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Levels of polychlorinated alkanes in food samples from the Swedish Market Basket Study 2022

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Sammanfattning

Klorparaffiner (CPs) används främst som flamskyddsmedel, mjukgörare och smörjmedel. De har visat sig vara persistenta och bioackumulerande, vilket gör dessa ämnen till potentiella miljö- och hälsorisker. Denna studie analyserade polyklorerade n-alkaner (PCAs), som är de huvudsakliga ämnena i CPs, i 17 livsmedelsgrupper från den svenska matkorgsundersökningen från 2022. PCAs-C_{10-30} detekterades i 11 livsmedelsgrupper, med de högsta nivåerna i fettrika livsmedel som bakverk (undre rapportgräns (LB) Σ PCAs-C_{10-30} 62 µg/g), ägg (LB Σ PCAs-C_{10-30} 51 µg/g), vegetabiliska köttersättningsprodukter (LB Σ PCAs-C_{10-30} 45 µg/g), kött (LB Σ PCAs-C_{10-30} 43 µg/g) och fet fisk (LB Σ PCAs-C_{10-30} 33 µg/g), vilket återspeglar de hydrofoba egenskaperna hos PCAs. Noterbart är även att fettsnåla livsmedel som grönsaker och frukt innehöll PCAs, vilket kan bero på förpackningar och andra kontamineringskällor. Dessa resultat påvisar en kontamineringsrisk av PCAs i livsmedelskedjan, och belyser behovet av kontinuerlig övervakning och reglering för att minska exponeringen. Sammanfattningsvis observerades en förändring i PCA-mönster jämfört med 2015 års undersökning, med större bidrag från PCAs-C_{14-17} och PCAs-C_{18-30}, troligen på grund av förbudet mot PCAs-C_{10-13} från år 2017 och deras ersättning med längre kedjehomologer.

Summary

Chlorinated paraffins (CPs), primarily used as flame retardants, plasticizers, and lubricants, are persistent and bioaccumulative chemicals of environmental and health concern. This study analyzed polychlorinated n-alkanes (PCAs), as the main components in CPs, in food items from the 2022 Swedish market basket study, covering 17 food categories. PCAs-C_{10-30} were detected in 11 groups, with the highest levels found in high-fat foods such as pastries (lower bound (LB)∑PCAs-C_{10-30} 62 µg/g), eggs (LB ∑PCAs-C_{10-30} 51 µg/g), meat substitute products (LB ∑PCAs-C_{10-30} 45 µg/g), meat (LB ∑PCAs-C_{10-30} 43 µg/g), and fatty fish (LB ∑PCAs-C_{10-30} 33 µg/g), reflecting the hydrophobic nature of PCAs. Notably, low-fat foods like vegetables and fruits also contained PCAs, potentially due to packaging and other contamination sources. These results highlight the presence of PCAs in the food chain and the need for ongoing monitoring and regulatory measures to mitigate dietary exposure. Overall, a shift in PCA patterns was observed compared to the 2015 survey, with greater contributions of PCAs-C_{14-17} and PCAs-C_{18-30}, likely due to the 2017 ban on PCAs-C_{10-13} and their replacement by longer-chain homologues.

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1. Background and frame of the study

Chlorinated paraffins (CPs) are mainly used as flame retardants, plasticizers in flexible polyvinyl chloride (PVC), and lubricants in metalworking fluids. They are high production volume chemical mixtures, with global output exceeding 1 million tonnes per year (Chen et al., 2022).

The technical mixtures of CPs primarily compose of polychlorinated n-alkanes (PCAs), with minor proportions of byproducts and contaminants (Fernandes et al., 2023). These are produced by chlorinating paraffins (hydrocarbon feedstock) with varying chain lengths, resulting in a vast number of homologues with different chain lengths and degrees of chlorination. Historically, they have been categorized into short-chain (C_{10}–C_{13}, SCCPs), medium-chain (C_{14}–C_{17}, MCCPs), and long-chain (C_{18}–C_{30}, LCCPs) chlorinated paraffins. Currently, "chlorinated paraffins" typically refers to the commercial mixtures, while "PCAs" is used for defined polychlorinated n-alkanes that are analytically determined in the samples.

Due to their persistence, potential for bioaccumulation, and toxicity to aquatic organisms, PCAs have raised environmental and health concerns. SCCPs were listed as persistent organic pollutants (POPs) under the Stockholm Convention in 2017, and MCCPs were nominated for listing in 2022. Dietary intake is considered one of the most significant exposure routes for the general population, accounting for about 60-88% of total PCA exposure (Yuan et al., 2022).

PCAs have been measured in a previous market basket study in 2015, where highest levels of PCAs were found in fish and oils/fats (Swedish Food Agency, 2017). This current report analyzed PCAs in food items collected in the Swedish market basket study from 2022.

2. Methodology

The new Swedish Market Basket Study was carried out in 2022 (Swedish Food Agency, 2024). For this study, the food groups with an average consumption of 0.5 kg per person per year or more were selected, covering approximately 90% of the total annual consumption (kg/person). The market basket represents more than 130 food items bought in major grocery stores, which were pooled together for each category. In total, the following 17 different categories were included: cereal products, pastries, meat, fatty fish, lean fish, lean dairy, fatty dairy, eggs, fat and oils, vegetables, fruits, potatoes, sugar and sweets, beverages, plant-based drinks, plant-based meat substitutes, and coffee and tea. Cereal product samples were processed in triplicates for quality assessment and control. The recovery rates (%) and method limits of detection (MDLs, ng/g) for each sample are listed in Table 1.

The sample preparation method was adapted from previous studies (Jensen et al., 2009, Swedish Food Agency, 2017). A mass or volume equivalent to 0.3 g of fat was weighed and spiked with 10 ng of the internal standard, $^{13}C_{10}$-1,5,5,6,6,10-hexachlorodecane. The samples were then categorized into three groups: solid samples, liquid dairy samples, and liquid samples and sweets. Slightly different extraction approaches were applied to each category.

Solid samples were homogenized using the Bead Ruptor Elite (Omni, US) bead mill homogenizer for two cycles of 30 seconds with 14 mL of hexane:acetone (14:35). These samples were then subjected to two solid-liquid extraction cycles with 10 mL of hexane:diethyl ether (9:1). Liquid (lean) dairy samples, previously dissolved in 6 mL of hexane:acetone (3:1), were extracted through two liquid-liquid extraction cycles with 6 mL of hexane:acetone (3:1) and one cycle with 10 mL of hexane:diethyl ether (9:1). The supernatants from the solid (fatty) and liquid (lean) dairy samples were dehydrated with 10 mL of aqueous 0.9% sodium chloride and 0.1 M phosphoric acid, followed by two liquid-liquid extraction cycles with 5 mL of hexane. The other liquid samples and sugar/sweets were extracted through two liquid-liquid extraction cycles with 6 mL of hexane:acetone (3:1) and one cycle with 10 mL of hexane:diethyl ether (9:1).

All sample extracts were then concentrated to 1 mL before the clean-up step. For clean-up, a multilayer column packed from bottom to top with 2 g of silica (deactivated with 2.5% H_2O), 6 g of 44% sulfuric acid silica, and 4 g of anhydrous sodium sulfate was used. The concentrated extracts were loaded onto the column and eluted with 15 mL of hexane:diethyl ether (1:1, v/v). The eluent was concentrated, and 10 ng of $^{13}C_{12}$-1,1,1,3,10,12,12-octachlorododecane was added as a recovery standard. The extracts were then solvent-exchanged to acetonitrile before instrumental analysis.

PCAs were measured using liquid chromatography coupled with quadrupole time-of-flight mass spectrometer (LC-qToF, Agilent 6546) in electrospray negative ionization mode. For quantifying PCAs-C_{10-30}, the $[M+Cl]^-$ ions were used, generated by adding 0.01 M of tetramethylammonium chloride to the mobile phases. The contribution of each PCA homologue group, after blank subtraction, was calculated using the deconvolution method proposed by Bogdal et al. (2015). For the pattern-deconvolution algorithm of PCA-C_{10-13} and PCA-C_{14-17}, single-chain standards (Chiron AS) for C_{10} (52.5% and 58.4% Cl), C_{11} (52.3% and 57.7% Cl), C_{12} (53.8% and 57.3% Cl), C_{13} (45.9% and 60% Cl), C_{14} (49.2% and 58.7% Cl), C_{15} (47.7% and 59.3% Cl), C_{16} (51.5% and 58.4% Cl), and C_{17} (56.3% Cl) were used. For PCA-C_{18-30} analysis, standard mixtures from Dr. Ehrenstorfer (Augsburg, Germany) containing 36.0% Cl and 49.0% Cl, and technical mixtures Uniclor40 from Neville Chemical Co (USA) and Paroil CW 40 from Dover Chemical Corporation (USA) were used.

3. Results and Discussion

A total of 17 food groups were analyzed for PCA, and 11 of them showed PCA levels above the method detection limits (MDL), Table 1. The highest levels were measured for ∑PCAs-C_{14-17}, followed by the ∑PCAs-C_{10-13} and lastly by ∑PCAs-C_{18-30}. These findings differ from the 2015 survey results, where ∑PCAs-C_{10-13} exhibited the highest levels (Swedish Food Agency, 2017). The increased contribution of PCAs-C_{14-17} and PCAs-C_{18-30} in the current patterns is likely due to the ban on PCAs-C_{10-13} in 2017, with PCAs-C_{14-30} serving as their replacements (Yuan and de Wit, 2022).

The highest ∑PCAs were measured for those items containing high fat content, such as pastries, meat, fatty fish and eggs. This can be attributed to the hydrophobic nature of PCAs which suggests that these groups of compounds will accumulate in the fat (Shen et al., 2023). Pastries exhibited the highest ∑PCAs-C_{14-17} levels, potentially due to the baking process, which may facilitate the incorporation of PCAs into these food products (Sprengel et al., 2021). Plant-based meat substitute products showed the second highest ∑PCAs-C_{14-17} content and the highest for ∑PCAs-C_{18-30}, this may be the result from the production procedure of these consumables which suffer several blending steps. The use of blenders has been seen to contribute to food PCA contamination (Yuan et al., 2017). Eggs are the food category which showed the second highest levels for ∑PCAs-C_{18-30}, these results align with other studies which have also described this pattern and explained bioaccumulation the tendency of PCAs, specially for the longer chain ones (Zeng et al., 2018).

Conversely, food categories with lower fat content and minimal prior processing, such as vegetables, fruits, and potatoes, were also found to contain PCAs. This contamination may arise from various sources, one of which could be the packaging commonly used for these food items in Sweden. The PCA profile in these foods, predominantly PCAs-C_{10-13}, aligns with the patterns reported in the packaging materials (Wang et al., 2019, EFSA, 2020).

Table 1: PCAs levels above MDL, and MDL in the food items. MDL was expressed as three times the standard deviation measured in the blanks. Samples with no observed PCA instrumental signal are marked as "not detected" (nd).

Food Group	Recovery %	PCAs-C_{10-13}		PCAs-C_{14-17}		PCAs-C_{18-30}		∑PCAs-C_{10-30}		
		Content ng/g	MDL ng/g	Content ng/g	MDL ng/g	Content ng/g	MDL ng/g	LB[2] ng/g	MB[2] ng/g	UB[2] ng/g
Cereal products[1]	112	7.0	6.5	12	5.4	4.6	2.3	24	24	24
Pastries	186	18	16	36	13	8.0	5.7	62	62	62
Meat	109	19	17	16	14	7.8	5.9	43	43	43
Lean fish	74	<11	11	16	8.8	4.0	3.8	20	25	30
Fatty fish	127	<17	17	21	14	12	6.0	33	41	50
Meat substitutes	144	nd	6.6	27	5.5	17	2.3	45	45	45
Lean dairy products	98	6.3	3.3	4.5	2.8	<1.2	1.2	11	11	12
Fatty dairy products	58	nd	163	nd	135	<58	58	0	29	58
Plant-based drinks	109	nd	2.2	<1.8	1.8	<0.8	0.8	0	1.3	2.6
Eggs	149	18	11	22	8.8	12	3.8	51	51	51
Fats/oils	102	<154	154	<128	128	<55	55	0	168	336
Vegetables	105	7.5	6.5	5.9	5.4	4.0	2.3	17	17	17
Fruits	68	10	6.5	7.3	5.4	3.9	2.3	22	22	22
Potatoes	71	11	6.5	7.8	5.4	3.2	2.3	22	22	22
Sugar and sweets	109	nd	33	nd	27	nd	12	nd	nd	nd
Beverages	204	nd	2.2	nd	1.8	<0.8	0.8	0	0.4	1.3
Coffee and tea	108	nd	2.2	<1.8	1.8	<0.8	0.8	0	1.3	2.6
					∑PCAs-C_{10-30} ng/g in the food basket			350	563	779

[1]*Mean of three replicates from the same pool of cereal products.*

[2]*Sum of all PCAs using lower bound (LB, <MDL=0), medium bound (MB <MDL=0.5*MDL) and upper bound (UB <MDL=MDL).*

4. Conclusions

This study analyzed PCAs in food items from the 2022 Swedish market basket study, revealing contamination in 11 out of 17 categories. The highest levels were found in high-fat foods like pastries, meat, fatty fish, eggs, and meat substitutes, reflecting the hydrophobic nature of PCAs. A shift in PCA patterns was observed compared to 2015, with higher contributions of PCAs-C_{14-17} and PCAs-C_{18-30}, likely due to the ban on PCAs-C_{10-13} in 2017. Low-fat foods like vegetables and fruits also contained PCAs, possibly from packaging materials and other sources. These findings underscore the persistence of PCAs in the food chain and demonstrate their presence in food items available in the Swedish market. This highlights the critical need for continued monitoring and regulatory measures to address potential public health concerns and ensure food safety.

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9. References

BOGDAL, C., ALSBERG, T., DIEFENBACHER, P. S., MACLEOD, M. & BERGER, U. 2015. Fast quantification of chlorinated paraffins in environmental samples by direct injection high-resolution mass spectrometry with pattern deconvolution. *Anal Chem,* 87**,** 2852-60.

CHEN, C., CHEN, A., ZHAN, F., WANIA, F., ZHANG, S., LI, L. & LIU, J. 2022. Global Historical Production, Use, In-Use Stocks, and Emissions of Short-, Medium-, and Long-Chain Chlorinated Paraffins. *Environmental Science & Technology,* 56**,** 7895-7904.

EFSA 2020. Risk assessment of chlorinated paraffins in feed and food. *EFSA Journal,* 18**,** e05991.

FERNANDES, A. R., KRÄTSCHMER, K., MCGRATH, T. J., YUAN, B., BRANDSMA, S., BRITS, M., CARIOU, R., LETCHER, R. J., MUELLER, J., MUIR, D., VETTER, W., WANG, T., YU, G. & BERGMAN, Å. 2023. Recommended terms and abbreviations for polychlorinated alkanes (PCAs) as the predominant component of chlorinated paraffins (CPs). *Trends Anal Chem,* 169**,** 117363.

JENSEN, S., LINDQVIST, D. & ASPLUND, L. 2009. Lipid Extraction and Determination of Halogenated Phenols and Alkylphenols as Their Pentafluorobenzoyl Derivatives in Marine Organisms. *Journal of Agricultural and Food Chemistry,* 57**,** 5872-5877.

SHEN, Y., KRÄTSCHMER, K., BOVEE, T., LOUISSE, J. & VAN LEEUWEN, S. P. J. 2023. Chlorinated paraffins (CPs) in vegetable oils from the Dutch market and the effects of the refining process on their levels. *Food Control,* 153**,** 109889.

SPRENGEL, J., RIXEN, S., KAPPENSTEIN, O. & VETTER, W. 2021. Transport of chlorinated paraffins (CPs) from baking oven doors into the food. *Food Chemistry: X,* 10**,** 100122.

SWEDISH FOOD AGENCY 2017. Swedish Market Basket Survey 2015 (Rapport 26 - 2017).

SWEDISH FOOD AGENCY 2024. Swedish Market Basket Study 2022 (L – 2024 nr 08).

WANG, C., GAO, W., LIANG, Y., JIANG, Y., WANG, Y., ZHANG, Q. & JIANG, G. 2019. Migration of chlorinated paraffins from plastic food packaging into food simulants: Concentrations and differences in congener profiles. *Chemosphere,* 225**,** 557-564.

YUAN, B. & DE WIT, C. A. 2022. Temporal Trends and Age-Dependent Sex Differences in Chlorinated Paraffin Accumulation in Moose. *Environmental Science & Technology Letters,* 9**,** 1044-1049.

YUAN, B., HAUG, L. S., TAY, J. H., PADILLA-SÁNCHEZ, J. A., PAPADOPOULOU, E. & DE WIT, C. A. 2022. Dietary Intake Contributed the Most to Chlorinated Paraffin Body Burden in a Norwegian Cohort. *Environ Sci Technol,* 56**,** 17080-17089.

YUAN, B., STRID, A., DARNERUD, P. O., DE WIT, C. A., NYSTROM, J. & BERGMAN, A. 2017. Chlorinated paraffins leaking from hand blenders can lead to significant human exposures. *Environ Int,* 109**,** 73-80.

ZENG, Y., HUANG, C., LUO, X., LIU, Y., REN, Z. & MAI, B. 2018. Polychlorinated biphenyls and chlorinated paraffins in home-produced eggs from an e-waste polluted area in South China: Occurrence and human dietary exposure. *Environment International,* 116**,** 52-59.