Chemosphere 363 (2024) 142907

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Risks associated with the presence of PFAS in FCM: An investigation of the Belgian market

Mélanie Di Mario [a,*], Laurent Bernard [a], Matthieu Legros [a], Florian Peltier [a], Salvatore Ciano [a], Séverine Goscinny [a], Jean-François Focant [b], Els Van Hoeck [a]

[a] *Organic Contaminants and Additives Service, Sciensano, Rue Juliette Wytsman 14, 1050, Brussels, Belgium*
[b] *Organic and Biological Analytical Chemistry Group, MolSys Research Unit, University of Liège, 11 Allée du Six Août, 4000, Liege, Belgium*

HIGHLIGHTS

- Food contact materials (FCM) contributes to human exposure to PFAS substances.
- Paper analogues FCM are more contaminated up to a factor 10 compared to paper and board FCM.
- Risk assessment highlighted risks for the consumers regarding a coffee cup and a food tray.

GRAPHICAL ABSTRACT

ARTICLE INFO

Handling editor: J. de Boer

Keywords:
PFAS
Food contact materials
Risk assessment
LC-MS/MS

ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of chemicals that have been widely used by various industries, including the food contact material industry. These substances are favoured for their ability to repel oil and resist moisture. However, exposure to PFAS has been linked to several health problems, including effects on the immune system. According to the European Food Safety Authority (EFSA), food contact materials (FCM) are likely to contribute to human exposure to PFAS. Therefore, this study investigated the exposure to PFAS from FCM. One hundred and ten FCM made of paper and board (e.g. straws, cups, bowls, boxes etc.), sugar cane or wheat pulp-based FCM, called paper analogues (e.g., cup, bowls, plates, hamburger boxes etc.) were carefully selected on the Belgian market and investigated using liquid chromatography coupled with high-resolution mass spectrometery. Out of the 25 PFAS targeted, 11 were detected in the samples, mainly perfluoroalkyl carboxylic acids (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA) and PFOS. It was found that all of the paper analogue samples contained PFAS, while 43% of the paper and board samples showed the presence of these chemicals. Except for one sample, most detections suggest contamination rather than intentional use. Finally, a risk assessment was conducted, which revealed potential risks for consumers related to a coffee cup made of paper and board and a food tray made of sugar cane.

* Corresponding author.
E-mail addresses: melanie.dimario@sciensano.be (M. Di Mario), Laurent.Bernard@sciensano.be (L. Bernard), Matthieu.Legros@sciensano.be (M. Legros), Florian.Peltier@sciensano.be (F. Peltier), Salvatore.Ciano@sciensano.be (S. Ciano), Severine.Goscinny@sciensano.be (S. Goscinny), JF.Focant@ULiege.be (J.-F. Focant), Els.Vanhoeck@sciensano.be (E. Van Hoeck).

https://doi.org/10.1016/j.chemosphere.2024.142907
Received 4 June 2024; Received in revised form 16 July 2024; Accepted 18 July 2024
Available online 20 July 2024

1. Introduction

Per- and polyfluoroalkyl substances (PFAS), commonly known as "Forever chemicals", are a large family of thousands of substances partially or totally fluorinated. Due to their particular physical properties, these substances are widely used by industries or applications (e.g., textiles, fire extinguishing foams, etc.). Indeed, these chemicals are resistant to degradation and remain stable due to the strong chemical bonds between the carbon and fluorine atoms (Straková et al., 2023; Lerch et al., 2022). However, they are subject to concern as they accumulate in living organisms and the environment (Pérez et al., 2013). PFAS are also potentially associated with a wide range of adverse health effects, including the development of various types of cancers, negative impact on fertility, immunotoxicity, abnormal fetal development, etc., but are also suspected to be endocrine disruptors (Straková et al., 2023; Dueñas-Mas et al., 2023; Schaider et al., 2017). In 2018, the European Food Safety Agency (EFSA) released a report on the harmful effects on human health of two well-known PFAS chemicals, PFOA and PFOS (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2018). Exposure to these chemicals can lead to increased cholesterol levels in serum of adults and reduced birth weight. Moreover, PFOS exposure can weaken the body's immune system, which can cause a decrease in the antibody response to vaccinations in children. PFOA can also negatively affect the liver by increasing the prevalence of high serum levels of an enzyme called alanine aminotransferase (ALT). In 2020, the EFSA CONTAM Panel conducted a risk assessment for the sum of four PFAS (PFOA, PFNA, PFHxS, and PFOS) due to their similar effects on animals, toxicokinetics, and observed levels in human blood (EFSA Panel on Contaminants in the Food Chain (EFSA CONTAM Panel) et al., 2020). Therefore, based on the outcome of the opinion, EFSA established a tolerable weekly intake (TWI) of 4.4 ng kg^{-1} body weight per week. It is worth noting that exposure to PFAS from food is considered one of the major sources of human exposure (Vera et al., 2024; Trudel et al., 2008). However, as described in the EFSA opinion, food contact materials (FCM) can also be a source of exposure to PFAS, even if it is considered that the contribution to human exposure is small compared to other sources (EFSA Panel on Contaminants in the Food Chain (EFSA CONTAM Panel) et al., 2020). Nevertheless, migrations of PFAS from FCM into food are not taken into account in the estimated dietary exposure, leading to an underestimation of the overall exposure. Non-sticky coating for paper and board is the most frequent application of PFAS in FCM (Bokkers et al., 2019; Peters et al., 2019) however, scarce information is available about the composition of the PFAS blend. (Lerch et al., 2023). Additionally, since the ban of certain single-use plastic products (e.g., straws, cutlery, plates) in all EU member states in July 2021 (Directive (EU), 2019), alternatives, considered as more sustainable, were introduced on the EU market (e.g., bagasse, wheat pulp, wood, paper and board etc.). However, the physical properties of plastic are often challenging to achieve without adding chemical substances to improve oil/grease and moisture resistance such as PFAS. Indeed, without a coating or treatment, certain materials like paper and board or paper analogues (e.g., made of sugar cane or wheat pulp) FCM cannot withstand certain types of food (e.g., fatty, liquid) (Mme Recyclage, 2024). The increased concerns about PFAS are leading regulatory authorities to act against the use of these chemicals. A few PFAS (PFOA, PFOS and PFHxS and their related salts) are listed in the Stockholm Convention, aiming to reduce or ban the use of persistent organic pollutants (POPs) (Idowu et al., 2013). In Europe, Regulation (EU) 2023/915 sets limits in food for 4 PFAS (PFOS, PFOA, PFNA, PFHxS) (Commission Regulation (EU), 2006). Nevertheless, there is currently no specific legislation regarding the use of PFAS in FCM. However, all FCMs must comply with Regulation (EC) No. 1935/2004. This regulation mandates that all materials and articles, under normal or foreseeable conditions of use, should not transfer their constituents to food in quantities that can endanger human health. (European Parliament and Council, 2004). In addition, Regulation (EU) 2020/784 entered into force, restricts the use of POPs with specific limits for PFOA and its salts of 0.025 mg kg^{-1} and 1 mg kg^{-1} for PFOA-related compounds (any substances that degrade to PFOA, including salts and polymers) (European Commission). Notwithstanding, only few substances are included in these documents compared to the number of PFAS potentially used. That is why the European Chemical Agency (ECHA) in collaboration with Germany, The Netherlands, Sweden and Denmark, proposed the broadest restriction proposal in history of roughly 10 000 PFAS. Currently, the ECHA committee is revising the restriction proposal (European Chemical Agency, 2023). The European Commission is slated to present the proposal to the Member States in 2025.

Even if various studies have been conducted in the past, especially in the last years to evaluate the levels of PFAS in different types of FCM, however, information about their presence in FCM is scattered (Phelps et al., 2024). In 2018, a study on the Norwegian market was conducted on 35 paper and board FCM migrated with simulant D1 (i.e. 50% Ethanol). The results highlighted the highest concentration in plates and the presence of fluorotelomer alcohols in 26% of the samples (Granby and Haland Tesdal, 2018). In 2020, Zabaleta et al. analysed 19 paper and board FCM, including baking papers, muffin cups, burger wrappers, French fries wrappers, burger boxes etc (Zabaleta et al., 2020). Migrations were performed with simulant D1, Tenax, and 95% ethanol. The outcome of the study showed a trend in terms of migration with short-chain PFAS tending to migrate more in simulant D1 than in 95% of ethanol. The contrary was observed with long-chain PFAS, and overall low migration of PFAS was observed with Tenax. Another study conducted in 2023 showed the migration of perfluorocarboxylic acids, fluorotelomer sulfonates and alcohols as well as polyfluoroalkyl phosphoate di-esters in samples, especially in plant-based samples advertised as biodegradable or compostable (Straková et al., 2023). In the same year, a study on food packaging from French fast-food restaurants, where samples were extracted with methanol, showed that 100% of the samples contained PFAS but in lower concentrations than in previous studies (Dueñas-Mas et al., 2023). Extraction with methanol of straws in the Belgian market was also conducted, revealing higher PFAS concentrations in paper and plant-based materials than in previous studies (Boisacq et al., 2023). Finally, in 2024, Vera et al. published a study on various FCMs, such as cardboard, biopolymer, paper, Teflon, etc., using Tenax migration, highlighting differences in PFAS concentration depending on the production location (Vera et al., 2024).

In the present study, the migration of PFAS from various FCMs made of paper and board and paper analogues present on the Belgian market is investigated. These samples include new applications of paper and board (analogues) like straws or takeaway applications, some of them replacing certain single-use plastics banned from the EU market. However, other applications like muffin moulds are also included. Moreover, similar articles from fast food chains will also be included since they have gained popularity. The study was conducted following harmonized methods developed by the European Reference Laboratory for FCM (EURL-FCM) to analyse paper and board FCM. Finally, the risks associated with these FCMs are assessed.

2. Materials and methods

2.1. Sampling

This present study focused on various types of FCM made of paper and board (e.g., straws, noodle boxes, cups etc.) and paper analogues made of bagasse or wheat pulp (e.g., plate, bowl, fork, catering plate etc.). A total of 110 samples were selected based on a web-based market study performed on the Belgian market (Ciano et al., 2023), articles purchased in Belgian retail stores (i.e. packaging containing a straw, like juice boxes) and finally, articles available in fast food restaurants. In order to cover a variety of articles available on the market, a lower number of the same items were purchased in favour of a higher diversity of the samples. An exhaustive description of the samples is provided in

Table 1
Applied test conditions.

Article material	Usage	Examples	Sample preparation	Simulant	Test conditions
Paper and board	Cold/ambient or hot use	Sandwich bag, hamburger box, cup, fries trays	Filling or cut speciment	Milli-Q water 95% Ethanol	24h at 23 °C 2h at 20 °C
	Only hot use	Muffin cup, roasting bag, baking paper		Milli-Q water 95% Ethanol	2h at 80 °C 2h at 60 °C
Paper analogues (bagasse, wheat pulp)	Only hot use	Cup Lid, hamburger box, bowl, plates	Filling, immersion or cut speciment	Simulant B 95% Ethanol	2h at 70 °C 2h at 70 °C
	Cold/Ambient or Hot use	Fork	Immersion	Simulant B 95% Ethanol	30 min at 70 °C 30 °C at 70 °C

Supplementary Table S1, including details on the type of FCM, presence of recycled fibers, coating, color, migration conditions, and whether the samples were purchased from a retail store, fast food restaurants or selected from the market study. Articles were purchased between September and October 2022.

2.2. Solvents, reagents, and standard solutions

Commercial stock solutions for all the targeted compounds of either 2 μg mL^{-1} or 50 μg mL^{-1} as well as isotopically labelled internal and external standards of 2 μg mL^{-1} were purchased from BCP instruments (Oullins, France) supplied by Wellington Laboratories (Guelph, Canada). Next, working solutions were prepared by appropriate dilutions of the stock solutions with methanol. All the solutions were stored at −20 °C and kept for two years. Solvents such as methanol (MeOH), acetonitrile (ACN) and ethanol (EtOH) were purchased from Biosolve (Valkenswaard, The Nederlands). Water was purified using a Millipore Milli-Q IQ 7000 system (Merck, Overijse, Belgium). Ammonia solution 28–30%, ammonium acetate and acetic acid (≥99%) were purchased from VWR (Darmstadt, Germany) and citric acid from Sigma Aldrich (Saint-Louis,USA). Solid phase extraction cartridges “Bond Elut PFAS WAX, 500 mg” were purchased from Agilent (Ketsch, Germany). The results were quantified using a calibration curve prepared in methanol ranging from 0.2 ng mL^{-1} up to 40 ng mL^{-1}. The targeted substances and internal standards with their associated mass spectrometer parameters can be found in Table S2 of the supplementary data. The limit of quantification (LOQ) are presented in Table S3 of the supplementary data. Fluorotelomer alcohols (FTOHs) and polyfluoroalkyl phosphate esters (PAPs) were not investigated in this study in favour of PFAS recommended for monitoring by Recommendation (EU) 2022/1431.

2.3. Sample preparation and analysis

First, the difference between migration and extraction should be highlighted to ensure consistency in the description of experiments. Migration involves the use of food simulants as described in Regulation (EU) October 2011. However, these simulants have been developed for plastic FCM and might not be suitable for other types of FCM. According to the EURL guidelines on testing conditions for kitchenware articles in contact with foodstuffs (European Commission, 2023), other simulants have been defined for paper and board FCM. These simulants are water and 95% ethanol, based on CEN standards EN 645 (EN 645, 1994) and EN 15519 (EN 15519, 2007). Although ethanol for paper and board FCM can also be considered an extraction, it does not correspond to an exhaustive extraction when using a more severe organic solvent (e.g., hexane). The term migration will be used in this manuscript to refer to these experiments.

The migration conditions (time and temperature) were selected according to the EURL guidelines (European Commission, 2023). When article filling (e.g.,bowl, cups) or immersion (e.g., straws) was possible, the intact article was migrated. If the article could not be filled or immersed (e.g. muffin cups, hamburger box), one dm^2 was cut and immersed in the food simulant. Table 1 summarises the test conditions applied depending on the type of articles.

For the analysis of PFAS, 25 mL of the aqueous fraction was combined with 25 mL of the organic fraction. The organic phase was dried under nitrogen, and the sample was reconstituted in 50 mL with the associated aqueous simulant. The extract was then purified using 500 mg Bond Elut PFAS WAX solid phase extraction (SPE) cartridges. The cartridges were conditioned with 4 ml of MeOH/NH4OH (95/5, v/v), followed by 4 ml of methanol and 4 ml of Milli-Q Water. Next, the samples were loaded, and the cartridges were washed with 6 mL of Water/ammonium acetate solution of 20 mM, followed by 6 mL of MeOH/2% acetic acid solution. The cartridges were dried for 5 min before the PFAS were eluted using 12 mL MeOH/NH4OH (95/5, v/v). Finally, the eluates were dried until 100 μL at 50 °C and 400 μL of MeOH was added, and the extract was transferred to a polypropylene vial. The final extract was then analysed by liquid chromatography coupled with high-resolution spectrometry (LC-HRMS). Recoveries and background contamination were assessed for each analysis batch through quality controls and blank procedures. Samples were analysed in single.

The chromatography and mass spectrometry details are available in the supplementary data section in Tables S2 and S4.

2.4. Expression of the results

The results are expressed in μg kg^{-1} food according to EURL guidelines (European Commission, 2023). The real surface-to-volume ratio in actual or foreseen use was applied except for articles for which less than 500 mL of simulant was used. In this case, a surface-to-volume ratio of 6 dm^2 per kg of food was applied.

2.5. Risk assessment

The risk assessment was performed using the EFSA RACE Tool (Fürst et al., 2019). This tool was originally developed by the EFSA Working Group to support risk managers in deciding whether a RASFF notification should be made. The EFSA RACE Tool is a decision tree that suggests a quick and reliable way to evaluate risks. The risk evaluation is based on assessing toxicological properties and dietary exposure. The outcome is determined by comparing the exposure level to a toxicological reference point resulting in “no risk”, “low probability of adverse health effects” or “low concern for public health”, “potential risk”, or “risk”. The terminology depends on the available toxicological data for the investigated substance. When a “potential risk” or “risk” is indicated, other investigations should be conducted as a concern for consumers is highlighted.

According to the latest scientific opinion of EFSA, a tolerable weekly intake (TWI) of 4.4 ng kg^{-1} body weight per week was established for the sum of 4-EFSA-PFAS (PFAS, PFOA, PFNA, PFHxS and PFOS). Two scenarios were considered: (i) sum of the 4-EFSA-PFAS and (ii) sum of all PFAS considering the relative potency factors (RPFs) developed by

Table 2
Overview of the selected samples.

Material	Category	Examples	Number
Paper and Board	Straw	Cocktail straw, juice straw, soda straw, etc.	20
	Takeaway - Hot use	Boxes (e.g. pizza, hamburger), Trays/bags (e.g. fries, snack) Wraps (e.g. tacos, hamburger), Cups (e.g. Coffee), Bowls (e.g. soupe), Foil/paper (e.g. baking papers, airfrier paper). Muffin cups	66
	Takeaway - Cold use	Bags (e.g. sandwich), Cups (e.g. soda), Bowls (e.g. ice cream), Utensil (e.g. spoon)	9
Paper analogues	Takeaway - Hot use	Boxes (e.g. hamburger), Trays, Bowls, Plates, cup and lid.	13
	Takeaway - Cold use	Bowls (e.g. salads), Utensil (e.g. fork)	2

RIVM in the Netherlands (Zeilmaker et al., 2018). The relative potency factors (Table S5) express the toxic potency of individual mixtures expressed as a comparable amount of a well-known substance in terms of toxicity and occurrences. In the RPF approach, which is similar to the use of Toxic Equivalency Factor (TEF) factors for dioxins, the ability of each PFAS to cause liver toxicity in rats is expressed relative to that of PFOA (as PFOA equivalents) (Zeilmaker et al., 2018). In this way, the calculated exposure can be compared to the health-based guidance value (HBGV) for PFOA on liver effect. The value is based on an estimated PFOA intake of 2.0 ng kg^{-1} bw/day which corresponds to critical exposure value of 14 ng kg^{-1} bw week (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2018). In line with the EFSA guidance, three age populations were considered, i.e. children (3–10 years old, 23 kg), teenagers (14–18 years old, 61 kg) and adults (18–64 years old, 70 kg) (EFSA Scientific Committee, 2024). For these three age categories, hypotheses on the consumption of food intended to be in contact with the targeted samples were determined. More details are described in Table S6. Finally, all information was combined to perform the risk assessment.

3. Results

Numerous studies have been conducted on per- and polyfluoroalkyl substances (PFAS) encompassing various matrices such as biological fluids, food contact materials, food, air, sediment, etc. The contribution of food to human PFAS exposure is now widely recognized. However, the European Food Safety Authority (EFSA) has raised concerns regarding the role of food contact materials (FCMs) in contributing to the population's exposure to PFAS. It is, therefore, essential to conduct a recent evaluation of the migration of PFAS from FCMs as well as a risk assessment to ensure consumer safety. As a result, a sampling of different FCM made of paper and board and analogues was undertaken. A total of 110 samples were selected to cover a wide range of categories available on the market. This selection was based first on a market study conducted on the Belgian market intended to inventory all the FCM intended to replace plastic FCM and particularly single-use plastic FCM. The results highlighted that FCM made of paper and board and analogues accounted together for 50% of the FCM intended to replace single-use plastic FCM (Ciano et al., 2023). The majority of these FCM made of paper and board and analogues, 58% and 98%, respectively, belonged to the takeaway category (Ciano et al., 2023). In parallel, similar samples were collected in fast-food restaurants and retail stores. Table 2 provides an overview of the samples.

An extensive overview of the samples is given in Supplementary Table S1. It includes information about the type of FCM, the presence of recycled fibres, coating, colour, migration conditions, and whether the samples were purchased from retail stores, fast food restaurants or selected from the market study.

3.1. Occurrence of PFAS in food contact materials

Currently, PFOA, PFOS, PFNA and PFHxS (4-EFSA-PFAS) are regulated in food under Regulation (EU) 2023/915 (Commission Regulation (EU), 2006). However, Recommendation (EU) 2022/1431 (Commission recommendation, 2022) advises all member states to test, if possible, similar compounds in as many as possible food matrices. Therefore, as PFAS can migrate from the FCM into food, 25 PFAS, including emerging PFAS mentioned in this recommendation, were included in this study.

3.2. Suspect screening of PFAS substances

Eleven PFAS, described in Table S2 of the supplementary data were part of a suspect screening method. However, none of the substances were detected in the samples.

3.3. Quantification of PFAS substances

Fourteen substances were targeted with a quantification method. The complete overview of the substances is dispayed in Table S2 of the supplementary data.

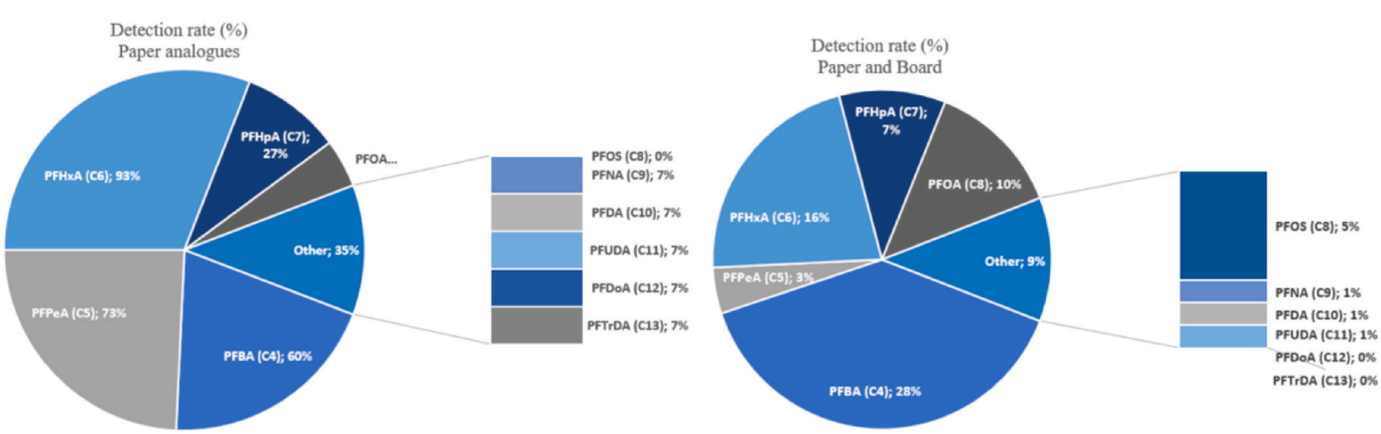

Fig. 1. Comparison of detection rate (%) of PFAS in paper and board samples and paper analogues samples.

Table 3
Overview of minimum, maximum, mean concentrations expressed in μg kg^{-1} and percentage of detection per PFAS and sample category.

	Paper and board						Paper analogues			
	Straws		Takeaway - Hot use		Takeaway - Cold use		Takeaway - Hot use		Takeaway - Cold use	
	Min **Max** (Mean) Std Dev	% Detection	Min **Max** (Mean) Std Dev	% Detection	Min **Max** (Mean) Std Dev	% Detection	Min **Max** (Mean) Std Dev	% Detection	Min **Max** (Mean) Std Dev	% Detection
PFBA (C4)	/	0	<LOQ **0.15** (0.013) 0.033	37.8	<LOQ **0.005** (0.003) 0.002	22.2	<LOQ **0.29** (0.13) 0.102	60.0	/	0
PFPeA (C5)	<LOQ **0.006** (NA) NA	5	<LOQ **0.005** (NA) NA	3.0	<LOQ **0,002** (NA) NA	11.1	<LOQ **0.14** (0.029) 0.046	60.0	<LOQ **0.01** (0.009) 0.001	13.3
PFHxA (C6)	<LOQ **0.005** (NA) NA	5	<LOQ **0.04** (0.01) 0.011	21.2	<LOQ **0,013** (0.008) 0.005	33.3	<LOQ **0.55** (0.13) 0.158	80.0	<LOQ **0.13** (0.13) 0.002	13.3
PFHpA (C7)	<LOQ **0.005** (NA) NA	5	<LOQ **0.002** (0.001) 0.0003	9.1	<LOQ **0,002** (0.002) 0.0003	22.2	<LOQ **0.38** (0.11) 0.183	26.7	/	0
PFOA (C8)	<LOQ **0.006** (0.004) 0.002	10	<LOQ **0.10** (0.02) 0.038	10.6	/	0	<LOQ **0.68** (0.342) 0.479	13.3	/	0
PFOS (C8)	/	0	<LOQ **0.002** (0.002) 0.0005	7.6	/	0	/	0	/	0
PFNA (C9)	<LOQ **0.006** (NA) NA	5	/	0	/	0	<LOQ **0.36** (NA) NA	6.7	/	0
PFDA (C10)	<LOQ **0.006** (NA) NA	5	/	0	/	0	<LOQ **0.32** (NA) NA	6.7	/	0
PFUDA (C11)	<LOQ **0.003** (NA) NA	5	/	0	/	0	<LOQ **0.29** (NA) NA	6.7	/	0
PFDoA (C12)	/	0	/	0	/	0	<LOQ **0.12** (NA) NA	6.7	/	0
PFTrDA (C13)	/	0	/	0	/	0	<LOQ **0.14** (NA) NA	6.7	/	0

(NA: not applicable due to only one sample with a detection).

Overall, 51% of the samples exhibit the presence of PFAS. Ten perfluoroalkyl carboxylic acids (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA) were found, while only PFOS represented the category of perfluoroalkyl sulfonic acids. Interestingly, no emerging PFAS were detected in the samples. The migration experiments highlighted the presence of 9 PFAS in paper and board samples and 10 PFAS in paper analogue samples. All paper analogue samples were found to contain at least one of the targeted substances, whereas 43% of the paper and board samples showed the presence of PFAS. In addition, except PFOS, all of the substances found in paper and board samples were also present in paper analogue samples. When considering the chain length, it is important to consider the official nomenclature. For perfluoroalkyl carboxylic acids, a chain length of C8 or more is considered a long chain, whereas for perfluoroalkyl sulfonic acids, a chain length of C6 or more is considered a long chain (ITCR - Interstate Technoloy Regulatory Council). Even though 63.6% of the detected substances are long-chain PFAS, it should be noted that the three most commonly detected PFAS are short-chain PFAS (i.e. PFBA, PFPeA and PFHxA) as displayed in Fig. 1. More specifically, when considering the two categories of materials together, PFBA was found to be the most frequently detected substance, present in 33% of the samples tested, followed by PFPeA (13%) and PFHxA (26%).

However, when comparing the detection rates per material type (Fig. 1), PFHxA was revealed to be the most commonly detected PFAS in paper analogue samples, with 93% of the samples containing this substance. Additionally, PFBA and PFPeA were also frequently detected in paper analogue samples, with 60% and 73% of the samples containing these substances, respectively. In contrast, PFBA was identified as the first PFAS detected in paper and board, with a detection rate of 28%.

Regarding the range of concentrations found, Table 3 displays the minimum, maximum, and mean concentrations found per category of sample as well as the percentage rate per PFAS. Supplementary Table S7 gives a complete overview of the results per sample.

Overall, paper analogue samples had higher PFAS concentrations than paper and board samples, with concentrations ranging from 0.003 μg kg^{-1} of PFPeA up to 0.29 μg kg^{-1} of PFBAcompared to concentrations ranging from 0.001 μg kg^{-1} of PFOA up to 0.15 μg kg^{-1} of PFBA in paper and board samples. However, one sample (FCM-107), a food tray made of bagasse containing 10 PFAS with higher concentration than any other sample ranging from 0.12 μg kg^{-1} of PFBA up to 0.68 μg kg^{-1} of PFOA. Out of all the paper samples analysed, only FCM-107 contains PFNA, PFDA, PFuDA, PFdoDA, and PFTrDA. On average, PFBA and PFHxA concentrations were 10 times higher in paper analogue samples than in paper and board followed by PFHpA 6 times higher and PFPeA 3 times higher also in paper analogues.

Regarding the 4-EFSA-PFAS, PFOA was found in 11 samples, PFOS in 5 and PFNA in 2 samples, while PFHxS was never found.

Additionally, no discernible pattern was noticed between the samples designated for use in hot versus cold conditions or between the different possible uses or types of intended food.

The presence of PFAS can come either from intentional use or residual background contamination from the environment. Dozens of manufacturers of paper and board or pulp were reportedly cited by the Forever Pollution Project as presumptive users of PFAS (Salmon et al., 2023). Nevertheless, no evidence of Belgian companies using PFAS was demonstrated. Considering the low volume and emissions of PFAS during the production stage in Belgian paper industry, the PFAS would have been introduced non intentionally by paper recycling, taking into account that 82% of paper and board packaging is recycled in Belgium (Salmon et al., 2023). In contrast, imported paper and board packaging are known to contain PFAS (Salmon et al., 2023).

To date, no European legislation exists to regulate PFAS in FCM. In 2020, Denmark became the first European country to ban the use of PFAS in paper and board FCM. A limit of 20 µg organic fluorine per gram of paper was set on the total organic fluorine content, while only a limited set of PFAS was included in this study. As a result, the analysis of these targeted PFAS will most probably underestimate the total fluorine content. However, if the sum of the concentration of the detected PFAS already exceeds the Danish limit, it would mean that there is probably a safety issue with that FCM. However, based on the results, no samples exceeded this limit.

Over the past decade, several studies have been carried out to investigate the presence of PFAS in food contact materials. These studies have mainly involved extraction experiments using methanol or a combination of methanol and ethyl acetate. Nonetheless, few studies performed migration experiments using Tenax®, simulant D1 or ethanol. In addition, only a few studies used the conventional assumption of 1 kg of food in contact with 6 dm^2 of FCM to express their results in µg kg^{-1} food as in the present study. The first study to express the concentration in µg kg^{-1} food was conducted in 2018 on 35 paper and board FCM from the Norwegian market, including the analyses of plates, cupcake cups, a cup, a popcorn beaker, bowls and a pizza tray (Granby and Haland Tesdal, 2018). In this study, migration experiments using ethanol or simulant D1 were performed. The comparison of the two studies showed that taking into account the same PFAS, the present study found much lower concentrations (minimum 10x lower) than Grandby et al., in 2018. One hypothesis is the origin country of the samples, or that the use of PFAS in the FCM industry has shifted since 2018. In 2024, Vera et al. published a study investigating FCM made of cardboard, biopolymer, paper and Teflon trays from various markets (Vera et al., 2024). The study found a total of 11 PFAS in the samples, with Chinese samples showing higher concentrations of PFAS than Spanish samples, showing the importance of the production origin. Similarly to the present study, pizza trays were analysed. No PFAS were detected compared to our findings. However, migration behavior of PFAS can differ significantly when using Tenax compared to water/ethanol migration. In addition, limits of quantification were at least a factor of 100 higher in Vera et al. (2024). More recently, in 2024, Loureiro et al. published a study on paper and board FCM including pizza box, muffin cups, cups etc. Their findings showed a higher level of PFAS and a higher number of PFAS per sample compared to the present study (Vázquez Loureiro et al., 2024).

Three other studies involving mainly extraction experiments expressed their results in ng g^{-1} of FCM. In 2020, Zabaleta et al. (2020) analysed 19 paper and board packaging materials, including baking papers, muffin cups, burger wrappers, French fries wrappers, burger boxes etc. Tenax®, Simulant D1 and ethanol were used to analyse the samples. When considering similar samples and substances targeted, Zabaleta et al., in contrast to the present study, didn't find similar results. Indeed, none of PFAS highlighted in the present study were found by Zabaleta et al.

Another study conducted in 2023 by Straková et al. analysed 119 single-use food packaging and tableware collected in 17 countries outside Europe (Straková et al., 2023). 54% of the samples contained PFAS. However, the most frequently found PFAS were not included in the present study (6:2FTOH). PFHxA was also mostly found in fast food paper wrappers, which was also observed in the present study. The highest concentrations were found in plant-based moulded fibre samples (e.g., bowls and plates) advertised as compostable or biodegradable. Paper analogues in the present study had concentrations (SUM of all the targeted PFAS) ranging from 0.23 up to 100 ng g^{-1} FCM, while in the study of Straková et al., the concentrations were around 1000 ng g^{-1}. However, fluorotelomer alcohols such as 6:2FTOH was the main contributor. When considering only the PFAS in common targeted in both studies, the concentrations found by Straková et al. are consistently close to the maximum concentrations found in the present study. This could be due to the origin of the FCM, mainly coming from outside of Europe in the study of Straková et al. or due to the extraction simulant used (mix of ethanol and ethyl acetate) potentially overestimating the concentrations.

A French study conducted in 2023, investigating food packaging from fast food restaurants (Dueñas-Mas et al., 2023). Among the 47 samples, all of them contained PFAS with PFHxA, 6:2 FTS, 6:2/6:2 diPAP found in all of the samples. PFHxA was found in concentrations ranging from 0.04 to 3.3 ng g^{-1} FCM. In the present study, PFHxA ranged from 0.08 up to 8.7 ng g^{-1} FCM in similar samples. The presence of PFHxA, frequently found in FCM could be explained by the degradation of other PFAS (6:2/6:2diPAP) in this substance (Lee et al., 2010).

Overall, the current study's findings are lower than those of previous studies. This could be attributed to a number of factors, such as the origin of the products, variation in the extraction/migration methods used, limits of quantification, and industries' inclination to substitute PFAS substances. A study conducted in 2023 by Lerch et al. showed preliminary results regarding factors influencing PFAS migration (e.g., thickness of the materials, misuse of the article, time, temperature) into food from FCM. High-temperature applications of FCMs associated with fatty matrices, such as muffins in muffin cups, seem to have a high risk of PFAS migration (Lerch et al., 2023). Additionally, Lerch et al. suggest that food simulants may not accurately represent migration results, such as Tenax®, which can lead to an underestimation of concentrations (Lerch et al., 2023). Nonetheless, it can be inferred that the intentional use of these chemicals is unlikely in the present study and that the contamination is most probably due to environmental background contamination, with the exception of one sample - a food tray made of sugar cane pulp. It is important to mention that this study did not specifically investigate fluorotelomer alcohols (FTOHs) and polyfluoroalkyl phosphate esters (PAPs), which are commonly present in food contact materials (FCM). Priority was given to PFAS recommended for monitoring by Recommendation (EU) 2022/1431.

3.4. Risk assessment

To date, no specific limits on the migration of PFAS from food contact materials exist at the European level. Nevertheless, food contact materials must be safe for consumers, regardless of the material. Consequently, a risk assessment was performed based on the migration results using the EFSA RACE Tool (Fürst et al., 2019). The potential risks were assessed for children, teenagers, and adults, considering two exposure scenarios. The first scenario focused on the sum of the 4-EFSA-PFAS (PFOA, PFOS, PFNA, PFHxS) regulated in food at the European level (Regulation (EU) 2023/915) and for which a TWI has been established. Next, scenario 2 was performed on the sum of the targeted PFAS, considering the relative potency factors. In 2018, the National Institute for Public Health and Environment in the Netherlands (RIVM) developed a methodology to assess the potency of a mixture of PFAS. Although PFOA is the most well-known PFAS substance, there is limited toxicological information available for other PFAS substances. As these substances often occur together in samples, the RIVM developed an approach based on the liver toxicity of PFAS. This approach allows the expression of PFAS as a PFOA equivalent using a relative potency factor

Table 4
Overview of the risk assessment results.

	Scenario 1 (EFSA-4-PFAS)			Scenario 2 (All PFAS)		
	Children	Teenagers	Adults	Children	Teenagers	Adults
Straws	No risk	No risk	No risk	No risk	No risk	No risk
Takeaway – Hot use Paper and Board	**No risk**	**Potential risk** *(>4.4 ng/kg bw/week) (coffee cup)*		No risk	No risk	No risk
Takeaway – Cold use Paper and board	No risk	No risk	No risk	No risk	No risk	No risk
Takeaway – Hot use Paper analogues	**Potential risk** *(>4.4 ng/kg bw/week) (food tray)*			**Potential risk** *(>14 ng kg^{-1} bw/week) (food tray)*		
Takeaway – Cold use Paper analogues	No risk	No risk	No risk	No risk	No risk	No risk

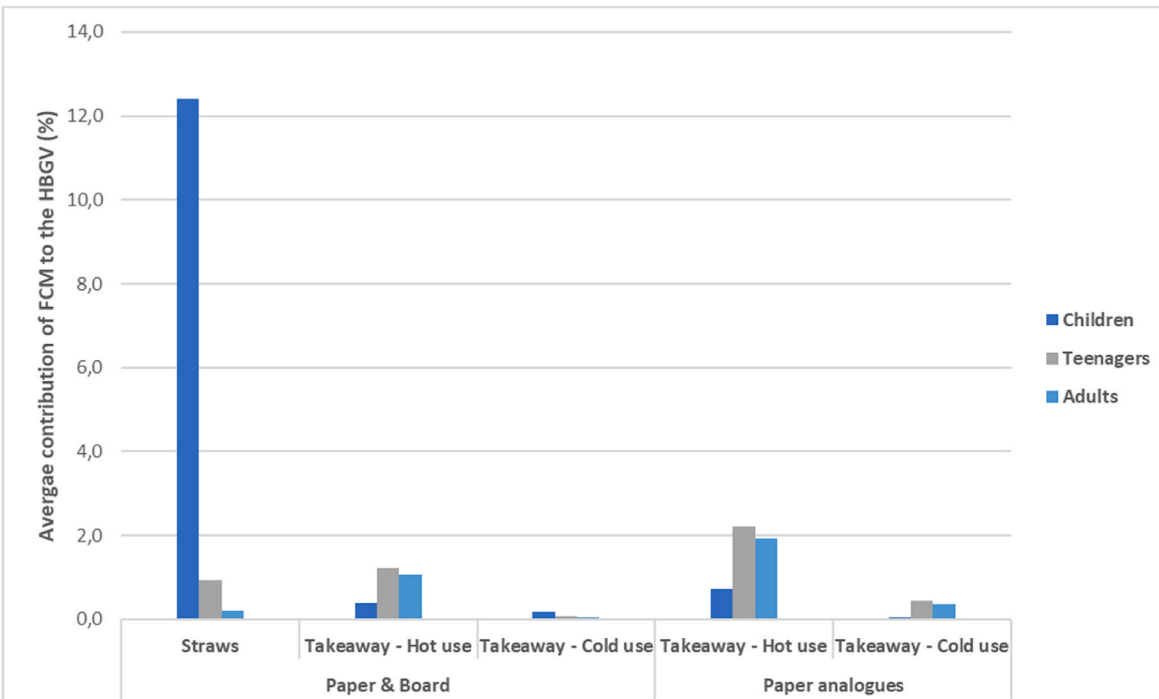

Fig. 2. Overview of the average contribution of FCM to the health-based guidance value (sample FCM-107 not taken into account (outlier)).

(available in Table S3) with PFOA set at 1 as the reference. By using this method, the calculated exposure can be compared with the health-based guidance value (HBGV) for PFOA on liver effect. The value is based on an estimated PFOA intake of 2.0 ng kg^{-1} bw/day which corresponds to critical exposure value of 14 ng kg^{-1} bw week (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2018).

Table 4 gives an overview of the potential risk associated with the different article types regardless the materials.

Among the 110 samples analysed from various types of articles, considering scenario 1 with the sum of the regulated PFAS in food and for which a TWI is available, only two samples, one coffee cup made of paper and board and a food tray made of sugar cane pulp are at potential risk for all populations. Regarding the results of the second scenario, the results of the calculated exposure were compared to the HBGV of 14 ng kg^{-1} bw week. Only the food tray made of sugar cane pulp is still at potential risk for all the population categories. However, the toxicological profile of most of the PFAS found is missing, and thus, no definitive conclusion can be drawn. Nonetheless, the exposure determined during the risk assessment can provide valuable information on the contribution of PFAS migration to the HBGV. To this end, the results of the exposure assessment determined with the scenario 2 will be used as it is the most refined. Fig. 2 displayed the contribution of the different FCM.

On average, most of the categories of food contact materials contribute to less than 2% of PFAS exposure among the population. However, it is important to pay attention to the use of straws, particularly for children, as they contribute to almost 12% of the health based guidance value. More specifically, coffee cups are also a concern for teenagers and adults as they account for around 11% of their total exposure to PFAS. Interestingly, cups made of pulp also contribute to around 9% of the HBGV, while cups made of paper and board contribute to less than 1% of the population. However, only one cup made of a mix of sugarcane and wood pulp was analysed. A food tray (FCM-107) made of bagasse in which the highest concentrations of PFAS were found is not represented on the graph as it is a clear outlier, and its contribution is over 1000%.

4. Conclusion & Perspectives

One hundred and ten food contact materials made of paper and board, bagasse or wheat pulp (paper analogues) were analysed to determine the potential migration of PFAS substances from these articles into food. The migration experiments highlighted the presence of 11 PFAS out of the 25 targeted. Even though 63.6% of the detected substances are long-chain PFAS, the three most commonly detected PFAS, were actually short chain PFAS (C4,C5 and C6). Overall, PFAS were detected in all of the paper analogue samples while 43% of paper and board samples contained them. The concentrations discovered in the study suggest that the presence of PFAS is probably unintentional and most likely due to environmental background contamination. However, one food tray is highly questionable due to higher concentrations than any other sample analysed. In the future, to confirm these findings, more samples of pulp based cup should be analysed.

The conducted risk assessment highlighted a potential concern for teenager and adults in only one sample, a coffee cup made of paper and board while a bagasse food tray is at potential risk for all the population categories. In addition, food contact materials contribute on average to less than 2% of the TWI but can be up to 12% of the TWI. To help in the success of the transition toward a safer and sustainable circular economy, the implementation of standardised monitoring approaches for PFAS in the near future will be decisive. In addition, designing sustainable alternatives remains challenging. While waxes or polymer film laminates made of polyethylene are not compostable or recyclable, biodegradable polymers like polylactic acid (PLA) could be a promising alternative even if they are not home-compostable (Glenn et al., 2021). Other alternatives made of chitosan, alginates, and plant proteins were tested, but unfortunately, they did not offer sufficient resistance to oil and grease. The rise of new sustainable alternatives in the market, driven by consumer demand to reduce their environmental impact, has introduced new potential risks of exposure to chemicals. Therefore, it is crucial to be able to assess the source of contamination for efficient monitoring. In addition, more toxicological data are necessary to refine exposure assessment.

CRediT authorship contribution statement

Mélanie Di Mario: Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Laurent Bernard:** Formal analysis. **Matthieu Legros:** Formal analysis. **Florian Peltier:** Formal analysis. **Salvatore Ciano:** Methodology, Formal analysis. **Séverine Goscinny:** Writing – review & editing, Supervision, Funding acquisition. **Jean-François Focant:** Writing – review & editing. **Els Van Hoeck:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

Acknowledgments

This study was funded by the Belgian Federal Public Service Health, Food Chain Safety and Environment (MIGRACARTO, FLUOREX (RT 21/6350), TREFCOM (RT 21/4)).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.142907.

References

Boisacq, P., De Keuster, M., Prinsen, E., Yunsun, J., Bervoets, L., Eens, M., et al., 2023. Assessment of poly- and perfluoroalkyl substances (PFAS) in commercially available drinking straws using targeted and suspect screening approaches. Food Addit. Contam.

Bokkers, B., van de Ven, B., Janssen, P., 2019. Per- and Polyfluoroalkyl Substances (PFASs) in Food Contact Materials. Rijksinstituut voor Volksgezondheid en Milieu RIVM [Internet]. https://rivm.openrepository.com/handle/10029/623023.

Ciano, S., Di Mario, M., Goscinny, S., Van Hoeck, E., 2023. Towards less plastic in food contact materials: an in-Depth overview of the Belgian market. Foods 12 (14), 2737.

Commission recommendation (EU) 2022/1431 of 24 August 2022 on the monitoring of perfluoroalkyl substances in food [Internet]. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32022H1431.

Commission Regulation (EU), 2006. 2023/915 of 25 April 2023 on Maximum Levels for Certain Contaminants in Food and Repealing Regulation. EC) No 1881.

Directive (EU), 2019. Of the European Parliament and of the Council of 5 June 2019 on the Reduction of the Impact of Certain Plastic Products on the Environment.

Dueñas-Mas, M.J., Ballesteros-Gómez, A., de Boer, J., 2023. Determination of several PFAS groups in food packaging material from fast-food restaurants in France. Chemosphere 339, 139734.

EFSA Panel on Contaminants in the Food Chain (CONTAM), Knutsen, H.K., Alexander, J., Barregård, L., Bignami, M., Brüschweiler, B., et al., 2018. Risk to human health related to the presence of perfluorooctane sulfonic acid and perfluorooctanoic acid in food. EFSA J. [Internet] https://data.europa.eu/doi/10.2903/j.efsa.2018.5194.

EFSA Panel on Contaminants in the Food Chain (EFSA CONTAM Panel), Schrenk, D., Bignami, M., Bodin, L., Chipman, J.K., del Mazo, J., et al., 2020. Risk to human health related to the presence of perfluoroalkyl substances in food. EFSA J [Internet] 18 (9) [cited 2024 Feb 19]. https://data.europa.eu/doi/10.2903/j.efsa.2020.6223.

EFSA Scientific Committee, 2024. Guidance on selected default values to be used by the EFSA Scientific Committee, Scientific Panels and Units in the absence of actual measured data. EFSA J. [Internet]. 2012 https://data.europa.eu/doi/10.2903/j.efsa.2012.2579.

EN 15519 - paper and board intended to come into contact with foodstuffs - Preparation of an organic solvent extract [Internet]. https://standards.iteh.ai/catalog/standards/cen/981004f1-05e0-4659-afbd-fa009f912d8a/en-15519-2007.

EN 645 - paper and board intended to come into contact with foodstuffs - Preparation of a cold water extract. Internet. https://standards.iteh.ai/catalog/standards/cen/24c9ce05-698b-4140-a01c-edb3cf05a703/en-645-1993.

European Chemical Agency, 2023. Annex XV restriction report - proposal for a restriction [Internet]. https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea.

European Commission. Commission Delegated Regulation (EU) 2020/784 of 8 April 2020 amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council as regards the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. Available from: https://www.legislation.gov.uk/eur/2020/784/introduction/adopted/data.pdf.

European Commission, 2023. Joint Research Centre. Testing Conditions for Kitchenware Articles in Contact with Foodstuffs: Plastics Metals, Silicone & Rubber, Paper & Board : the EURL FCM Harmonised Approach Series. Publications Office [Internet]. LU. https://data.europa.eu/doi/10.2760/80698.

European Parliament and Council, 2004. REGULATION (EC) No 1935/2004 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC [Internet]. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02004R1935-20210327.

Fürst, P., Milana, M.R., Pfaff, K., Tlustos, C., Vleminckx, C., Arcella, D., et al., 2019. Risk evaluation of chemical contaminants in food in the context of RASFF notifications. EFSA Support Publ [Internet] 16 (5) [cited 2024 Feb 6]. https://data.europa.eu/doi/10.2903/sp.efsa.2019.EN-1625.

Glenn, G., Shogren, R., Xing, J., Orts, W., Hart-Cooper, W., Olson, L., 2021. Per- and polyfluoroalkyl substances and their alternatives in paper food packaging. Compr. Rev. Food Sci. Food Saf.

Granby, K., Haland Tesdal, J., 2018. Per-and polyfluorinated alkyl substances (PFAS) in paper and board Food Contact Materials - selected samples from the Norwegian market 2017 [Internet]. https://backend.orbit.dtu.dk/ws/files/192717049/Per_and_polyfluorinated_alkyl_substances_PFAS_in_paper_and_board_Food_Contact_Materials_2017.pdf.

Stockholm convention on persistent organic pollutants (POPs). In: Idowu, S.O., Capaldi, N., Zu, L., Gupta, A.D. (Eds.), 2013. Encyclopedia of Corporate Social Responsibility [Internet]. Springer Berlin Heidelberg, Berlin, Heidelberg, 2336–2336. http://link.springer.com/10.1007/978-3-642-28036-8_101506.

ITCR - Interstate Technoloy Regulatory Council. Naming Conventions for Per- and Polyfluoroalkyl Substances (PFAS). Available from: https://pfas-1.itrcweb.org/wp-content/uploads/2022/09/NamingConventions_PFAS_Fact-Sheet_083122_508.pdf.

Lee, Y chi, Lo, S.L., Chiueh, P te, Liou, Y.H., Chen, M.L., 2010. Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation. Water Res. 44 (3), 886–892.

Lerch, M., Nguyen, K.H., Granby, K., 2022. 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. Food Chem. 393, 133375.

Lerch, M., Fengler, R., Mbog, G.R., Nguyen, K.H., Granby, K., 2023. Food simulants and real food – what do we know about the migration of PFAS from paper based food contact materials? Food Packag. Shelf Life 35, 100992.

Mme Recyclage, M., 2024. Functionalisation of paper and cardboard. How to male paper/Cardboard impervious for packaging? [Internet]. https://rethinkplasticalliance.eu/wp-content/uploads/2024/02/FunctionalisingCardboard_V5.1_EN.pdf.

Pérez, F., Nadal, M., Navarro-Ortega, A., Fàbrega, F., Domingo, J.L., Barceló, D., et al., 2013. Accumulation of perfluoroalkyl substances in human tissues. Environ. Int. 59, 354–362.

Peters, R.J.B., Groeneveld, I., Sanchez, P.L., Gebbink, W., Gersen, A., de Nijs, M., et al., 2019. Review of analytical approaches for the identification of non-intentionally added substances in paper and board food contact materials. Trends Food Sci. Technol. 85, 44–54.

Phelps, D.W., Parkinson, L.V., Boucher, J.M., Muncke, J., Geueke, B., 2024. Per- and polyfluoroalkyl substances in food packaging: migration, toxicity, and Management Strategies. Environ. Sci. Technol. 19 acs.est.3c03702.

Salmon, T., Huppertz, T., Le Bihan, M., 2023. PFAS in Belgian Industry Market Study.

Schaider, L.A., Balan, S.A., Blum, A., Andrews, D.Q., Strynar, M.J., Dickinson, M.E., et al., 2017. Fluorinated compounds in U.S. Fast food packaging. Environ. Sci. Technol. Lett. 4 (3), 105–111.

Straková, J., Brosché, S., Grechko, V., 2023. Forever Chemicals in Single-Use Food Packaging and Tableware from 17 Countries.

Trudel, D., Horowitz, L., Wormuth, M., Scheringer, M., Cousins, I.T., Hungerbühler, K., 2008. Estimating consumer exposure to PFOS and PFOA. Risk Anal. 28 (2), 251–269.

Vázquez Loureiro, P., Nguyen, K.H., Rodríguez Bernaldo de Quirós, A., Sendón, R., Granby, K., Niklas, A.A., 2024. Identification and quantification of per- and polyfluorinated alkyl substances (PFAS) migrating from food contact materials (FCM). Chemosphere 360, 142360.

Vera, P., Canellas, E., Dreolin, N., Goshawk, J., Nerín, C., 2024. The analysis of the migration of per and poly fluoroalkyl substances (PFAS) from food contact materials using ultrahigh performance liquid chromatography coupled to ion-mobility quadrupole time-of-flight mass spectrometry (UPLC- IMS-QTOF). Talanta 266, 124999.

Zabaleta, I., Blanco-Zubiaguirre, L., Baharli, E.N., Olivares, M., Prieto, A., Zuloaga, O., et al., 2020. Occurrence of per- and polyfluorinated compounds in paper and board packaging materials and migration to food simulants and foodstuffs. Food Chem. 321, 126746.

Zeilmaker, M.J., Fragki, S., Verbruggen, E.M.J., Bokkers, B.G.H., Lijzen, J.P.A., 2018. Mixture exposure to PFAS: a relative potency factor approach [cited 2024 Feb 6]. http://rivm.openrepository.com/rivm/handle/10029/622164.