

# Baking ovens are a relevant source of medium-chain chlorinated paraffins (MCCPs) in household kitchens

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## Introduction

The growing use and importance of electronic equipment in daily life has been accompanied by improved safety standards regarding flammability mitigation; most consumer products are required to contain some sort of physical or chemical mechanism to decrease flammability. Chlorinated paraffins (CPs) are currently the most frequently used industrial polyhalogenated compounds with a production volume of 13 million metric tons between 1935-2012<sup>1</sup>, that is ~10-fold the global production volume of polychlorinated biphenyls (PCBs),<sup>2</sup> and CP production rates are still on the rise.<sup>1</sup> Previous studies on the contamination of CPs in fat deposits in kitchen hoods and dishcloths have indicated significant concentrations of CPs in German kitchen environments.<sup>3,4</sup> Baking ovens may represent particular culprits of CP introduction to the kitchen environment, as they are present in nearly every household kitchen and are explicitly in place to heat food to high temperatures. Thus, they require commensurate flame retarding measures. The aim of this study was to quantify CPs on the inner oven door surfaces of baking ovens from German household kitchens. Twenty-one baking ovens were sampled (one both before and after pyrolysis program) and samples were collected by means of standardized wipe tests. In addition, one disused baking oven was dismantled and different parts were analyzed on CPs.

## Materials and methods

**Chemicals and Standards.** Silica gel 60, *iso*-octane (for pesticide residue analysis) and anhydrous sodium sulfate (*p.a.*, ≥99%), cyclohexane (≥99.5%) and ethyl acetate (≥99.5%) were from Sigma-Aldrich. Cyclohexane (≥99.5%) and ethyl acetate (≥99.5%) were azeotropically distilled (C/E mixture, 46:54, w/w). Acetone (*p.a.*, ≥99%) and *n*-hexane (for pesticide residue analysis, ≥99%) were from Th. Geyer (Renningen, Germany), conc. sulfuric acid (>98%) was from BASF (Ludwigshafen, Germany), and demineralized water was produced in-house with an ELGA purelab classic ultrapure water system (Celle, Germany). Technical mixtures of short-chain chlorinated paraffins (SCCPs) and medium-chain chlorinated paraffins (MCCPs) were from Dr. Ehrenstorfer (Augsburg, Germany). SCCPs (51.5%, 55.5% and 63% avg. chlorine content) and MCCPs (42%, 52% and 57% avg. chlorine content) were mixed to give additional SCCP mixtures with 53.5% and 59.3% and MCCP mixtures with 47% and 55% chlorine content, respectively. BCIS (6'-MeO-BDE 66) and perdeuterated hexachlorocyclohexane ( $\alpha$ -PDHCH) were used as internal standards.<sup>3</sup>

**Samples and sampling.** Twenty-one baking ovens from private households in Stuttgart (Germany) were sampled by volunteers between February-April 2016 by means of wipe tests (see below). Participants were not informed beforehand of the aims of his study and sampling was conducted using ovens in the condition in which they were found. Information on the baking ovens was collected by means of a questionnaire, but no information was available about cooking and cleaning frequencies. Wipe tests were performed with cotton pads (diameter: 6 cm, obtained from a retail store in Stuttgart and previously tested to be free of CPs), which were stored in aluminum foil until use. Directly before the sampling, the cotton pads were wet with 5 mL *n*-hexane and the entire surface area of the oven door was sampled by wiping the wet cotton pad in a continuous circular pattern across the entire area. The sample cotton pads were then placed in 20 mL brown glass vials and were stored at -20 °C in darkness until sample preparation.

Components (inside of door, surfaces of the cable insulation, circuit board housing, exhaust shaft located at the backside, and thermal insulation) of one disused baking oven were sampled in the same way by wipe tests with cotton pads. The samples were stored as described above.

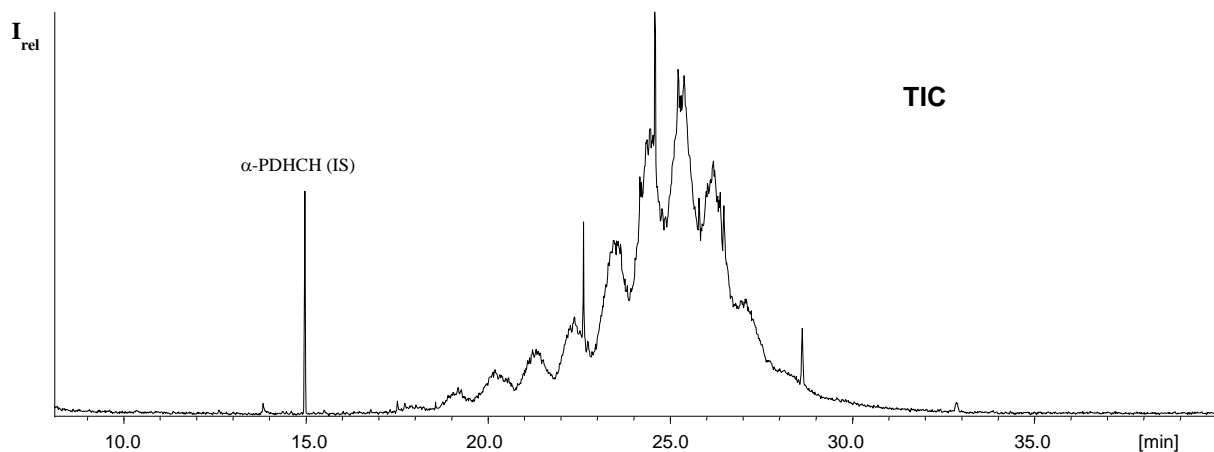
**Sample clean-up.** After sampling, cotton pads were cold-extracted (5 min in ultrasonic bath) 3x with 15 mL *n*-hexane. Combined extracts were carefully evaporated to dryness and re-dissolved in 3 mL *n*-hexane and supplemented with 107 ng of the IS  $\alpha$ -PDHCH and 5 mL concentrated sulfuric acid. After at least 1 h reaction, the organic layer was removed and the sulfuric acid phase was re-extracted twice with 5 mL *n*-hexane. The combined organic extracts were evaporated to <1 mL and subjected to adsorption chromatography (1 cm i.d. glass column, filled with 3 g silica gel deactivated with 30% water, topped with ~0.5 cm water-free Na<sub>2</sub>SO<sub>4</sub>).<sup>5</sup> Target compounds were eluted with 60 mL *n*-hexane and the final volume was set to 1 mL. An 800  $\mu$ L aliquot of this sample was concentrated to 80  $\mu$ L (nitrogen stream, 35 °C) and spiked with 5  $\mu$ L BCIS (2.0 ng/ $\mu$ L, internal standard, diluted in *iso*-octane) before instrumental analysis (see below).

**Quality control.** Before use, all glassware was thoroughly pre-cleaned with hot water, detergent, demineralized water, acetone and C/E mixture (46:54, w/w). Amber or clear glassware covered with aluminum foil was used to minimize exposure to light. At least one procedural reagent blank was performed after 4-6 samples to verify that contamination did not occur during the clean-up. Field blank samples ( $n=5$ ) were collected by wetting unused cotton pads with 5 mL *n*-hexane and storing them like the samples. Procedural reagent blanks and field blanks were found to be free of CPs (<limit of detection, LOD). Recovery of the volatile recovery standard  $\alpha$ -PDHCH was  $87\pm 17\%$ . Initial spiking experiments with CPs (analyzed after spiking into cotton pads) resulted in recovery rates of 81% or higher. CP levels in samples were not recovery-corrected.

**Gas chromatography with electron capture negative ion mass spectrometry (GC/ECNI-MS).** Analyses were performed with an Agilent 7890/5975c system (Waldbronn, Germany) equipped with a Gerstel CIS-4 programmed temperature vaporizing (PTV) injector (Mülheim, Germany).<sup>6</sup> A 30 m Agilent HP-5 MS UI column (0.25 mm internal diameter, 0.25  $\mu$ m film thickness, J&W Scientific, Folsom, CA, USA) using the GC parameters reported previously was used for the measurements.<sup>6</sup> SCCPs and MCCPs were quantified according to Reth *et al.*<sup>7,8</sup> but with BCIS as the internal standard. The LOD was defined by a signal-to-noise ratio of three ( $S/N=3$ ) and the limit of quantification (LOQ) by  $S/N=10$ , whereas the method detection limit (MDL) and quantification limit (MQL) was calculated by the mean sample weight of all samples.

## Results and discussion

**Characterization of the samples.** Nineteen baking oven models from eight manufacturers (age: 1-25 years) were present in the 21 kitchens. The weight of fat residues collected from the inner surface of the baking oven doors ranged from 1.0-200 mg (mean/median: 81/61 mg) with an average wiped surface area of 3,300 cm<sup>2</sup>. In the following discussion, levels of polyhalogenated compounds will generally be based on the sample weight and not on the wiped area, because in a previous study on kitchen hood fat deposits it has been shown that concentration of polyhalogenated compounds correlated with the amount of deposited fat.<sup>3</sup> CPs were detected in ten samples, and if present the concentrations were much higher than those of any other polyhalogenated compound (**Figure 1**).



**Figure 1: Typical GC/ECNI-MS full scan chromatogram of a CP-positive baking oven sample. MCCPs dominated while other polyhalogenated compounds were several orders of magnitude lower concentrated.**

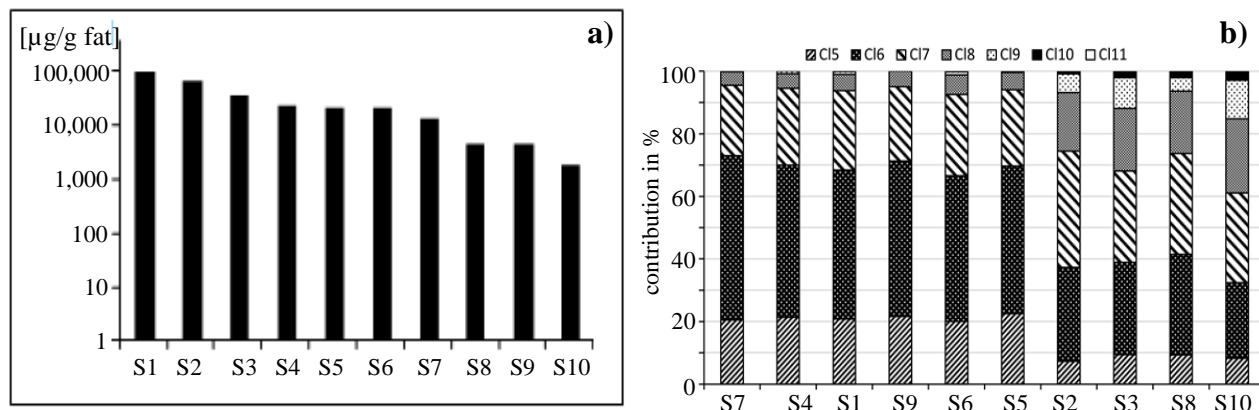
In the ten CP-positive samples (S1-S10, **Figure 2a**) MCCPs were generally more abundant and also more frequently detected than SCCPs. MCCP concentrations ranged from 1,900-93,200  $\mu$ g/g fat (mean 12,600  $\mu$ g/g). SCCPs were only present in three samples at 320 (sample S10, 17% of MCCPs), 1,800 (sample S2, 2.9% of MCCPs) and 1,900 (sample S3, 5.3% of MCCPs)  $\mu$ g/g fat, respectively. Six of the ten samples contaminated with MCCPs showed very similar MCCP patterns with dominance (48-52%) of hexachlorinated homologs (MCCP pattern #1, Cl<sub>6</sub>-isomers, **Figure 2b**).

Slight fluctuations in the MCCP congener group composition were observed for example within samples with MCCP pattern #1 which may be the result of different stability or volatility of selected MCCP congeners. No correlation was observed between MCCP pattern and age of the baking ovens.

The MCCP pattern of three further samples (S2, S3 and S8) was slightly shifted towards equally high or higher proportions of heptachlorinated homologs (MCCP pattern #2, Cl<sub>7</sub>-isomers: 29-38%, Cl<sub>6</sub>-isomers: 29-31%, **Figure 2b**). Noteworthy, two of the samples with MCCP pattern #2 also featured SCCPs. The 10<sup>th</sup> and last positive baking oven sample (S10) showed a similar chlorination pattern as the samples of MCCP pattern #2 but S10 was unique in that it only featured C<sub>14</sub>- and C<sub>15</sub>-alkanes with equal proportions of hexa- and heptachlorinated homologs

(MCCP pattern #3, **Figure 2b**). This sample was the one with the lowest concentration in MCCPs of all positive findings (**Figure 2a**).

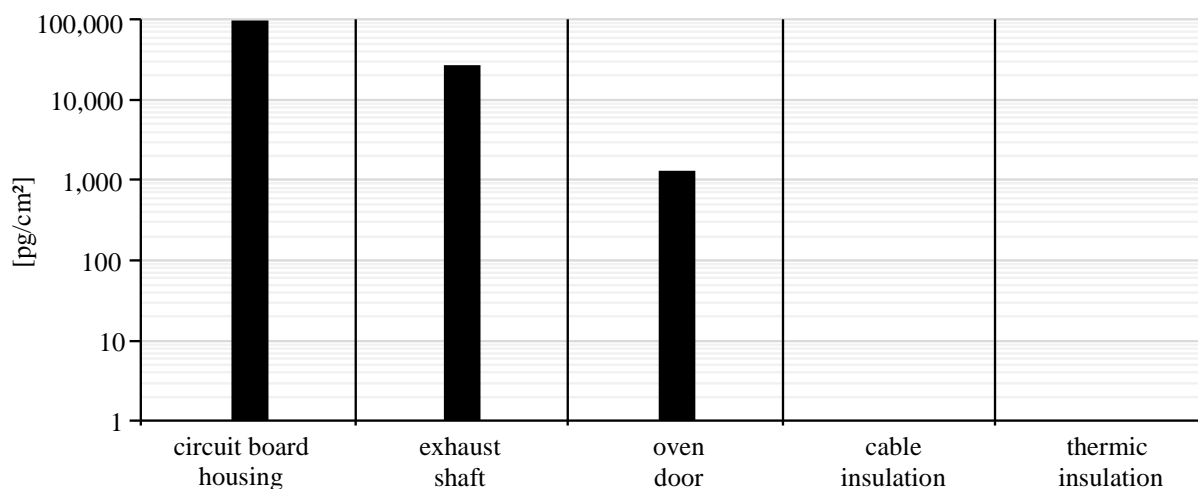
Four baking ovens with MCCP pattern #1 were from the same manufacturer “A” (S7, S4, S1, S9) and had an age of 1-25 years. However, six further samples from baking ovens of manufacturer “A” were free of MCCPs. It is possible that some of ten baking ovens of manufacturer “A” (altogether eight different models) were produced in different plants, possibly even in different countries. Moreover, different suppliers may provide different flame retardants (or different components treated with different flame retardants) to different plants. Similarly, only one of three baking oven models from manufacturer “D” was MCCP-positive (S5). Hence, no relationship was found between age and presence of MCCPs.



**Figure 2:** (a) Concentrations of chloroparaffins (CPs) in CP-positive baking ovens in German households (sorted by decreasing concentrations) and (b) chlorination pattern of three types (see text) sorted by pattern, producer and age.

If detected, mean CP concentrations in the baking ovens more than 1,000 fold higher than previously found in kitchen hood fat deposits (mean CP level: 3,500 ng/g kitchen hood fat).<sup>3</sup> Interestingly, the detection frequency was similar and, if present, CPs dominated in all types of samples (kitchen hood fat deposits, dishcloths, baking ovens). These coincidences and the fact that the CP concentrations in the baking ovens were orders of magnitude higher and that the wiping tests were performed on the insides of the baking ovens produced strong incidence that the baking ovens itself were the source of the CPs.

In order to further verify this hypothesis, one disused baking oven (ten years old, stored for >1 year in the basement) was also analyzed on CPs. The oven door wipe test sample of this baking oven showed the characteristic MCCP pattern #1 which was also found in another model from this manufacturer (S5). Following the initial wipe test, the discarded baking oven was dismantled and further wipe tests were performed on the backside thermal insulation, a circuit board housing, a cable insulation, and an exhaust shaft. MCCPs were only detected from samples taken on the thermal insulation, the exhaust shaft, and the baking oven door (**Figure 3**).



**Figure 3:** Concentrations of CPs in different parts of a disused baking oven dismantled for this study.

Due to very low sample lipid weights within samples taken beyond the oven door, MCCP concentrations were calculated in relation to the wiped area to enable comparison of concentrations detected across the different oven components. The highest MCCP concentration ( $\sim 96 \mu\text{g}/\text{cm}^2$  wiping area) was measured on the circuit board housing, whereas levels on the exhaust shaft and on the oven door surface (which were located close to the circuit board housing, **Figure 3**) were only  $\sim 1/3^{\text{rd}}$  and  $1/100^{\text{th}}$  of this value, respectively.

All three components showed similar MCCP pattern #1. Decreasing MCCP concentrations from circuit board to the oven door indicated that MCCPs were likely released from the circuit board or from adjacent components, most likely due to coercion from high temperatures during the heating/baking process. Liberated MCCPs from heated components would then re-condense on the exhaust shaft and, to a lower extent, on the more remote oven door, whereas no MCCPs were detected on the most remote cable insulation and thermal insulation. Based on fat weight (9.2 mg) collected from the wiped oven door, the MCCP concentration ( $\sim 38,000 \mu\text{g}/\text{g}$  fat) of the dismantled baking oven was typical for samples with MCCP pattern #1. This verified that release from the baking oven itself had occurred.

A comparably high or even a higher detection frequency (DF) of CPs (with predominance of MCCPs) has been observed in dishcloth samples commonly used in kitchens (DF: 58%)<sup>4</sup> and kitchen hood fat deposits (DF: 100%).<sup>3</sup> Although the samples (baking ovens, dishcloths, kitchen hood fat deposits) from the three studies originated from different households, the high frequency of CP contamination in these matrices may be explained by exposure to or contact with CP-treated baking oven components. Ostensibly CPs may be transferred to dishcloths through wiping of the oven surface or transferred to hoods via the outflow of contaminated hot air from baking oven.

Hence, release of CPs from the baking ovens seems to be a major source contributing to the high levels previously detected in kitchen hoods and dishcloths.<sup>3,4</sup> Likewise, CPs released from components of the baking oven housing into the oven chamber may enter foodstuff baked within the oven. In either case, release from the baking oven will most likely contribute to the human exposure to CPs both by inhalation of contaminated air and by consumption of food contaminated during the baking process.

While SCCPs are expected to be classified as POPs in 2017, no ban or regulation is currently proposed for MCCPs. Our results further indicate that MCCPs are a much bigger problem than SCCPs in (German) kitchen households. Accordingly, the use of MCCPs in ovens should not be considered innocuous, and exposure evaluations and appliance safety stands should be revised accordingly. For safety reasons, product requirements should include tests which confirm that MCCPs are not released during baking processes. Such standards should also be established for other kitchen appliances and equipment.

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