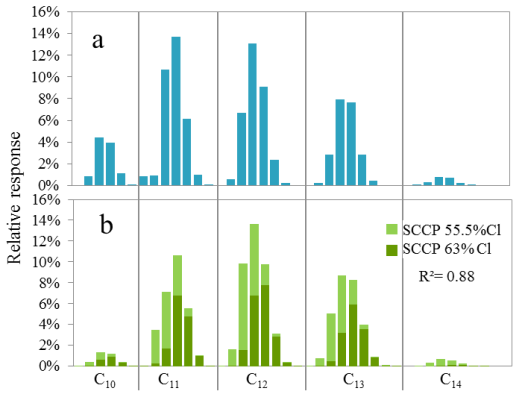

Figure 1. Relative response CP homologue patterns of (a) processed coconut oil and (b) technical SCCP mixtures.

CP levels in raw foods were in good agreement with levels reported in earlier studies from Sweden[3], Great Britain[4] and Japan[5], although with some very high levels for fish and vegetable oils (Table 1). Only eggs showed a tenfold higher CP amount in our study than in all other studies, though the reasons for this finding are as of yet still unknown. Noteworthy, the type of farming (organic, conventional) or cut of meat did not have a strong impact on CP levels throughout the food group, although varying lipid levels resulted in differing results when calculated in ng/g wet weight (ww).

Table 1. Total CP amount in raw food analysed for market basket studies 2005-2019 given as ranges for each food group. Results from Japan are SCCPs only.

	Total CP amounts from market basket studies [ng/g ww]			
Food group	Present study (no. of samples)	Sweden 2015[3]	UK 2009[4]	Japan 2005[5]*
Meat and offal	1.4-12 (17)	n.d.	<2.0-12	6.6-7.0
Eggs	14-23 (5)	n.d.	n.d.	2.0-2.7
Milk and dairy	0.5-17 (6)	n.d.	4.1	0.8-1.6
Fish	1.8-360 (13)	9.7	<2.0-38	16-17
fats and oils	15-800[#] (8)	14.5	-	140-150

n.d. = not detected/below method limit of detection *results are sum of SCCPs only [#]assuming 100% fat content

Full meal and total diet samples

The analysis of full meal samples yielded much lower CP concentrations than for the raw food components (Table 2). On one hand, this was expected because the full meals often also included other, mostly plant-based components like vegetables, rice or bread which de-facto diluted any possible CP contamination of food components of animal origin. Additionally, a cooking study showed that CPs can be reduced during the heating and cooking of meals[8]. This might be the case also in our meal samples. On the other hand, even fried food or meals with several components containing CPs when analysed as raw food had very low total CP levels. It is possible that a certain amount of CPs was not properly extracted by the cold extraction method applied here, which is supported by a markedly lower level of recovery for full meal samples than for raw food samples. Thus, further investigation into better suited extraction methods might be beneficial to this kind of survey in the future.

Table 2. Sum of CP, SCCP and MCCP amount determined in full meal samples given in ng/g ww. Numbers of samples analysed per group are indicated in brackets.

Sample group	sum of CP [ng/g ww]	SCCP [ng/g ww]	MCCP [ng/g ww]
Full meal			
- Meat-based (8)	2.7-17	1.8-8.9	1.0-7.8
- Vegetarian (2)	1.8-3.7	1.2-1.9	0.6-2.0
Total diet samples			
- Light diet (3)	1.1-2.7	1.0-2.1	0.4-1.1
- Full diet (2)	8.9-9.0	4.0-4.7	4.3-4.8

Interestingly, the total diet samples with cooked and uncooked foods only showed in one case a recognizable CP homologue pattern that could be matched with raw food samples; in this case, the pattern was similar to CPs in Chester or soft cheese (Figure 2). This fits the menu plan, as cream cheese and a cheese salad as well as a gratin with cheese were served to vegetarians that day. In general, the number of full meal and total diet samples that could be matched to raw food was relatively low, partly because not all major components were available as raw food samples for comparison, partly due to the very low percentages and comparatively high number of individual components in the meals obscuring distinctive patterns. Full meal samples had a few more matches among the raw food samples, as the percentages of these foods in the serving were higher. In two of those cases, pork from a roast served with vegetables and rice and minced beef from Greek-style meat balls with vegetables seem to have been the dominant CP sources in the samples. Still, not the whole pattern could be explained with the available raw food patterns, thus pointing towards further relevant ingredients or procedural contamination from the cooking process causing the unexplained MCCP contamination.

It is furthermore to be noted that the full diet samples had a higher contamination than the light diet, regardless of them being vegetarian or including meat. This can be explained by the meal plan – a full diet includes a major protein source for lunch and dinner (e.g. beef and ham or potato gratin and cheese salad). Based on our findings in raw foods, these particular foods are also major CP sources due to a higher fat content. Contrary to expectation, the light diet samples did not show an increase in CP content even if they mostly contained fish-based meals for lunch. Additionally, the percentage of fish in the samples was too low to allow for characteristic fish homologue patterns to emerge. Since part of the light diet approach includes smaller portions, this might have factored in to the de-facto dilution of any contamination.

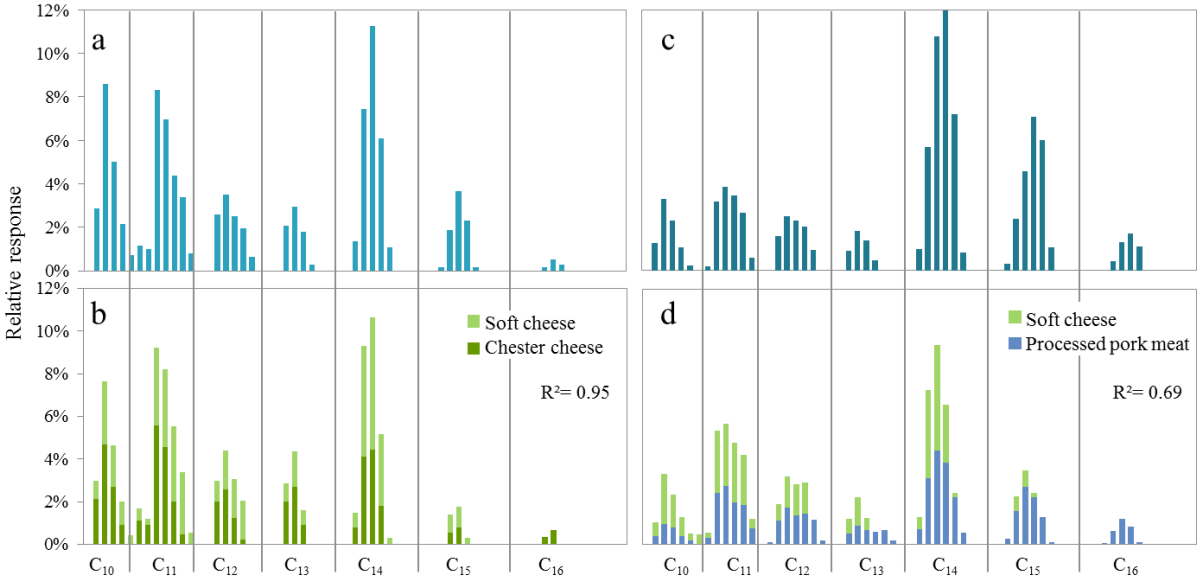

Figure 2. Relative response CP homologue patterns of total diet and full meal samples with corresponding raw food patterns. The total diet sample (a) could be well matched to a combination of soft cheese and Chester cheese (b), while the full meal "pig roast filled with ham and cheese, served with vegetable rice" (c) could not completely be explained by processed pork meat and soft cheese (d), as evidenced by the low correlation.

Exposure estimation

Using the mean and maximum total CP levels for each raw food group, the estimated exposure for the mean and 95th percentile of consumers was calculated for adults in Germany based on official data on food consumption[11,12]. As not all consumers have a high consumption in all food categories, a marker for total exposure through food was calculated using the 95th percentile for consumers of only the two food categories contributing most to daily intake added to the mean exposure of the total population for the remaining categories as described elsewhere[11]. This approach has proven to give an appropriate 97.5th percentile of total exposure. The calculated total exposure to CPs based on raw food for adults in Germany was 0.24-0.86 µg/kg bw/day. The highest contribution to that exposure was made by highly contaminated processed vegetable oils (Table 3).

Table 3. Exposure estimation for adults in Germany based on consumption data of consumers and the total population (includes also persons that to not consume a given product group, e.g. vegan people). Given are the results for mean and maximum total CP contamination of each food or sample group.

Food group/ Sample group	consumers only [ng/kg bw/day]			total population [ng/kg bw/day]		
	mean	95th perc.	97.5th perc.	mean	95th perc.	97.5th perc.
Meat	8.3-18	20-42	24-52	7.7-17	19-42	23-51
Eggs	6.2-9.0	15-21	17-25	1.5-2.2	8.4-12	12-18
Milk and dairy	21.6-46	61-130	75-160	21-45	60-130	75-160
Fish	42-320	100-780	120-930	11-81	65-490	82-620
Fats and oils	64-250	160-630	210-790	62-240	160-620	200-780
Full meal (meat)	7.6-38	23-110	27-130	4.3-22	19-94	24-120
Full meal (vegetarian)	4.2-6.1	12-18	15-22	2.4-3.5	104-15	13-19
Total diet (light)	61-150	160-370	190-450	47-110	140-330	170-410
Total diet (full)	220-250	570-630	690-760	170-190	510-560	620-690

Total CP exposure based on full meals was calculated using the consumption data for the category 'composite food' which comprised only 9.3% of total daily food consumption for the adult population in Germany[12], leading most likely to an underestimation of the CP intake. Therefore, the 97.5th percentile of total CP exposure based on composite food was only 0.024-0.12 µg/kg bw/day for meals including meat and 0.013-0.019 µg/kg bw/day for vegetarian meals. In comparison, the total diet samples amounted to 0.17-0.41 µg/kg bw/day (light diet, 97.5th percentile) and 0.62-0.69 µg/kg bw/day (full diet, 97.5th percentile) for the adult population in Germany.

This lower calculated exposure based on total diet samples shows the need for further contemplation about the choice of sampling method for exposure assessment for CPs, at least until reliable factors are available to convert raw food contamination in actual CP intake after food preparation. Further cooking and degradation studies are needed in this regard.

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