LEVELS OF PERFLUORINATED CARBOXYLIC ACIDS (PFCA), PERFLUORINATED SULFONIC ACIDS (PFSA), AND FLUORINATED TELOMERS (FTOH) IDENTIFIED IN PAPER-BASED FOOD CONTACT MATERIALS FROM THE GERMAN MARKET

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Introduction

Perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) have been detected in tissues of background exposed humans all over the world. Several authors identified food as a major exposure route for these compounds.[1,2] Besides environmental sources food contact materials are discussed to contribute to the overall dietary exposure of fluorinated and perfluorinated compounds. Several authors reported PFOS and PFOA levels in paper based packaging from LOD to 3500 ppb.[3,4] Additionally, fluorinated telomers (FTOHs), precursor substances of PFCA, have been identified in paper based popcorn bags.[5]

According to Empfehlung XXXVI of the German Bundesinstitut für Risikobewertung (BfR) the positive list of food contact materials contains about 10 fluorine based materials for grease proofed paper and cardboard based packaging. These materials contain side groups based on FTOH, which may potentially be degraded into PFCAs including PFOA, both in the atmosphere or in biological systems.

Therefore, it was the aim of the present work to identify and quantify the levels of fluorinated and perfluorinated compounds including PFCA, PFSA and FTOH from food contact materials intended for both, baking applications and food packaging.

Material and methods

154 paper-based food contact materials were collected mainly in Freising, a small town north-east of Munich in Bavaria, Germany. Using screening methods presented elsewhere in this issue, 47 fluorine-positive samples were identified und subjected to a detailed analysis for FTOH, PFCA, and PFSA.

Therefore, samples were fortified with isotope-labelled standards of PFCA, PFSA and FTOH and extracted with methanol by pressurized liquid extraction (PLE, ASE 200, Dionex, Germany). In order to avoid cross contaminations, the PLE apparatus was equipped with Teflon-free tubes and carefully checked for blanks. The methanol extracts were split into two equal aliquots.

One aliquot was subjected to GC-(CI)-MS (TSQ 7000, Thermo) analysis using methane for chemical ionisation. The other aliquot was cleaned by SPE (Oasis WAX) and measured by LC-(ESI)-MS/MS (LC Quattro, Waters). For both analytical approaches quantification was based on an isotope dilution method.

Results and discussion

A statistical description of the measured levels of PFCA, PFSA and FTOH is presented in Tab. 1. 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were identified in all fluorine positive samples at levels ranging from 9 to 39500 ng/g, whereas 4:2 FTOH where only quantified in about 25% of the samples (maximum value 54 ng/g).

Concentrations of PFCA were considerably lower and ranged from LOD (<1) to 619 ng/g PFOA, LOD (<1) to 1500 ng/g PFNA, and LOD (<1) to 390 ng/g PFDA. These ranges are comparable to previously reported levels of PFCA in food contact materials.[3,4]

PFSA were not found in any sample at levels above 1 ng/g, which may indicate at a switch from FOSE-based coatings to FTOH containing macromolecules in industrial practise. .

Fig 1 displays the contributions of PFCA congeners to the total PFCA concentration calculated from the 10 highest concentrated samples. Three patterns can be distinguished and may indicate to at least three different mother compounds, i.e. fluorine based paper coatings:
Pattern A, dominated by more or less equal amounts of PFOA, PFDA and PFDoA,
Pattern B dominated by PFOA and PFNA followed by PFHpA and PFDA
Pattern C, clearly dominated by PFHxA.

Fig 2 displays the contributions of 6:2, 8:2 and 10:2 FTOH to the total FTOH concentration calculated from the 10 highest concentrated samples. Whereas 7 out of these 10 samples are dominated by 6:2 and 8:2 FTOH, 8:2 FTOH exceeded the other FTOH in the other three samples by far.

Using the EU cube approach[6] (1 kg of food is packed into 6 dm² food contact material) and assuming total migration from the sample into the food stuff, food levels from 50 to 150 ng/g FTOH and from 0.4 to 5.6 ng/g PFCA may have to be expected. These levels exceed PFCA levels found in food duplicate samples obtained in a German dietary exposure study within the same geographic area by a factor of 8 to 110. This indicates clearly, that food packaging may serve as a relevant source of fluorinated and perfluorinated compounds in food and that packaging-related FTOH and PFCA may contribute to the overall PFCA levels in food. Furthermore is important to investigate the migration of PFCA and FTOH into food stuff in more detail.

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References

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Tab. 1: Statistic description of levels of PFCA, PFSA and FTOH (ng/g) identified in fluorine-positive paper-based packaging.

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFDOA	PFUDA	PFTeDA	PFOS
Arith. Mean	5	8	39	31	57	62	44	30	35	13	< 1
Min	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
25%Quantile	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Median	1	< 1	5	2	12	3	8	5	< 1	< 1	< 1
75%Quantile	4	5	23	9	28	15	26	21	7	11	< 1
90%Quantile	19	16	198	28	140	35	113	76	20	37	< 1
Max	48	81	270	394	619	1506	389	290	957	148	< 1

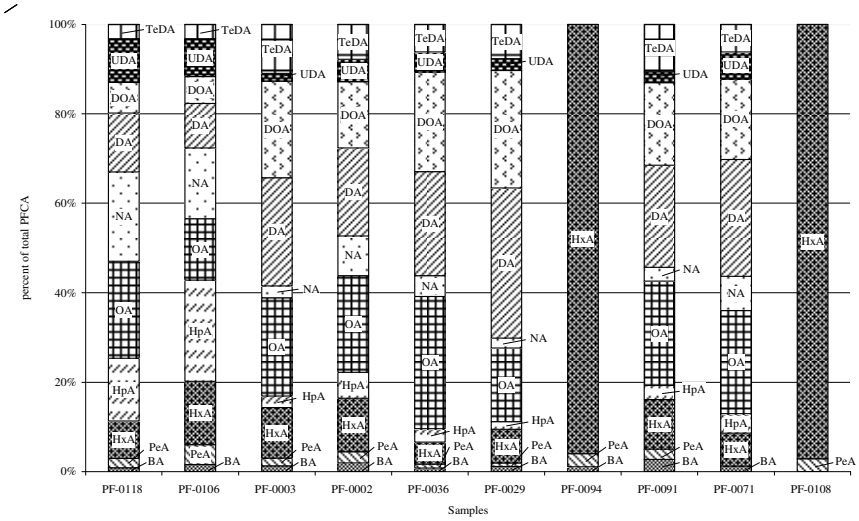

Fig. 1: Contribution of 10 different PFCA congeners to the total PFCA concentration measured in the 10 highest concentrated samples (BA= PFBA, PeA= PFPeA, HxA= PFHxA, …..).

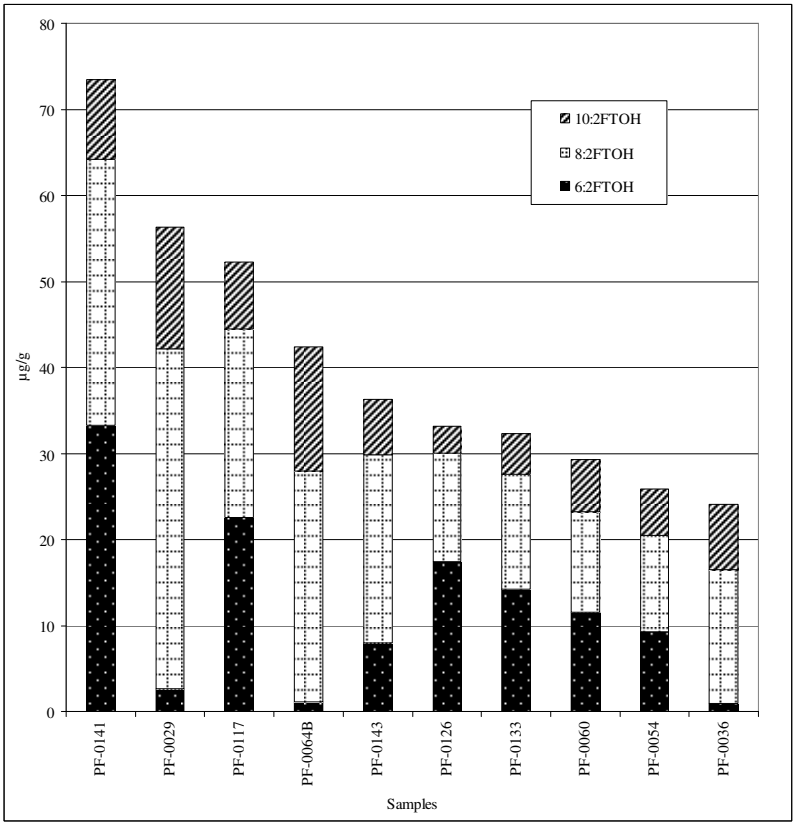

Fig. 2: Contribution of 6:2, 8:2 and 10:2 FTOH to the total FTOH concentration measured in the 10 highest concentrated samples.