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KITCHEN STORIES: POLYHALOGENATED COMPOUNDS IN DISHCLOTHS AFTER REGULAR USE IN HOUSEHOLDS

W. Vetter[1], C. Gallistl[1], B. Lok[1], A. Schlienz[1]

[1]*University of Hohenheim, Institute of Food Chemistry, Stuttgart, Germany*

Introduction

Chemicals in indoor environments are increasingly recognized as harmful contamination sources which constitute a risk to human health.[1] Different polyhalogenated compounds widely used as flame retardants in electronic equipment and plastic materials are utilized in various home movables and kitchen facilities. Release of polyhalogenated compounds from equipment along with improved thermal insulation and limited ventilation in homes are causing increased pollutant concentrations indoors. As a consequence, polyhalogenated compounds have already been identified in dust and indoor air.[2] Recently, we noticed that the insides of household kitchen hoods were generally clogged with cooking fat.[3] In this deposited fat we found a range of polyhalogenated compounds. Each sample had its own contamination pattern with chloroparaffins being the most abundant substance class.[3] It was proposed that the polyhalogenated compounds were attracted by the vent in the kitchen hood, and that they originated from different sources within the kitchen and possibly neighbored rooms. In this study we wished to determine if dishcloths regularly used in the households are polluted with polyhalogenated compounds. Dishcloths are used for cleaning kitchen spaces and possibly tables after cooking and eating. During their use they are collecting leftovers of food, fat, splashes and dust and typically they are used without hands being protected by gloves. The design of the study was collecting a set of dishcloths (Fig. 1) from different households after normal use and substituting them with new dishcloths which were collected again after 14 days in use.

Materials and methods

Samples and Chemicals. Nineteen samples of dishcloths from private households were collected in May 2015 in and around Stuttgart (Germany). The original dishcloths used in individual homes (and which were different in size and material) were collected for analysis (first sampling) and substituted with uniform dishcloths (Fig. 1) bought at a retail store (and tested for absence of target compounds before sampling) in Germany. Participants were asked to use the dishcloths as normal but not to wash them in a washing machine. After fourteen days, the dishcloths were collected again (second sampling) and analyzed in duplicate as shown below. Origins of chemicals used for sample preparation are shown in Bendig et al. (2013).[3]

Sample Cleanup. Dishcloths were halved and both parts were individually cut to pieces of ~1 cm^3 in size. Pieces from half dishcloths were placed in a 250 mL Erlenmeyer flask, the 1st internal standard perdeuterated α-HCH (α-PDHCH; IS-1) was added and samples were extracted with 80 mL ethyl acetate/ cyclohexane (azeotrope, 54:46, w/w). The solvent was evaporated to >1 mL, substituted with n-hexane (with some iso-octane as keeper) and transferred to a test tube with further 6 mL of n-hexane before treatment with 3 mL concentrated sulfuric acid overnight. The organic layer was separated and the acid phase was twice re-extracted with n-hexane (each 3 mL). Hexane extracts were combined, washed with 5 mL dest. water, dried over Na2SO4 and evaporated to a final volume of 1 mL. Finally an aliquot (250 µL) was concentrated to 50 µL and the 2nd IS standard 6´-methoxy-2,3´,4,4´-tetrabromodiphenyl ether (6´-MeO-BDE 66 or BCIS; IS-2) was added before analysis via GC/MS. Recoveries of the internal standard α-PDHCH were 87±12% (69-106%).

GC/MS parameters. GC/ECNI-MS analyses were performed with a 7890/5975C system (Agilent) according to Bendig et al.[3] A 30 m, 0.25 mm i.d., 0.25 d_f HP-5MS UI column (Agilent) was installed in the GC oven which was programmed from 50 °C (hold time 1 min) at 10 °C/min to 300 °C (hold time 19 min).3 BDE-209, TBBPA, TBBPA and its derivatives, HBCD and DBDPE were measured on a 15 m, 0.25 mm i.d. and 0.1 d_f ZB-1 column (Phenomenex) with the same oven program. In the GC/ECNI-MS full scan mode, m/z 50-800 was recorded. Identification and quantification of different polyhalogenated compounds was reported elsewhere.[3]

Results and discussion

General observations. Several polyhalogenated compounds were detected in each of the 19 samples and at both samplings. Yet, both the pollutant pattern and the total contaminant load varied from sample to sample. Excluding chloroparaffins at this point (see however below), the sum of all chlorinated compounds ranged by two orders of magnitude from 9-1,210 ng/dishcloth (Table 1, overall mean ~190 ng). Compared to that the mean sum of all brominated compounds (~2,600 ng) was about ten-fold higher (up to 12,600 ng/dishcloth (Table 1). Surprisingly, in most of the samples, PBDEs amounted only for ~10% of the load of polybrominated compounds (see below). The mean value was moderately higher than the median which indicated some impact of (few) highly contaminated samples on the mean value. Differences were also noticeable between the two samplings. The first sampling reflected the non-influenced conventional use of dishcloths in the kitchen by the participants in the study. No previous instructions were made. Hence, it is unknown how frequently (and when for the last time) the dishcloths were cleaned before the sampling was taking place. In contrast, the second sampling was more standardized (uniform dishcloths were applied for the same period) and the results were better for inter-comparisons. In 30-50% of the samples compound-to-compound differences between sampling 1 and 2 were within a factor of ~2. In selected cases, and more pronounced for polybrominated compounds, the two samples from the same kitchen could differ by more than the factor 10 and up to factor 55. If concentrations were higher, then most frequently in the first sampling (Table 1). While the pattern differed from sample to sample, the frequency of detection was usually similar in the first sampling and the second sampling.

Detailed residue patterns. A total of 15 chlorinated compounds or compound classes and 15 polybrominated compounds (PBDEs counted one) were detected in the 19 samples with different levels and frequency of detection. The individual residue patterns in samples from different kitchens were partly completely different (Fig. 2a,b). Sample 12-2 (Fig. 2a) represented one of the few examples where PBDEs were among the most relevant pollutant classes. The residue pattern of dishcloth sample 7-1 was dominated by extremely high levels of medium-chain chloroparaffins (Fig. 2b). The medium-chain chloroparaffin levels exceeded the sumPBDE level in sample 12-2 (Fig. 2a) by several orders of magnitude (chloroparaffins were not abundant in this sample). Extraction of m/z 79 (and m/z 81) from the GC/ECNI-MS full scan chromatogram enabled us to verify the presence of several polybrominated compounds including TBA, PBT and HBB, but no prominent peaks from PBDEs (Fig. 2c). Interestingly, sample 7-1 featured four unknown polybrominated compounds (labeled U1 to U4 in Fig. 2c) in the retention time range of penta- to heptaBDEs. Accordingly, the molecular weights of U1-U4 were most likely in the range of m/z 450-650. Although many BFRs were available as reference standards, these did not match with the GC/MS data of compounds U1-U4. It is most likely that these unknown polybrominated compounds were metabolites of larger molecules (used as BFR). All four compounds (U1-U4) showed the $[Br_2]^-$ fragment ion at m/z 158, which excluded structural relationship with PBDEs. The $[Br_2]^-$ fragment ion has been linked with an aliphatic substructure in the molecules.[4] Further samples also featured unknown compounds.

Polychlorinated compounds – variety and frequency. Two types of polychlorinated compounds were detected in the sample. On one hand, the class of classic outdoor pollutants such including chloropesticides (penta- and hexachlorobenzene, hexachlorocyclohexane isomers, DDE, chlordane-related compounds) and on the other hand more relevant indoor pollutants such as industrial chemicals (pentachlorophenol (PCP) and –anisole (PCA), chlordane plus and dechlorane plus (syn and anti), as well as chloroparaffins). Surprisingly, PCBs only played a minor role and were not quantified in this study. Pentachlorobenzene (PCBz) and hexachlorobenzene (HCB) were detected in all samples, it followed in detection frequency trans-chlordane (95% of all samples), lindane, and dechlorane plus syn and anti (both 89% of all samples). PCA was present in 68% of the samples and α-HCH only in four samples. Finally, PCP was only detected in one sample and DDE (26%) had the lowest frequency of all compounds. CPs were detected in 92% of all samples. Apart from chloroparaffins, the highest median concentrations were detected for lindane and HCB but the concentrations scarcely exceeded 100 ng/dishcloth.

Chloroparaffins. CPs were detected in 18 of the 19 samples (first sampling). CP concentrations were the predominant contaminant in four samples (microgram-amounts/sample, Fig. 2b). In addition, CP levels

were moderate in further three samples (comparable to other major compounds/compound classes and low in six samples. Traces only were detected in five samples (Fig. 2a).

Dechlorane plus. Despite being present in 17 samples (first sampling), the concentrations were mostly <20 ng and only three samples revealed higher levels of ~35-60 ng. The syn/anti ratio ranged from 0.5 to 2.6. The mean (median) of anti-dechlorane plus was slightly higher with 12.3 ng (5.4 ng) vs. 12.0 ng (5.0 ng) for syn.

Polybrominated compounds – variety and frequency. As mentioned above, brominated flame retardants were usually more prominent than chlorinated compounds. In addition, they were more differently distributed from kitchen to kitchen. For instance, notably high decabromodiphenylethane (DBDPE, Fig. 3) concentrations were detected in four samples (#9, #14, #18, #19 of the first sampling) with 360-3,600 ng/dishcloth while DBDPE was < LOD (34 ng) in the remaining 15 dishcloth samples. A similar situation was observed for BDE 209 (five detections in #3, #9, #16, #18, #19 with 140-1,220 ng/dishcloth, 14 non-detections). Hexabromocyclododecane (HBCD was detected only in seven samples, i.e. #4, #6, #7, #14, #16, #17, #19 but, if detected, the concentration was high (140-6,400 ng). As can be seen from the listed sample numbers, DBDPE, HBCD and BDE 209 were only detected once at high levels, respectively. It is obvious from these results that individual items in kitchen/indoor were responsible for the contamination. The highest frequency was observed for allyl-tribromophenyl ether (ATE) and pentabromotoluene (PBT) (95%), 79% 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and 74% tribromoanisole (TBA).

Concentrations of DPTE, BATE, and ATE. ATE (mean 129 ng) and BATE (mean 100 ng) are known metabolites of DPTE (251 ng), and all three compounds were detected with high frequency. In contrast to previous information,[5] DPTE is still being used in Germany. There is at least one supplier available on the German market and it appears that the product is frequently used and evenly distributed although the concentrations were lower than for other BFRs. This indicates that the DPTE group is used in one product group used in all kitchen/households but which does not lead to extremely high levels. Although ATE has also been used as BFR itself, the co-presence of DPTE and BATE in most samples indicates that it is either used together with DPTE or that DPTE has been partly metabolized. Noteworthy, the ratio of the three compounds was not constant. In some samples DPTE was dominant, in others BATE or ATE. Possibly, the ratio of DPTE, BATE and ATE may serve as an indicator for old sources (higher abundance of BATE and ATE) and new sources (dominance of DPTE).

Tetrabromobisphenol A (TBBPA) and tetrabromobisphenol diallyl ether (TBBPA-DE). TBBPA and TBBPA-DE (Fig. 3) showed a similar distribution pattern. TBBPA had a higher frequency, and all except one sample positive for TBBPA-DE also contained TBBPA.

Concentrations of PBDEs. The PBDE pattern (concentrations 19-1,550 ng/dishcloth) was dominated by hexa- to octabrominated congeners, which pointed towards the use of technical octaBDE (DE-79). However, there were distinct differences noticeable between the PBDE pattern of sample and DE-79. For instance, the sample featured prominent octaBDEs not present in DE-79 which indicated that these were metabolites of decaBDE (BDE 209). PBDEs other than BDE 209 were dominated by higher brominated congeners (Fig. 2a). These samples did not feature the PentaBDE patterns classic for fish and other marine organisms. This can be seen from the fact that the typical metabolites of octaBDE and decaBDE, BDE 49 and BDE 66,[6] were detected in nine vs. five samples, frequently at higher concentration than BDE 47.

Conclusions. Polyhalogenated compounds were detected in all dishcloth samples, typically in the ng range. The compound patterns and the kitchen-to-kitchen variations resembled the observations made during the analysis of kitchen hood residues. Dishcloths are usually used without gloves and uptake of pollutants via the skin cannot be excluded. The results verify the widespread presence of polyhalogenated compounds in kitchens with potential health risks, especially for cooks.

References.

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Fig. 1: Photo of a dishcloth before use.

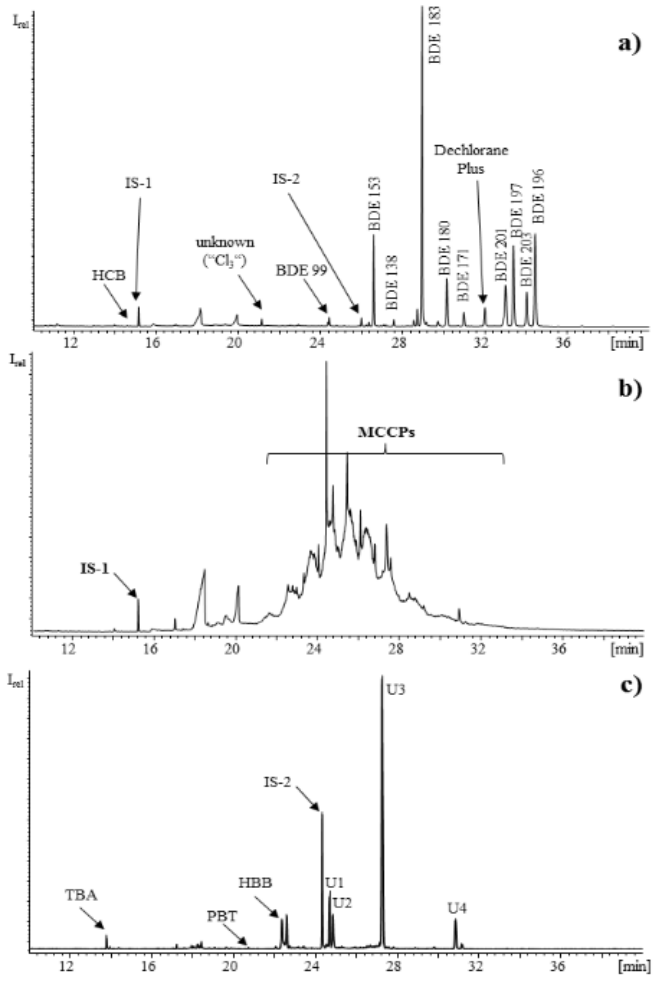

Fig. 2: GC/ECNI-MS chromatograms of dishcloth extracts. (a) full scan of sample 12-2 as well (b) full scan mode (*m/z* 50-800) and (c) *m/z* 79 extracted from the full scan chromatogram for the monitoring of BFRs of sample 7-1

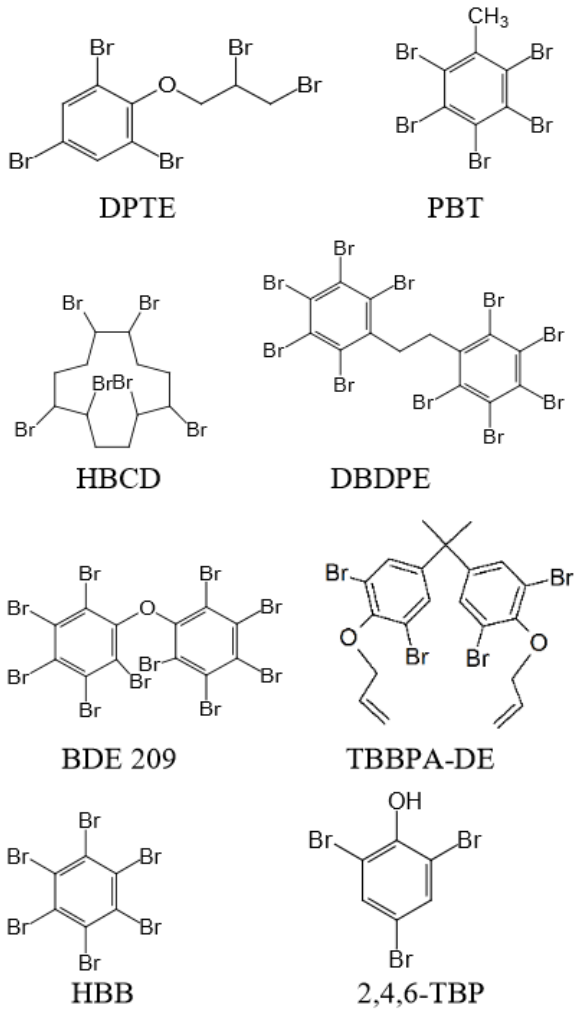

Fig. 3: Structures of selected polybrominated compounds detected in this study

Table 1: Sum concentration (ng/sample) of all chlorinated (except chloroparaffins) and brominated compounds in 19 dishcloth samples from Stuttgart/Germany after use in the kitchen (for the calculation of mean and median values, non-detections were taken into account with LOD/2)

	Σchlorinated compounds		Σbrominated compounds	
values in ng/dishcloth	first sampling	second sampling	first sampling	second sampling
mean	214	161	3,720	1,520
median	156	38	2,740	1,260
min - max	14 - 706	9 - 1,210	n.d. – 12,600	131 – 4,730