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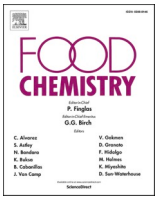

Is the use of paper food contact materials treated with per- and polyfluorinated alkyl substances safe for high-temperature applications? – Migration study in real food and food simulants

Michaela Lerch *, Khanh Hoang Nguyen, Kit Granby

Technical University of Denmark, National Food Institute, 2800 Kgs. Lyngby, Denmark

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ABSTRACT

Migration of per- and polyfluorinated alkyl substances (PFAS) from paper food contact materials (FCMs) can pose a consumer risk. However, risk assessment procedures typically do not consider PFAS contribution from FCMs. Moreover, migration studies are often limited to one subclass of PFAS or simplified by using food simulants (FS). To assess the risk comprehensively, migration of three PFAS subclasses (perfluorinated carboxylic acids/ sulfonic acids (PFCAs/PFSAs), polyfluoroalkyl phosphate esters (PAPs), and fluorotelomer alcohols (FTOHs)) from six FCMs were investigated to FS (50% and 20% ethanol) and food (oatmeal porridge, muffins, and tomato soup) under high-temperature conditions. Migration of PFCAs and FTOHs to all food samples was observed. Migration of PFCAs and FTOHs to 50% ethanol was significantly higher than migration to real food whilst FTOHs did not migrate into 20% ethanol. Estimated dietary PFAS exposure for children (1.06 – 5.67 ng/kgbw/day) exceeded EFSA's proposed safety threshold (0.63 ng/kgbw/day), risking consumer health.

1. Introduction

Cancer (Steenland & Winquist, 2021) and thyroid hormone disruption (Preston et al., 2020) are just two examples of possible adverse health effects related to per- and polyfluorinated alkyl substances (PFAS). This diverse group of chemicals includes more than 5000 different compounds all containing a minimum of one completely fluorinated methylene or methyl carbon atom (United States Environmental Protection Agency, n.d.; OECD, 2021). The high stability of the covalent carbon–fluorine bonds results in thermal and biological stability of PFAS. These man-made chemicals often consist of a hydrophobic fluorinated carbon backbone and a hydrophilic functional group granting the molecules amphiphilic and surfactant properties. The combination of these industrially attractive characteristics leads to a multitude of applications for instance in paper based food contact materials (FCMs) (Trier, 2017).

Treatment of paper FCMs with PFAS provides non-sticky grease and waterproof materials usable for example for fast food packaging. Direct application of paper as FCMs would be difficult since the porous raw material has poor liquid resistance, low heat stability, and low resistance to chemical migration. Improvement of the physicochemical properties can be achieved by impregnating the paper for instance with PFAS (by internal or external sizing, or coating). PFAS can be used for internal as well as external impregnation of the paper products making them versatile. Traditionally, PFAS coatings can contain fluorotelomer alcohols (FTOHs) and/or polyfluoroalkyl phosphate esters (PAPs) mixtures. However, a definite list of applied PFAS in the production of FCMs does not exist (Trier, 2017; Deshwal et al., 2019; OECD, 2020). Some countries provide lists of PFAS that can be used for the production of FCMs e.g., the *German risk assessment institute* listed 12 PFAS (BfR, 2022). Nevertheless, currently, no clear global legislation regarding the use of PFAS in FCMs exists.

Over the years, more and more possible health concerns associated with PFAS have been reported. For instance, FTOHs and PAPs have been linked to the inhibition of sex hormone synthesis (Rosenmai et al., 2013) and other PFAS groups such as perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) have shown hepatotoxicity (Bil et al., 2021). Moreover, the toxicity of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) resulted in their inclusion in the *Stockholm Convention* (in 2009 and 2020, respectively) to minimize their use and production (Downie, 2012). Encompassing 152 countries, this regulation is the most global approach for PFAS management attempted. The high toxicity of PFCAs is especially concerning since other PFAS classes (namely FTOHs and PAPs) can be transformed into

* Corresponding author.
E-mail address: mile@food.dtu.dk (M. Lerch).

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the more toxic products (Jiao et al., 2021). Generally, longer chained PFCAs/PFSAs (e.g., PFOA) are assumed to be more harmful to human health than shorter chain compounds (e.g., perfluoro-*n*-butanoic acid, PFBA) leading to increased industrial use of the smaller molecules.

The toxicity of PFAS combined with their use in FCMs is particularly problematic since it allows direct contact between the chemicals and the food products. This can result in the migration of PFAS into food. For example, PAPs were found to migrate from paper FCMs into various fast-food products such as popcorn, hamburgers, and potato chips (Gebbink et al., 2013; Zabaleta et al., 2020), also, FTOHs were found in muffins after baking in paper muffin cups (Fengler, 2011). Most often PFCAs/PFSAs were seen to migrate into foods (Begley et al., 2008; Elizalde et al., 2018; Moreta & Tena, 2014). However, migration studies typically focus on only one or two of these subclasses. The occurring migration is a diffusion process, therefore, dependent on contact conditions (time, temperature, and type), and the properties of the food matrix and migrants (Castle, 2006). One of the most impactful migrant characteristics influencing the migration is the mobility of the chemicals. Typically, chemicals with a higher molecular weight are less volatile and less mobile. Accordingly, short chain PFCAs/PFSAs such as PFBA (C4 chain, vapor pressure 899 Pa at 25 °C) are expected to show higher migration than longer chain homologs e.g., perfluoro-*n*-nonanoic acid (PFNA, C9 chain, vapor pressure 3.5 Pa at 25 °C) (Bhhatarai & Gramatica, 2011; Ding & Peijnenburg, 2013). Corresponding, boiling points of the PFCAs cover a range from 121 °C (at 101.325 kPa) for PFBA to 218 °C (at 101.325 kPa) for PFNA, an increase of the chain length by a –CF2 unit increased the boiling point by roughly 20 °C (Table S1). Besides the characteristics of the migrants, the transfer of the chemicals also depends on the food matrix in contact with the FCMs. Exemplified, influential food components such as water content (Fengler, 2011) and the presence/ absence of emulsifiers (Begley et al., 2008) were reported to impact migration behavior. Even though chemical migration is depending on a plethora of factors, food simulants are often used to simplify the investigation of PFAS migration from paper FCMs (Chiang, 2012; Yuan et al., 2016; Xu et al., 2013). The quantitation of PFAS in real food samples often requires intensive extraction and clean-up procedures to enable instrumental detection (e.g., using mass spectrometry). Therefore, chemically clearly defined substitutes are used to mimic the real food matrices e.g., 50% ethanol to imitate food with medium lipophilic character (European Commission, 2011). These food simulants were primarily developed for migration tests of plastic FCMs and not for paper based FCMs. As a result, the established transferability of the migration conditions allowing the replacement of real food with the defined food simulants cannot be guaranteed (Trier, 2017). Furthermore, a comparison of the migration from PFAS containing FCMs to rice, cereals, and whole milk powder (Zabaleta et al., 2020; Elizalde et al., 2018) with Tenax® (food simulant for dry food) resulted in an underestimation of PFAS migration. Similarly, the application of oil (mygliol) to simulate the PFAS migration tests for highly lipophilic foods such as butter has also proven to be problematic (Begley et al., 2008). Migration of PFAS from FCMs into food can contribute to the consumer's dietary exposure to these potentially hazardous chemicals and thereby pose a health risk (Tittlemier et al., 2006; Jiao et al., 2021). However, risk assessments regarding PFAS in dietary exposure typically investigate the detected PFAS in food products without elaborating on the contribution of paper based FCMs (Schrenk, 2020).

Consequently, this study investigates the migration of all three PFAS classes (PFCAs/PFSAs, PAPs, and FTOH) and assesses the risk to the consumer solely caused by migration from paper based FCMs. Migration tests are performed under realistic high-temperature applications with real food samples as well as food simulants and migration conditions recommended by European Commission (EC).

2. Materials and methods

2.1. Chemicals, reagents, and materials

All solvents and analytical standards used for the analysis were obtained at the highest purity commercially available. Acetonitrile and methanol were purchased from Honeywell (Seelze, Germany). Milli-Q water was generated using a Milli-Q Elix & QPOD System from Millipore (18.2 Ωcm). Ethanol, 25% ammonia solution (EMSURE® grade), ammonium acetate, and chemicals used for the dispersive solid phase extraction: anhydrous magnesium sulfate, sodium chloride, Supercleanᵀᴹ ENVI-Carbᵀᴹ, Discovery® DSC-18 were purchased from Merck KGaA (Darmstadt, Germany). Whatman Mini-UniPrepᵀᴹ polypropylene filter vials were purchased from GE Healthcare Bio-Sciences AB (Hatfield, United Kingdom).

The native standards of 11 perfluoroalkyl carboxylic acids (PFCAs), 4 perfluoroalkyl sulfonic acids (PFSAs), 4 polyfluoroalkyl phosphate esters (PAPs), and 4 fluorotelomer alcohols (FTOHs) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Characteristic details of each compound are provided in Table S1.

PFCAs and PFSAs were bought as mixture at 2 μg/mL in methanol containing PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDeA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, PFHxS, PFOS, and PFDS. The stock solution was diluted to 50 ng/mL to prepare a working solution. The PAPs stock solutions containing 6:2 MonoPAP, 8:2 monoPAP, 6:2 DiPAP or 8:2 DiPAP were bought separately at 50 μg/mL in methanol. The stock solutions were then used to prepare a working solution of 50 ng/mL in methanol containing all compounds. FTOHs stock solutions of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were also bought separately at 50 μg/mL in methanol and used to prepare a working solution at 100 ng/mL in methanol.

Stable isotope labeled analogs of 7 PFCAs, 2 PFSAs, 2 PAPs, and 2 FTOHs were used as internal standards for quantification of the corresponding native analytes (Table S6) and were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). A stock solution mixture of labeled PFCAs and PFSAs (MPFCAs & MPFSAs) was obtained at 2 μg/mL in methanol and diluted to prepare a working solution at 31.25 ng/mL in methanol. All stock solutions of labeled PAPs (MPAPs) and labeled FTOHs (MFTOHs) were bought separately at 50 μg/mL in methanol and used to prepare one working solution mixture for each compound class at 31.25 ng/mL or 200 ng/mL, respectively.

Six-point calibration curves were prepared for each compound group: PFCAs/PFSAs 0–5.0 ng/mL, PAPs 0–5.0 ng/mL, and FTOH 0–75 ng/mL. All calibration standards also contained their corresponding internal standards (MPFCAs/MPFSAs 1 ng/mL or 0.5 ng/mL for FS analysis, MPAPs at 2.5 ng/mL, and MFTOH 20 ng/mL). To match the final sample extracts as closely as possible, calibration standards were prepared in acetonitrile for real food extracts quantification or in ethanol:Milli-Q (50:50, v:v) for food simulants quantification.

2.2. Food contact materials (FCMs) collection

Investigation of PFAS migration was performed on six paper based FCMs: three types of microwavable disposable paper plates (A-C) and three types of muffin cups (A-C). FCMs were sampled on the Scandinavian market in 2017 and early 2019. Paper plates A-B as well as muffin cups A-C were part of previous studies (Danish Veterinary & Food, 2019; Granby and Håland, 2018) and are known to contain PFAS (detailed descriptions of the FCMs are in Table S2). Additionally, two blank FCMs were used to establish background contaminations (one type of paper plate and one type of muffin cup). The blank FCMs were part of the aforementioned studies and known to not contain PFAS.

2.3. Migration tests

Migration tests were performed on both real food matrices and food

simulants to compare their performance in the investigation of PFAS migration from the collected FCMs. Since the intended use of those FCMs is for high-temperature applications (e.g., microwaving and baking), the food matrices were chosen accordingly to design the migration tests as realistic as possible: muffin for muffin cups, ready-meal tomato soup (TS), and simple to prepare oatmeal porridge (OMP) for paper plates. The selection of the food simulants and the migration conditions followed EC regulation regarding migration tests for plastic FCMs (European Commission, 2011). However, some adjustments in the migration conditions (contact type, time, and temperature) were made as the properties of the food simulants did not allow the exact reproduction of the migration conditions of the food preparation.

2.3.1. Migration from muffin cups into muffins

Muffin dough was selected to investigate the PFAS migration from muffin cups; the following muffin dough recipe was used: 150 g butter, 525 g wheat flour, 15 g baking powder, 3 eggs, 300 g sugar, and 300 mL milk (3.5% fat) to bake 24 muffins. All ingredients were bought in Danish supermarkets (Table S3 and Table S4). Eggs and sugar were combined and stirred with a hand mixer until the batter was completely smooth. Afterward, butter was added in small pieces to the mixture followed by flour, baking powder, and milk. The whole batter was mixed until it was completely homogeneous. The dough was then transferred into the muffin cups (filled about ¾) that were placed in a steel baking tray (KADAX, China) to provide stability. The muffins were baked for 13 min at 200 °C in a ChefTop^{TM} ventilated baking oven from UNOX. Then, the muffins were cooled to room temperature for about 20 min and the muffin cups were removed. The muffins were stored at −20 °C (in a freezer) until chemical analysis or directly processed further (see section 2.4.1).

2.3.2. Migration from paper plates into oatmeal porridge (OMP) and tomato soup (TS)

It was assumed that disposable microwavable paper plates are intended for the preparation of simple meals or heating of pre-prepared meals. Therefore, TS purchased as ready-meal and simple to prepare OMP were selected to investigate the migration of PFAS into real food. The OMP was prepared directly on the paper plates by combining 50 g oatmeal, 5 g butter, 0.5 g salt (sodium chloride), 100 mL milk (3.5% fat), and subsequent stirring with a spoon. The TS carton was opened and 200 mL TS was transferred into each paper plate. All ingredients were bought in Danish supermarkets (Table S3 and Table S4). The food-filled paper plates were microwaved for 1 min at 800 W in a kitchen microwave oven from Samsung. After heating, the food was stirred thoroughly and cooled down to room temperature (about 15 min). The cold food was then transferred into plastic beakers and further processed (see section 2.4.1).

2.3.3. Migration tests – food simulants

Based on the EC-regulation for migration tests for plastic FCMs, food simulants and migration conditions were selected. 50% ethanol solution (food simulant D1) was designated to imitate muffin dough and OMP during the heat treatment. The food simulant D1 is intended to simulate "food with lipophilic character". To mimic TS during the heating process a mixture of 20% ethanol (food simulant C) was used due to the lower fat content of TS. Food simulant C should be applied for food containing "relevant amounts of organic ingredients that render the food more lipophilic" (European Commission, 2011).

Regarding the contact type during the migration, the characteristics of the paper based FCMs did not allow a single-sided migration test (the ethanol solutions penetrated the paper FCMs completely) therefore an immersion-based migration test was performed. Furthermore, migration conditions had to be adjusted. The overall migration of PFAS from FCMs was investigated using contact time and temperature that were based on the standardized testing conditions "OM3", heating for 2 h at 70 °C (The European European Commission, 2011). This condition was selected for the microwaving process since it is recommended to simulate short-term (max. 15 min) heating up to 100 °C. For baking muffins, the recommended condition of "OM 7", 2 h at 175 °C, could not be used as the boiling point of the ethanol-based food simulants (78 °C) was below the recommended temperature. To keep the experimental procedure as simple as possible and reduce the risk of contamination with omnipresent PFAS, the "OM 3" testing conditions were selected. For all of the final food products, direct consumption after cooling to room temperature was expected.

For the simulation of PFAS migration into muffins or OMP, an area of 6 cm^2 (2 cm × 3 cm) of either muffin cups or paper plates was cut to ribbons, placed in a 15 mL polypropylene (PP)-tubes and soaked with 6 mL of ethanol:water (50:50, v:v). For the simulation of the migration into TS, 6 mL of ethanol:water (20:80, v:v) was added to paper plate cutouts. In all cases, the samples were mixed for 2 min and incubated for 2 h at 70 °C in a pre-heated water bath. Subsequently, the FCMs were removed with a tweezer, and the extract was stored in a freezer (-20 °C) until chemical analysis or further processed (see section 2.4.2). The described procedure followed the validated migration test methodology available at the National Food Institute. However, the immersion volume was adjusted to match the expected ratio between the food volume and the contact area of the FCMs (Table S2).

2.4. Sample preparation

2.4.1. Sample preparation of real food samples

PFAS extraction and sample clean-up of muffin, porridge, and soup samples were based on a dispersive solid phase extraction (dSPE) approach developed by the *European Reference Laboratory for Halogenated Persistent Organic Pollutants in Feed and Food* (Freiburg, Germany) (Zielinski & Riemenschneider, 2020).

The food samples were homogenized with a hand blender and 2 g of each food homogenate was weight in a 50 mL PP-tube (Sarsted, Numbrecht, Germany). Internal standards (MPFCAs/MPFSAs 0.5 ng, MPAPs 1.25 ng, and MFTOH 10 ng) were added to the samples before extraction. Solvent extraction was performed by shaking with 5 mL acetonitrile for 3 min at 1500 rpm in a GenoGrinder® from SPEX Sample prep®P (Metuchen, NJ, USA), then centrifuging for 10 min at 3500 rpm (5 °C, Heraeus Multifugex3FR centrifuge, Thermo Scientific, Waltham, MA, USA). The supernatant was collected and the extraction was repeated once. The combined supernatant was then frozen overnight (-20 °C), defrosted, and centrifuged when still cold (5 min at 3500 rpm, 5 °C) to remove fat and waxes. Then the organic phase was transferred to another PP-tube containing the dSPE materials consisting of 2 g anhydrous magnesium sulfate, 0.5 g sodium chloride, 0.1 g ENVI-Carb, and 0.1 g DSC-18. The sample was shaken for 2 min and centrifuged for 20 min (4000 rpm, 5 °C). The cleaned-up organic phase was transferred to a 15 mL PP-tube and evaporated to 500 μL (under nitrogen at 40 °C). Furthermore, samples were again frozen (-20 °C), defrosted, and centrifuged (10 min, 4000 rpm, 5 °C) and the organic layer was transferred into filter vials.

2.4.2. Sample preparation of food simulant samples

No further sample extraction was needed for the food simulant samples. For that reason, the sample extracts were vortexed, sonicated (10 min in a water bath), and then transferred into three separate filter vials, depending on the targeted PFAS group: 210 μL for PFCAs/PFSAs analysis, 230 μL for PAPs analysis, and 225 μL for FTOH analysis were transferred. Finally, the corresponding internal standard was added to each vial to obtain the final volume of 250 μL (final concentration 0.5 ng/mL for MPFCAs/MPFSAs, 2.5 ng/mL for MPAPs, or 20 ng/mL for MFTOHs).

2.5. Detection of PFAS by LC-MS/MS

Quantitation of PFAS extracted from real food and food simulants

was performed using liquid chromatography separation followed by tandem mass spectrometric detection (LC-MS/MS). An Ultimate 3000 LC-system from Thermo Fisher Scientific (Waltham, MA, USA) equipped with an Acquity UPLC® CSH^{TM} C18 (130 Å, 1.7 μm, 2.1x100 mm) as an analytical column for separation of analytes and an Acquity UPLC® BEH C18 (130 Å, 1.7 μm, 2.1 × 50 mm) as delay column to separate systematic PFAS contamination (e.g., PFAS in eluents) from the analytes.

Different LC-MS/MS methods for each compound group were used to allow optimal separation based on their chemical characteristics to increase sensitivity due to increased analysis time during MS/MS. For the analysis of both PFCAs/PFSAs and PAPs, 2 mM ammonium acetate in Milli-Q:methanol (90:10, v:v) adjusted with 25% ammonia solution to pH 9 as aqueous eluent and methanol as organic eluent were used. The separation of FTOHs used 2 mM ammonium hydroxide also adjusted with 25% ammonia solution to pH 9 and methanol as organic eluent.

For all methods, 5 μL of the sample was injected onto the analytical column (heated to 50 ± 1 °C). More separation details for all three methods are provided in Table S5. MS/MS detection of PFAS was performed on an EVOQ Elite triple quadrupole from Bruker Corp. (Billerica, MA, USA), operated in multiple reaction monitoring mode (MRM). Ionization of the analytes was achieved by heated electrospray ionization (HESI) in negative mode. Spray voltages of −3000 V for the FTOHs and PFCAs/PFSAs analysis and −3500 V for the PAPs analysis were applied. The cone temperature (350 °C), cone gas flow (20 mL/min), probe temperature (350 °C), probe gas flow (50 mL/min), and nebulizer gas flow (50 mL/min) were identical for all analysis. The corresponding collision energies and MRM transitions are listed in Table S6. Data acquired by LC-MS/MS was processed and quantified with the *MS-Data Review* application of the *MS-Workstation 8*.

All results for PFAS migration were reported in ng of PFAS per g food (ng/g food). For the conversion of the food simulant results, the concentration (ng/mL) in the simulant was converted to ng/dm^2 FCM; and then further converted to ng/g food using estimated contact areas between the food and the FCMs. A list of the considered areas, food amounts, and an example for the calculations are provided in Table S2. Comparison of the migration results was calculated with a one-tailed student *t*-test assuming unequal variance between the samples.

2.6. Quality assurance and quality control

All calibration curves (forced through 0 and weighted 1/x) showed $R^2 > 0.99$. The lower limit of quantitation (LOQ) was defined as the validated level where the deviation from the expected concentration was less than 35%. The LOQs were 0.1 ng/mL for all PFSAs/PFCAs, 10 ng/mL for 4:2 FTOH and 6:2 FTOH, 5 ng/mL for 8:2 FTOH and 10:2 FTOH, and 0.3 ng/mL for monoPAPs and diPAPs.

Due to the omnipresent nature of PFAS in the environment, identification of PFAS migration was only reported after comparison with instrument and matrix blanks. Instrument blanks (pure methanol) were run at the start, in between samples, and at the end of each analysis sequence. Matrix blanks for food samples were produced by baking muffins directly in a stainless steel muffin tray or microwaving TS/OMP in a glass beaker. The matrix blanks were extracted in the same manner as samples obtained from migration tests for real foods. Two matrix blanks were analyzed for each food matrix and injected in duplicate (n = 4). Matrix blanks for the analysis of food simulants were prepared by extraction of blank FCMs known to not contain PFAS with the assigned food simulants. Overall, no carryover was observed and almost all targeted analytes were not identified in instrument or matrix blanks, except PFHpA and PFHxA. Both compounds were detected in food simulants (<LOQ), the concentration was estimated to be 0.01 ng/mL and used for blank subtraction. Furthermore, samples with concentrations above the upper limit of quantitation were diluted to fit into the quantitation range for final quantitation.

To ensure the validity of the quantitation data, quality control samples (QC-samples) were included. For the analysis of the food simulants, native as well as internal standards were spiked directly into 50% ethanol and quantified using the calibration curves. The maximal deviation from the expected concentrations was 18% for PFCAs/PFSAs at 2.5 ng/mL, PAPs at 4 ng/mL, and for FTOHs at 10 ng/mL.

In order to assess the data quality for the real food samples, the recovery was determined. Internal standards and native standards were spiked into 2 g of each blank food matrix and processed with the described methodology (section 2.4.1 and section 2.5). Recoveries of the three food matrices were generally within 70 – 130% for the investigation of PFCAs/PFSAs (3 ng/mL), FTOHs (20 ng/mL), and diPAPs (4 ng/mL). However, some compounds showed recovery values over 130%, namely, 6:2 FTOH in OMP as well as 10:2 FTOH, PFHpA, PFPeA, and 8:2 FTOH in muffins. For these compounds, their concentration in the samples was corrected using factors obtained from recovery samples. Both monoPAPs could only be extracted from TS, with a maximum recovery of 61%. No recovery correction was necessary since the compounds were not detected in the samples. Furthermore, the extraction of 4:2 FTOHs was only possible from muffins (recovery 98%). All extracted recovery samples also showed good precision with the coefficient of variation (CV) below 28%. All described analytical detection methods are validated and accredited methodologies for PFAS migrates from FCMs developed at the National Food Institute.

2.7. Risk assessment

Consumer risk from the food servings was assessed based on dietary exposure from the migrated PFAS and comparison with safety guidelines. The dietary exposure was calculated for adults (age 18–65 years, body weight 70 kg) and children (age 3–10 years, body weight 23.1 kg) using equation (1).

$$Dietary\ \ exposure = \frac{\sum\left(PFAS\ \left[\frac{ng}{g\ food}\right]\right)\ x\ \ weight\ \ of\ \ each\ \ serving\ [g]}{body\ \ weight\ \ [kg]} \quad (1)$$

For a comprehensive risk assessment, three different approaches were used to calculate dietary exposure, varying in *Σ (PFAS)*. The total *Σ (PFAS)*, *Σ (PFOA, PFNA, PFOS, PFHxS)*, or *Σ (PFOA equivalent)* were considered. Conversion of PFAS concentration to PFOA equivalents was based on the relative potency factor (RPF) approach developed by Bil et al. (2021). To estimate a worst-case scenario, PFPeA was factored with RPF 0.05, PFHxA and PFHpA with RPF 0.01, PFNA and PFDeA with RPF 10, PFUnA with RPF 4, PFDoDA with 3, 6:2 FTOH and 6:2 DiPAP with RPF 0.02, 8:2 FTOH and 10:2 FTOH with RPF 0.04, and PFOA was considered as base value with RPF 1. In the case of PFAS concentrations below the lower limit of quantitation (<LOQ) the LOQ was assumed: 0.025 ng/g food for PFCAs, 0.075 ng/g food for PAPs, and 2.5 ng/g food for FTOHs.

3. Results and discussion

The use of PFAS in paper based FCMs can result in migration of the hazardous chemicals into food and thus pose a risk to the consumer. Consequently, results of PFAS migration to real foods prepared at high temperatures in PFAS treated paper based FCMs are presented.

These results were compared with the results of migration tests to food simulants performed on the same FCMs. Finally, the risk of PFAS exposure solely caused by migration from those FCMs to real foods was assessed.

3.1. Migration test – real food

The migration of PFCAs/PFSAs, PAPs, and FTOHs from three different microwavable disposable paper plates (paper plate A-C) and three muffin cups (muffin cup A-C) during high-temperature applications was investigated. OMP and TS were used for the migration from

Table 1
Concentrations of PFAS migrated into real food samples (oatmeal porridge, tomato soup, and muffins) from disposable paper plates or muffin cups after microwaving (1 min at 800 W) or baking (13 min at 200 °C).

	Paper Plate A		Paper Plate B		Paper Plate C		Muffin Cup A	Muffin Cup B	Muffin Cup C
	Oatmeal Porridge [ng/g food]	Tomato Soup [ng/g food]	Oatmeal Porridge [ng/g food]	Tomato Soup [ng/g food]	Oatmeal Porridge [ng/g food]	Tomato Soup [ng/g food]	Muffin [ng/g food]	Muffin [ng/g food]	Muffin [ng/g food]
PFPeA	0.35 ± 0.06	0.71 ± 0.18	0.24 ± 0.02	0.74 ± 0.12	0.40 ± 0.05	0.81 ± 0.05	N.d.	N.d.	N.d.
PFHxA	1.96 ± 0.12	2.63 ± 0.43	1.49 ± 0.05	2.57 ± 0.24	1.71 ± 0.20	1.89 ± 0.20	N.d.	N.d.	N.d.
PFHpA	0.06 ± 0.01	0.16 ± 0.05	0.04 ± 0.00	0.19 ± 0.03	0.03 ± 0.01	0.07 ± 0.01	N.d.	N.d.	N.d.
PFOA	< LOQ	N.d.	<LOQ	0.04 ± 0.00	N.d.	< LOQ	0.03 ± 0.01	0.13 ± 0.03	0.03 ± 0.02
PFNA	N.d.	N.d.	N.d.	N.d.	N.d.	< LOQ	< LOQ	0.04 ± 0.00	0.03 ± 0.01
PFDeA	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	0.02 ± 0.01	0.11 ± 0.01	< LOQ
PFUnA	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	0.03 ± 0.00	N.d.
PFDoDA	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	<LOQ	0.08 ± 0.00	N.d.
6:2 FTOH	3.66 ± 0.47	N.d.	2.83 ± 0.43	N.d.	4.26 ± 1.24	11.3 ± 1.37	N.d.	N.d.	3.41 ± 0.65
8:2 FTOH	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	1.55 ± 0.12	3.17 ± 0.27	N.d.
10:2 FTOH	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	1.18 ± 0.53	1.45 ± 0.05	< LOQ
6:2 DiPAP	< LOQ	N.d.	< LOQ	N.d.	< LOQ	N.d.	N.d.	N.d.	N.d.

paper plates and muffin dough was baked in the muffin cups. As briefly touched upon in section 2.3.3 OMP and muffin dough were considered to have lipophilic properties. This was based on the estimated fat content of 8% and 15% in OMP and muffin dough (Table S4). The fat was mainly contributed by butter (water-in-oil-emulsion), milk (oil-in-water emulsion), and also eggs in the case of muffins. Both emulsions are stabilized due to naturally occurring emulsifiers such as polar lipids (e.g., phospholipids), which are also present in egg yolk. With a fat content of 3% TS was considered a food with light lipophilic character. Components contributing to natural emulsifiers are skimmed milk and cream. No additional emulsifiers were listed as ingredients (Table S4).

Migration of PFAS to all three food matrices was observed to different degrees (Table 1). After contact with paper plates, A-C investigated foods mostly contained short chained PFCAs (PFPeA C5 to PFHpA C7) with the highest concentration of PFHxA (C6). Also, 6:2 FTOH was found in OMP and TS after contact with these FCMs. In contrast, migration from muffin cups A and B into muffins mainly resulted in the detection of longer chained PFCAs (PFOA C8 to PFDoDA C12) in rather low concentrations (max. 0.13 ± 0.03 ng/g food). Here, the longer chain FTOHs (8:2 FTOH and 10:2 FTOH) were detected with the highest concentration from 8:2 FTOH. This indicates that the PFAS-coating for muffin cups A and B contained higher amounts of longer chained PFAS than the coating used for the paper plates. However, it could also indicate that the shorter chained PFCAs are lost during the baking process i.e., evaporate out of the muffins (further discussion see section 3.3.3). The migration pattern of muffin cup C differs from the other two samples. Only PFOA, PFNA, and PFDeA were detected for the PFCAs in the muffins from cup C and the highest concentration was observed for 6:2 FTOH instead of 8:2 FTOH. Multiple causes could be responsible for the differences in the migration pattern such as the country or year of production. Muffin cups A and B were produced in China and purchased in 2017 whilst muffin cup C was produced in the EU and purchased in 2019. For confirmation of either assumption, additional data would be required.

Not only dependent on the FCMs materials of choice, the migration of PFAS was also influenced by the composition of the food matrix and physiochemical properties of the migrant. PFCAs from paper plates migrate with significantly higher concentrations ($p < 0.05$) into TS than into OMP; Except for the PFHxA migration from paper plates A and C, where the mean concentrations were higher in TS, but not significantly ($p = 0.07$ and $p = 0.2$). Contrarily to the migration behavior of the PFCAs, migration of FTOHs resulted in higher concentrations observed in OMP. Migration from paper plate A-C showed a comparable migration of 6:2 FTOH (highest in plate C) into OMP whilst only for paper plate C a migration into TS was observed. Similar results were obtained for 6:2 diPAP, where the detection was only possible in OMP (<LOQ). Considering the higher fat content of OMP (8%) compared to TS (3%) the preferences in migration can be explained by the differences in lipophilicity between the migrants. The octanol/water partition coefficient (K_{OW}) from PFPeA (log K_{OW} 0.09), PFHxA (log K_{OW} 0.70), and PFHpA (log K_{OW} 1.31) are considerably lower than for 6:2 FTOH (log K_{OW} 4.54) (Ding & Peijnenburg, 2013), indicating a higher affinity towards hydrophilic solutions. No data regarding the log K_{OW} -value for 6:2 diPAP was found, however, the molecular structure (Table S1) would suggest higher lipophilicity than 6:2 FTOH because of the high share of non-polar CF-chains in the molecule.

The migration of 6:2 FTOH from paper plate C into TS, however, exceeded the migration into OMP. A possible explanation could be found by considering the FCMs itself. The coating composition (higher concentration of 6:2 FTOH) of paper plate C and the paper quality could vary from the other analyzed paper plates. These differences could result in a less tight sealing of the paper and therefore provide a larger contact surface between the food and the FCMs. TS has a higher viscosity than OMP allowing a better interaction with the irregularities of the paper.

Table 2
Concentrations of PFAS detected in food simulants (20% ethanol and 50% ethanol) after migration tests on disposable paper plates (2 h at 70 °C).

	Paper Plate A		Paper Plate B		Paper Plate C		Muffin Cup A	Muffin Cup B	Muffin Cup C
	50% Ethanol [ng/g food]	20% Ethanol [ng/g food]	50% Ethanol [ng/g food]	20% Ethanol [ng/g food]	50% Ethanol [ng/g food]	20% Ethanol [ng/g food]	50% Ethanol [ng/g food]	50% Ethanol [ng/g food]	50% Ethanol [ng/g food]
PFPeA	3.03 ± 0.86	2.24 ± 0.71	2.78 ± 0.35	2.78 ± 0.46	5.00 ± 0.29	5.58 ± 0.66	< LOQ	< LOQ	N.d.
PFHxA	31.1 ± 10.4	27.1 ± 9.51	37.3 ± 2.56	35.7 ± 4.56	36.0 ± 2.01	36.7 ± 6.87	<LOQ	0.30 ± 0.05	N.d.
PFHpA	0.81 ± 0.31	0.62 ± 0.27	0.89 ± 0.07	0.97 ± 0.16	0.48 ± 0.06	0.58 ± 0.15	< LOQ	< LOQ	N.d.
PFOA	< LOQ	< LOQ	0.33 ± 0.03	0.30 ± 0.03	< LOQ	< LOQ	0.54 ± 0.06	0.69 ± 0.07	N.d.
PFNA	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	N.d.	< LOQ	< LOQ	N.d.
PFDeA	< LOQ	N.d.	< LOQ	N.d.	N.d.	N.d.	0.54 ± 0.10	0.57 ± 0.08	N.d.
PFUnA	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	< LOQ	< LOQ	N.d.
PFDoDA	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	0.32 ± 0.04	0.47 ± 0.06	N.d.
PFTrDA	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	< LOQ	< LOQ	N.d.
PFTeDA	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	< LOQ	0.19 ± 0.02	N.d.
6:2 FTOH	27.3 ± 8.55	< LOQ	36.0 ± 6.25	N.d.	210 ± 40.0	N.d.	N.d.	N.d.	N.d.
8:2 FTOH	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	19.2 ± 4.48	21.9 ± 6.07	N.d.
10:2 FTOH	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	50.9 ± 1.71	37.1 ± 11.8	N.d.

3.2. Migration test – food simulants

The use of food simulants to mimic real food is a typical approach for migration tests on FCMs. These food simulants have a clearly defined chemical composition and therefore simplify the sample preparation procedures required for the instrumental detection. Selection of the food simulants is based on the characteristics of food in contact with the FCMs. OMP and muffins were imitated with a solvent composition of 50% ethanol and TS was mimicked with 20% ethanol. Migration into all investigated food simulants was observed (Table 2). For migration from paper plates, PFCAs (PFPeA C5 to PFDeA C10) were detected with the highest concentration of PFHxA (C8). A comparison of the migration of PFCAs into 20% and 50% showed no significant difference ($p > 0.19$). However, severe discrepancies in the migration of 6:2 FTOH were observed. Migration of 6:2 FTOH was high in 50% ethanol (up to 210 ng/g food) but not quantifiable in 20% ethanol. A possible reason could be the high log K_{OW} of 6:2 FTOH with 4.54 in combination with the lower extraction strength and higher hydrophilicity of 20% ethanol (Danish Environmental Protection Agency, 2008). Additionally, it should be mentioned that the highest detected concentrations in 50% ethanol was detected for paper plate C. The migration tests from muffin cups A-B using 50% ethanol resulted in the detection of PFCAs (PFPeA C5 to PFTeDA C14), 8:2 FTOH, and 10:2 FTOH. No PFAS were detected in the muffin cup C migration test (discussion see section 3.3.3).

3.3. Migration in food versus food simulants

In the European Union (EU), all FCMs have to comply with the framework regulation 1935/2004 (European Commission, 2004). Additionally, regulation EC 10/2011 specifies testing procedures on plastic FCMs including the choice of food simulants and migration conditions (European Commission, 2011). However, no regulation exists for the testing of paper FCMs. Hence, the suitability of the application of these “plastic migration test conditions” was investigated by comparing the migration of PFAS in food simulants (50% ethanol and 20% ethanol) and real food (OMP, TS, and muffins).

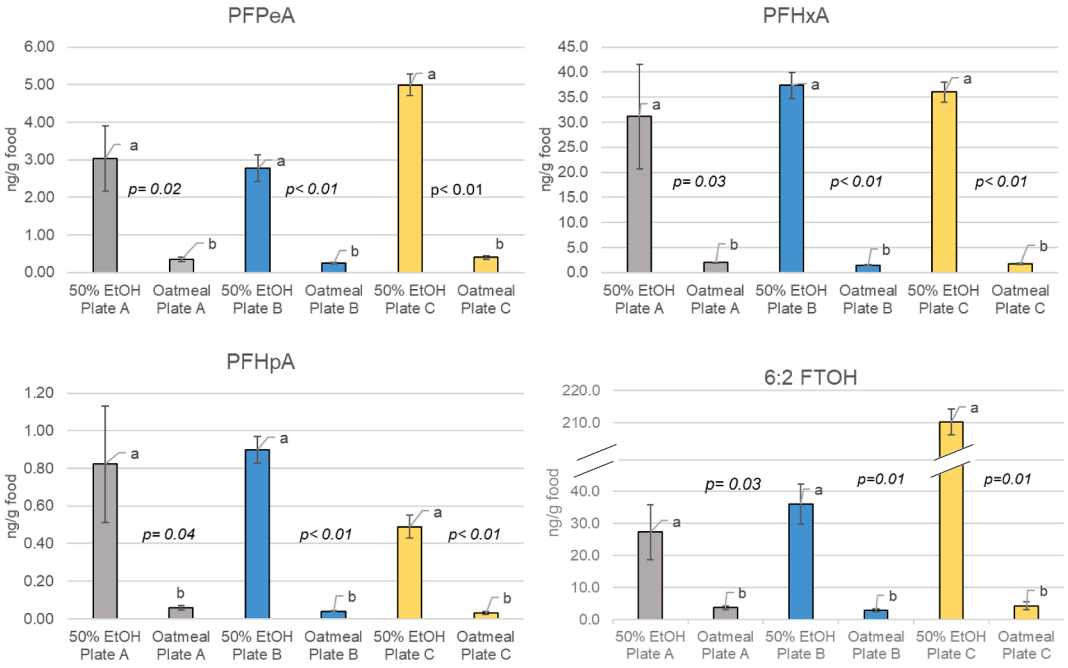

Fig. 1. Comparison of PFAS (ng/g food) migrated into 50% ethanol as food simulant (left column) and oatmeal porridge as real food matrix (right column) from paper plates A (grey), B (blue), and C (yellow). p-values were determined by the use of an independent student *t*-test. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3.1. PFAS migration into oatmeal porridge versus 50% ethanol

Migration from paper plates A-C showed significantly higher concentrations of PFCAs (PFPeA C5 to PFHpA C7) and 6:2 FTOH migrating to 50% ethanol than to OMP (Fig. 1). Additionally, detection of PFOA, PFNA, and PFDeA (<LOQ) was only possible in the food simulant but not in real food. These results indicate that 50% ethanol could be safely used as a food simulant to investigate the migration of PFCAs and FTOHs from paper plates. In the context of consumer safety, an over-estimation of migration of the hazardous chemicals would be preferable to an under-estimation. On the contrary, 6:2 diPAP was only detected (<LOQ) in OMP.

Besides the lipophilicity of the molecule, previously mentioned in section 3.1, it should also be considered that most PFAS show surfactant activity due to their amphiphilic character. Consequently, PFAS can form micelles with themselves or other surfactants present in the matrix when their concentration reaches or exceeds the critical micelle concentration. As a result, the migration of 6:2 diPAP into OMP could be simplified due to the lower surface tension caused by the natural emulsifiers in the matrix. Begley et al first reported increased migration of PFAS in the presence of emulsifiers in 2008 (Begley et al., 2008).

This could indicate the need for alternative food simulants to investigate the migration of PAPs from paper FCMs. An alternative food simulant could be an oil-in-water emulsion. Similar to the mixture of oil with added emulsifiers (e.g., miglyol with Tween60) that was reported by Begley et al (Begley et al., 2008) to simulate butter (an water-in-oil emulsion).

3.3.2. PFAS migration into tomato soup versus 20% ethanol

The migration of PFCAs from paper plates A-C is significantly higher in 20% ethanol than into TS ($p < 0.04$) except for PFHpA migrated from paper plate A (Fig. 2). Observed mean migration was higher in 20% ethanol but not significantly ($p = 0.07$). The similar or higher migration of PFCAs into 20% ethanol would again suggest the suitability for the application of the food simulant to predict the migration of PFCAs from paper FCMs.

However, the migration of 6:2 FTOH does not follow this trend. Quantitation of the compound was only possible in TS after contact with paper plate C and not in the 20% ethanol simulant.

As presented in sections 3.1 & 3.2 has 6:2 FTOH a high log K_{OW} –values indicating a preferred migration into nonpolar systems. As a result, it is possible that 20% ethanol is too polar to allow migration of 6:2 FTOH. Although, TS is more polar than the other food matrices it still contains about 3% fat including natural emulsifiers that could have supported the migration of 6:2 FTOH. The high concentrations of 6:2 FTOH observed in 50% ethanol could suggest the use of this food simulant as an alternative to 20% ethanol.

3.3.3. PFAS migration into muffin versus 50% ethanol

Comparison of the migration of PFCAs into muffins and food simulant (50% ethanol) from muffin cups A and B showed significantly higher migrations into 50% ethanol for PFOA, PFDeA, PFDoDA, 8:2 FTOH, and 10:2 FTOH (Fig. 3). Additionally, PFPeA, PFHxA, PFHpA, PFTrDA, and PFTeDA were only detected in the food simulants.

As touched upon in section 3.1, smaller molecular weight PFCAs, PFPeA (C5), PFHxA (C6), and PFHpA C7) were not detected in muffins. However, they were detected in food simulants. It is hypothesized that lighter PFCAs in the FCMs might migrate into food and evaporate during the muffin baking process. During such a process, the high applied temperature of 200 °C could enable the evaporation of the mobile PFCAs (boiling points of 140 °C, 157 °C, and 177 °C) into the air (open system). Fengler et al. reported similar observations (Fengler, 2011). In the case of PFTrDA and PFTeDA with boiling points up to 270 °C evaporation is not considered. It is more likely that the concentrations were too low to be extracted from the real food samples. This could indicate the suitability of the use of 50% ethanol to mimic PFAS migration into muffins.

The migration pattern from muffin cup C does not follow the described trends. No migration into 50% ethanol was observed and only low concentrations of PFOA, PFNA, PFDeA, 6:2 FTOH, and 10:2 FTOH were detected in the muffins. All compounds have been seen to migrate into 50% ethanol therefore the suitability of the food simulant is not likely the cause of lacking migration. Furthermore, the rigorous use of blanks rules out that the detected PFAS in the muffins are contaminants. Similar to paper plate C the irregularities in migration could be caused by variation of the FCMs. For the entire analysis, muffin cups were sampled randomly out of the available FCMs from the same brand therefore, it is possible that not all muffin cups contained the same

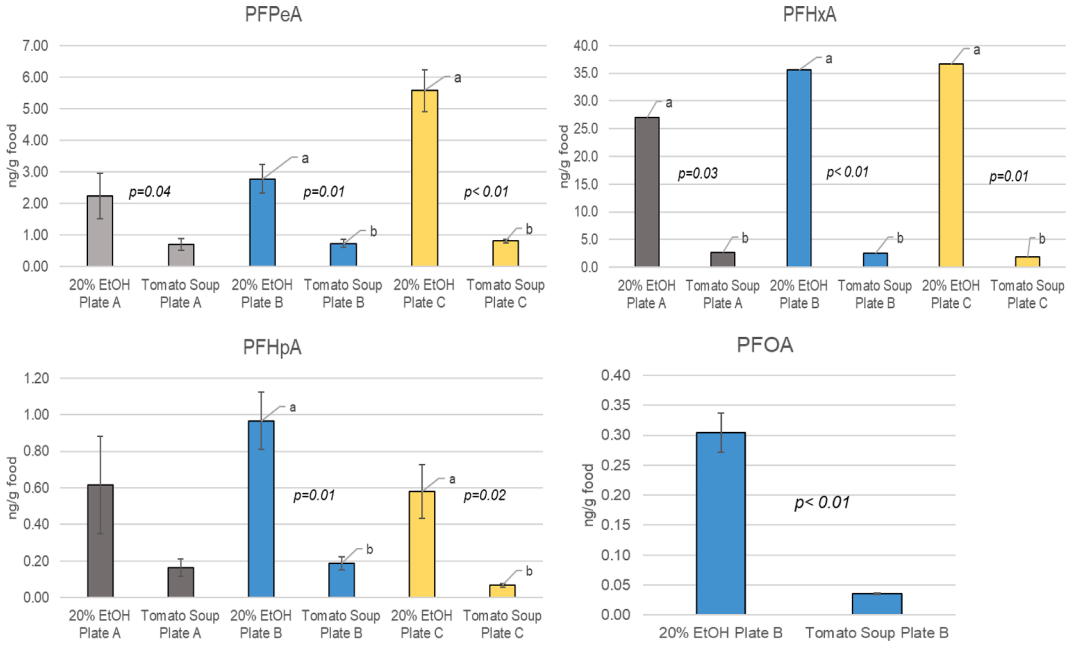

Fig. 2. Comparison of PFAS (ng/g food) migrated into 20% ethanol as food simulant (left column) and tomato soup as real food matrix (right column) from paper plates A (grey), B (blue), and C (yellow). P-values were determined by the use of an independent student *t*-test. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

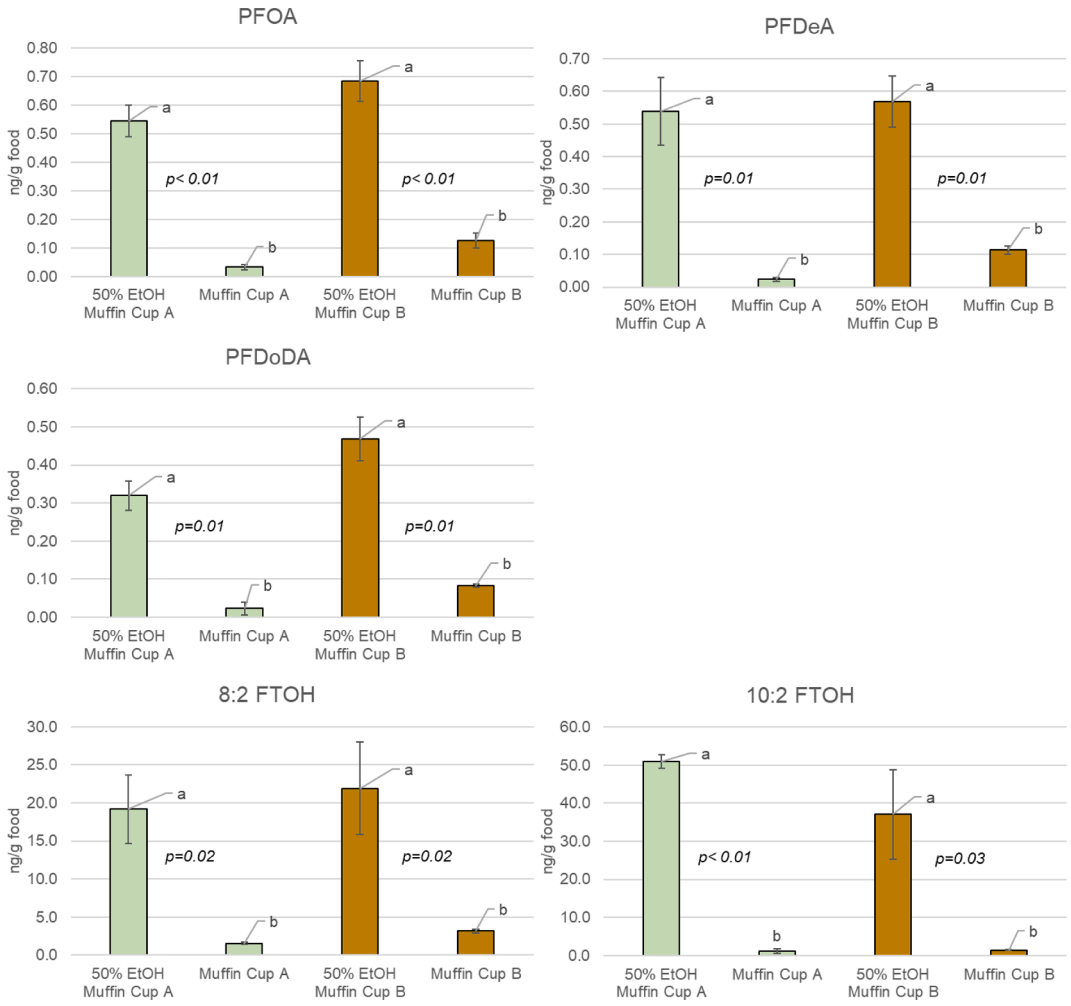

Fig. 3. Comparison of PFAS (ng/g food) migrated into 50% ethanol as food simulant (left column) and muffins as real food matrix (right column) from muffin cups A (green) and B (orange). P-values were determined by the use of an independent student *t*-test. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

amount/composition of PFAS. This suggests that PFAS present in muffin cup C could be added not intentionally but be residues in the production system.

3.3.4. *PFAS migration – can real food be simulated with food simulants?*

Comparison of the migration test results for real food with the migration to food simulants indicates a suitable performance of 50% ethanol to mimic food with lipophilic properties such as OMP and muffins. The food simulant originally proposed by the EC for migration tests on plastic food contact materials showed significantly higher migration of PFCAs and FTOHs than their respective migrations into real food. In the context of consumer safety, an overestimation of migration is preferable. Therefore, the application of the EC proposed migration conditions appears to be appropriate for use on migration tests investigating the transfer of PFCAs and FTOHs from paper FCMs.

Furthermore, the use of 20% ethanol to mimic food with light lipophilic properties such as TS provides comparable results for the migration of PFCAs but not for FTOHs.

Concluding, the application of migration test conditions developed for plastic FCMs, cannot be directly extrapolated to study the migration of all three PFAS groups from paper based FCMs. The physicochemical properties within the large group of chemicals are too diverse to predict the migration behavior without preparative experiments.

3.4. *Estimation of dietary exposure and risk assessment*

The migration of PFAS from paper based FCMs into food products can cause health risks for the consumer. To determine if this is the case for the observed migrated PFAS, the dietary exposure for each food product was estimated (Table 3) and compared to currently available safety thresholds. The EFSA Panel on Contaminants in the Food Chain proposed a tolerable weekly intake (TWI) of 6 ng/kgbw/week for PFOA (0.9 ng/kgbw/day) in 2018 (Knutsen et al., 2018) and a new total lower TWI for Σ (PFOA, PFNA, PFHxS, PFOS) of 4.4 ng/kgbw/week (0.63 ng/kgbw/day) in 2020. The focus was thereby placed on the most toxic and frequently occurring PFAS in food (Schrenk, 2020). In the present study, all dietary exposures were calculated per serving of food: average weight TS 208 g, average weight OMP 164 g, average weight muffin with muffin cup A 43.3 g, average weight muffin with muffin cup B 43.3 g, and average weight muffin with muffin cup C 42.7 g. The assumption was made that only one portion of the food serving was consumed daily, e.g., consumption of one muffin baked in muffin cup A per day.

Following the EFSA recommendations, the combined dietary exposure for PFNA and PFOA was estimated since neither PFOS nor PFHxS were found to migrate into food from the investigated FCMs. The dietary exposure (Table 3, "sum of PFOA/PFNA") for adults (age 18–65 years) varied from 0 to 0.15 ng/kgbw/ per day with the maximal exposure caused by the consumption of TS prepared on paper plate C. None of the estimated exposure values exceeded the tolerable daily intake of 0.63

Table 3
Estimated dietary exposures for PFAS migration from paper based FCMs in real food (oatmeal porridge, tomato soup, and muffins).

			Paper Plate A		Paper Plate B		Paper Plate C		Muffin Cup A Muffin	Muffin Cup B Muffin	Muffin Cup C Muffin
			Oatmeal Porridge	Tomato Soup	Oatmeal Porridge	Tomato Soup	Oatmeal Porridge	Tomato Soup			
Total PFAS		Total *Σ (PFAS)* [ng/g food]	6.13	3.50	4.70	3.54	6.48	14.1	2.83	5.01	6.00
	Adult	Dietary exposure per serving [ng/kgbw/day]	14.3	10.4	11.0	10.5	15.1	41.9	1.75	3.10	3.65
	Child	Dietary exposure per serving [ng/kgbw/day]	43.4	31.5	33.3	31.8	45.9	127	5.30	9.38	11.1
Sum of PFOA/PFNA		*Σ (PFOA/PFNA)* [ng/g food]	0.03	0.00	0.03	0.04	0.00	0.05	0.06	0.17	0.06
	Adult	Dietary exposure per serving [ng/kgbw/day]	0.06	0.00	0.06	0.12	0.00	0.15	0.03	0.11	0.04
	Child	Dietary exposure per serving [ng/kgbw/day]	0.18	0.00	0.18	0.36	0.00	0.45	0.10	0.32	0.11
RPF Approach		*Σ (PFOA equivalent)* [ng/g food]	0.20	0.22	0.15	0.29	0.15	0.63	0.66	2.17	0.75
	Adult	Dietary exposure per serving [ng/kgbw/day]	0.46	0.66	0.35	0.87	0.36	1.87	0.41	1.34	0.46
	Child	Dietary exposure per serving [ng/kgbw/day]	1.39	1.99	1.06	2.63	1.09	5.67	1.24	4.07	1.38

ng/kgbw/day of Σ (PFOA/PFNA/PFOS/PFHxS). For children (age 3–10 years) the maximum estimated exposure was with 0.45 ng/kgbw/day around 3 times higher than for adults but still within the threshold limits. However, this approach of dietary exposure estimation only considered two out of 12 PFAS that were observed migrating into food.

To highlight the severity of the neglected concentrations of PFAS, the total PFAS concentration in food (Table 3 "total PFAS") was used to calculate the dietary exposure for adults and children. The estimated daily exposure for adults varies from 1.75 to 41.9 ng/kgbw/day and for children from 5.30 to 127 ng/kgbw/day. The high differences in the detected sum concentrations of "total PFAS" and "sum of PFOA/PFNA" highlighted the need for a more comprehensive form of risk assessment. Therefore, the relative potency factor (RPF) approach developed by Bil et al (Bil et al., 2021) was used to convert the concentrations of each PFAS to a PFOA equivalent. The conversion factors were determined based on the liver toxicity of the PFAS (Bil et al., 2021). The summarized PFOA equivalents were then used to calculate the dietary exposure per serving (Table 3, "RPF approach"). The estimated dietary exposure for adults is between 0.35 ng/kgbw/day and 1.36 ng/kgbw/day. Servings for TS and muffins baked in muffin cup B exceeded the safety threshold of 0.63 ng/kgbw/day Σ (PFOA, PFNA, PFOS, PFHxS). Also, all daily dietary exposures calculated for children (1.06 to 5.67 ng/kgbw/day) exceeded the guide value by up to nine times. The differences in the dietary exposures determined with the two assessment approaches (sum PFOA/PFNA and RPF approach) emphasized the necessity to apply a mixture-based procedure to gain a comprehensive insight into the potential risk to the consumer.

This study, however, only investigated the application of targeted PFAS treated FCMs selected among samples with elevated levels of total organic fluorine (TOF). Hence, concerning the selection of FCMs worst case scenarios were estimated. Between 2015 and 2019, around 70% of paper based FCMs on the Danish market were found to contain detectable levels of TOF that indicate the intentional addition of PFAS to FCMs. In Denmark, this percentage is expected to decrease further since in 2020 a national ban on PFAS treated FCMs was issued by the Danish government, with a maximum limit of 20 μg F/g FCMs (Danish Veterinary and Food Administration, 2020). Additionally, in the last years, replacements for PFAS have been reported e.g., waxes of polyethylene (Glenn et al., 2021). Still, no comparable international regulations for the use of PFAS in FCMs exist. Furthermore, the performed migration tests and risk assessment only analyzed a small number of PFAS that are typically investigated in control procedures. The diverse nature of the group of PFAS (more than 5000 compounds) could result in the presence of additional PFAS in FCMs that were not included in the targeted analysis. The validity of this assumption has been shown for alternative application fields of PFAS for instance in firefighting foam (Rotander et al., 2015).

Nonetheless, PFAS migration from paper FCMs during high-temperature applications contributes considerably to the dietary exposure of the consumer. More importantly, based on the RPF approach result for the dietary exposure it can be assumed that the migration of PFAS can pose a risk to the consumer, especially children.

4. Conclusion

"Is the use of paper FCMs treated with PFAS safe for high-temperature applications?" Based on the presented comprehensive risk assessment using the dietary exposure estimations calculated with the RPF approach, the answer is no.

All estimated dietary PFAS exposures for children (1.06 to 5.67 ng/kgbw/day) exceeded the safety threshold (0.63 ng/kgbw/day Σ (PFOA, PFNA, PFOS, PFHxS) by up to nine times. This highlights the necessity to use comprehensive risk assessment approaches. Otherwise, the risk to the consumer could be underrated as shown by the dietary exposure Σ (PFOA, PFNA). This comprehensive form of risk assessment requires comprehensive migration studies investigating multiple PFAS subclasses like the applied dSPE-based sample preparation method that already allowed the combined investigation of three PFAS subclasses (PFCAs/PFSAs, PAPs, and FTOHs). Considering the plethora of factors that can already influence the migration of PFAS into real food (e.g., food composition, PFAS characteristics), the application of food simulants, to simplify the analysis procedures should be approached with caution, especially for the analysis of FTOHs in food with light lipophilic character. However, the use of 50% ethanol to simulate OMP and muffins could lead to an overestimation of the PFCAs and FTOH migration and the related risk. This would be preferable to predict consumer safety.

However, the most reliable way to avoid the unnecessary exposure of the consumer to PFAS would be to prohibit the addition of PFAS to FCMs.

CRediT authorship contribution statement

Michaela Lerch: Methodology, Investigation, Data curation, Writing – original draft, Visualization, Validation, Software. **Khanh Hoang Nguyen:** Writing – review & editing, Methodology, Supervision, Resources. **Kit Granby:** Conceptualization, Funding acquisition, Supervision, Project administration, Methodology, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.133375.

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