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LEAKAGE OF CHLORINATED PARAFFINS FROM HAND BLENDERS SOLD ON THE SWEDISH MARKET

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Introduction

Chlorinated paraffins (CPs) are complex mixtures of straight alkane chains with different degrees of chlorination. They have been used for a long time as lubricants, plasticizers, flame retardants and metal cutting fluids. Depending on the alkane chain length, CPs are divided into short chain (C₁₀₋₁₃), medium chain (C₁₄₋₁₇), and long chain (C₁₈₋₃₀) products, commonly referred to as SCCPs, MCCPs and LCCPs.¹ In 2006 the SCCPs were proposed to be included in the Stockholm Convention list of persistent organic pollutants (POPs) and are currently under review for inclusion.² The European Chemical Agency has also included the SCCPs in the candidate list of substances of very high concern.³

During a research project run at Stockholm University it was discovered that a newly bought hand blender used to prepare samples for extraction contaminated samples with CPs. To see if other types of hand blenders also leaked CPs, twelve new blenders were bought and tested. Typical patterns of CPs were seen in eight of the tested blenders when analysing the samples using a gas chromatograph (GC) with an electron capture detector (ECD). For the samples showing the highest intensity of CPs confirmation was also done using GC mass spectrometry (MS) (full scan, ECNI). No quantification was however performed due to the limitations of the instruments used and the many challenges associated with CP analysis.⁴ The report of the first study is available online.⁵

The aim of the present study was to repeat the test using the blenders bought back in 2014 showing typical patterns of CPs, and some newly bought blenders aiming to both quantify and determine the pattern of CPs. The recently published method used included chlorine enhanced direct injection negative ion APCI quadrupole time of-flight high-resolution MS (APCI-qTOF-HRMS) operated in full scan mode.⁶

Materials and methods

The blenders used were purchased from retailers in the Stockholm area in 2014 (n = 8) or 2016 (n = 4). Eight different brand were tested, and in some cases different models were included in the test. Five of the brands were manufactured in China, one in Poland and for two brands this information was not specified. Prior to analysis the hand blenders were cleaned according to the written instructions from the manufacturers. To test any potential leakage of CPs, approximately 1g of cooking oil was mixed with 100 mL of water under the recommended maximum running time for fluids or soft ingredients specified in the instructions. In cases where no such information was available the hand blenders were used for 1 min. The oil water mixture was spiked with Dechlorane-603 as a surrogate standard and extracted using isohexane:acetone (3:1), lipids were removed using concentrated sulfuric acid. The samples were further cleaned up by applying a silica gel column impregnated with sulfuric acid.

Instrumental Analysis: Samples were directly injected into APCI-QTOF-MS (QTOF Premier, Waters, UK). Instrument settings described previously⁶ were applied with several adjustments. The collision energy was 0.7 V, the cone voltage 20 V, and the source temperature 100 °C. The mass scan range was m/z 250 – 1000, and the observed resolution was over 8000. A total of 277 m/z ratios corresponding to CP congener groups from C₉Cl₃ to C₃₁Cl₁₂ were considered to form a congener group pattern.

Quantification: CP congener group patterns of a set of CP technical products (n = 40) were initially analyzed, and a sub-set of eighteen products were selected for quantification in this study, consisting of five SCCPs, seven MCCPs and six LCCPs. CP congener group pattern of each sample was reconstructed

by a deconvolution algorithm from CP patterns of the selected products. An example of pattern reconstruction is shown in Figure 1. In this study, CP patterns in the tested hand blenders were satisfactorily reconstructed ($R^2 > 0.90$). Relative contributions of the products were then used to calculate instrument response factors of SCCPs, MCCPs and LCCPs in the sample. Detailed deconvolution procedure has been given in Bogdal et al.⁶

Results and discussion

CPs were present above the limit of quantification (LOQ) in samples mixed with nine out of the twelve blenders tested, with concentrations ranging from <LOQ to 120 µg/g oil, see Table 1. SCCPs were the dominant components from four of the blenders, accounting for 52% to 56% of the total CP content. MCCPs were the dominant components from the other five blenders, with a percentage composition varying from 67% to 91%. LCCPs were only observed from one of the tested blenders (i.e. brand#6.1). The chlorine content of SCCPs and MCCPs from the blenders ranged from 57% Cl to 60% Cl and from 49% Cl to 55% Cl, respectively.

CP congener group patterns from four blenders are shown in Figure 2. Among SCCPs, C₁₂ was the most abundant chain observed in SCCP-dominant samples (e.g. blender#3.3 and blender#6.1, Figure 2), while C₁₃ was the most abundant in MCCP-dominant samples (e.g. blender#1 and blender#5.1, Figure 2). Among MCCPs, C₁₄ was the most abundant chain observed in all samples. C₉ congeners were observed in one blender (blender#6.1, Figure 2), although they have not been produced intentionally.⁷

Attempts were made to see if the amount of CPs leaking out decreased with increasing time of usage. Two of the blenders (brand#3.3 and brand#6.1, Table 1) were tested repeatedly, showing no decreasing levels after approximately twenty and forty minutes of usage, respectively (every fifth run was extracted and analysed for CP leakage). The time tested was however quite limited and probably need to be increased significantly to be able to see any decreased levels.

The results presented in this study is in line with a recent publication from Germany where fat from kitchen hoods were analysed for different types of environmental contaminants. CPs were present at the highest levels (140 – 15 000 ng/g fat, n = 15) of the compounds analysed, and the use of CPs in kitchen- and indoor environments was suggested as the source.⁸

As previously mentioned may CPs be used as sealants, and the leakage we see from the blenders in the present study might possibly originate from the use CP containing sealant oil. CPs are persistent and bioaccumulative chemicals, and CPs with an average carbon chain length of twelve and with an average degree of chlorination of 60% (i.e. SCCP products) are listed as possible carcinogens in humans (Group 2b) by IARC (International Agency for Research on Cancer).⁹ The results presented indicate a risk for human exposure to CPs, including the SCCPs, when eating food prepared using the hand blenders leaking CPs. The presence of CPs in these types of household appliances is unacceptable and quite alarming since they are often recommended for preparation of baby food.

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Table 1. Concentrations and chlorine contents of CPs from the hand blenders and country of origin.

Sample	Year	Total conc CP (µg/g oil)	Percentage composition (%)			Chlorine contents (%Cl, w/w)				Prod country
			SCCPs	MCCPs	LCCPs	Total	SCCPs	MCCPs	LCCPs	
Brand#1	2014	1.4	9.0	91	–	54	57	52	–	China
Brand#2	2014	0.68	12	88	–	51	59	50	–	Unknown
Brand#3.1	2014	21	56	44	–	56	57	54	–	Unknown
Brand#3.2	2014	100	52	48	–	56	57	55	–	Unknown
Brand#3.3	2016	84 ^a	53	47	–	56	56	54	–	Unknown
Brand#4	2014	0.65 ^b	19	81	–	55	60	53	–	Poland
Brand#5.1	2014	4.6	33	67	–	55	57	54	–	China
Brand#5.2	2016	<LOQ								China
Brand#6.1	2014	32 ^c	55	42	3.0	57	57	54	53	China
Brand#6.2	2016	<LOQ								China
Brand#7	2014	<LOQ								China
Brand#8	2016	1.0	12	88	–	51	59	49	–	China

^a Average of five runs, range 55 – 120 µg/g oil. ^b Average of two runs. ^c Average of five runs, range 8.0 -58 µg/g oil.

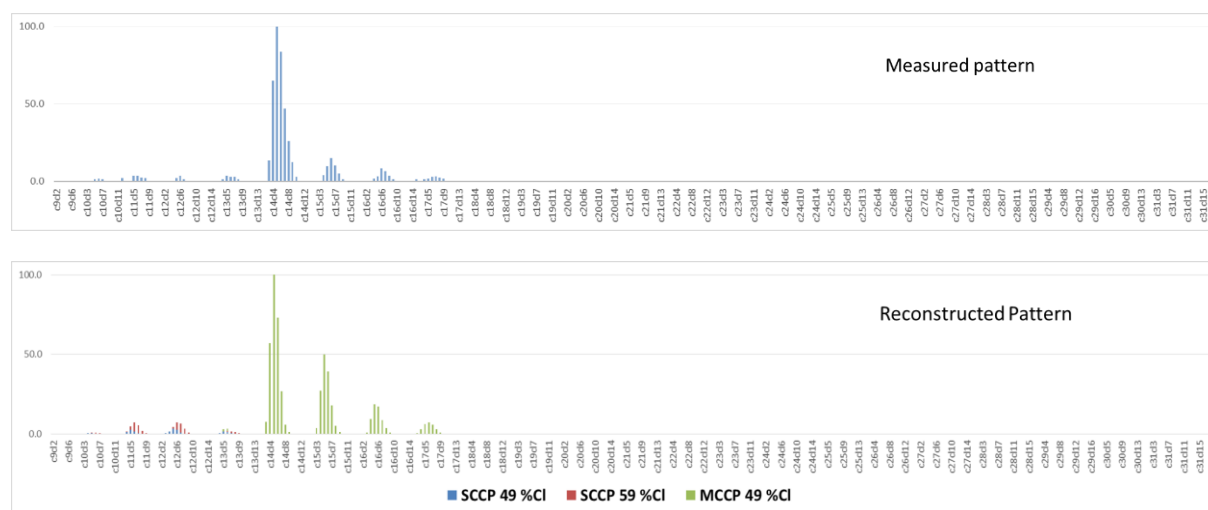


Figure 1. CP pattern reconstruction in the sample Brand#2 ($R^2 = 0.91$). Relative contributions of technical products SCCP 49 %Cl, SCCP 59 %Cl and MCCP 49 %Cl are 4%, 8% and 88%, respectively.

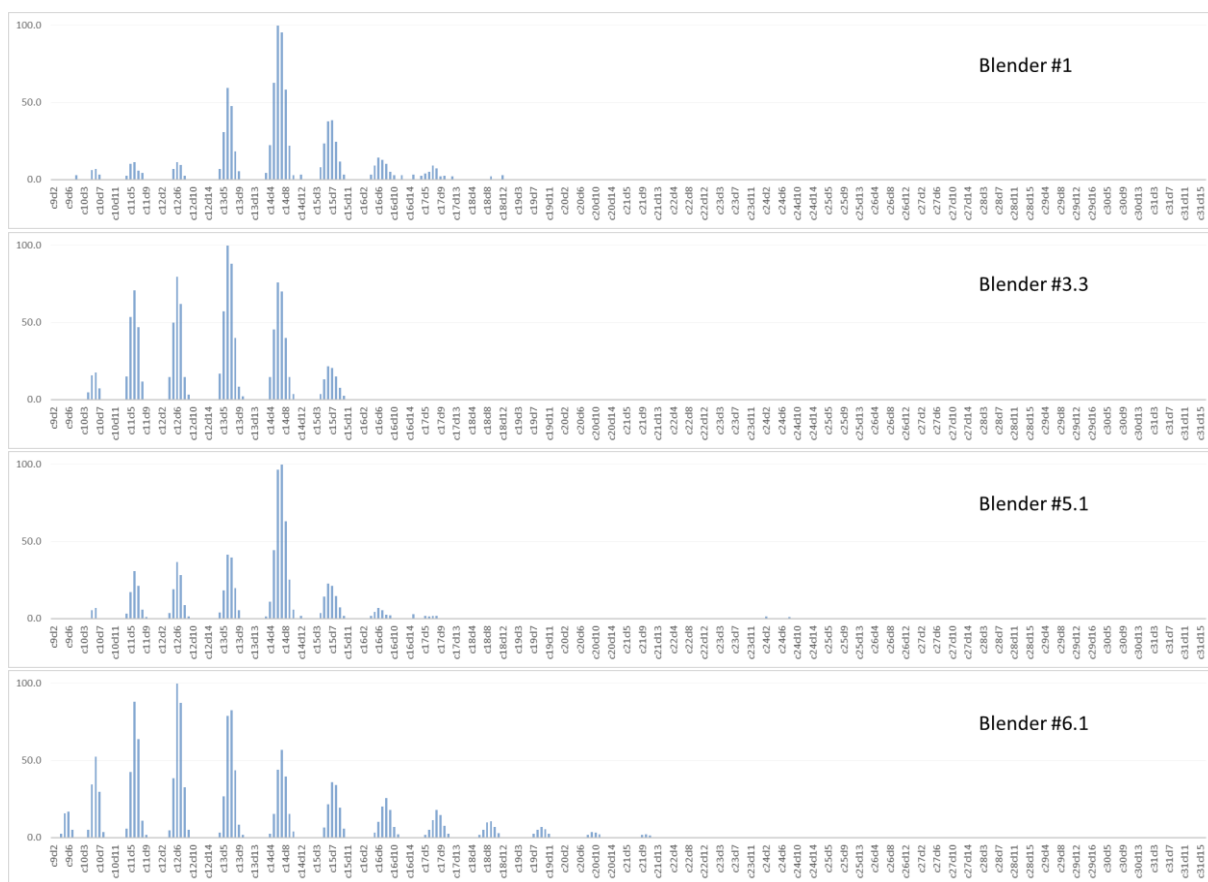


Figure 2. CP congener group patterns in four blenders of different brands.