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Food Additives & Contaminants: Part B
Surveillance

ISSN: 1939-3210 (Print) 1939-3229 (Online) Journal homepage: https://www.tandfonline.com/loi/tfab20

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To cite this article: Ana Lorena Monge Brenes, Greg Curtzwiler, Philip Dixon, Kamel Harrata, Joey Talbert & Keith Vorst (2019): PFOA and PFOS levels in microwave paper packaging between 2005 and 2018, Food Additives & Contaminants: Part B, DOI: 10.1080/19393210.2019.1592238

To link to this article: https://doi.org/10.1080/19393210.2019.1592238

Published online: 04 Apr 2019.

FOOD ADDITIVES & CONTAMINANTS: PART B
https://doi.org/10.1080/19393210.2019.1592238

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ARTICLE

PFOA and PFOS levels in microwave paper packaging between 2005 and 2018

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ABSTRACT

Per- and polyfluoroalkyl substances are synthetic environmental pollutants previously used for packaging applications as a grease, oil, and water-resistant coating. Exposure reported in previous studies highlighting potential concerns with public health. This study evaluated performance of coated paper packaging used for microwave popcorn, snacks, and sandwich bags for presence of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Current paper packaging materials: seven popcorn bags and three snack and sandwich bags were analysed for PFOA and PFOS and compared to concentrations in microwave popcorn bags between 2005 and 2018. Only two microwave popcorn bags had average PFOA content above the limit of quantitation of 5.11 ng g^{-1} paper. All other sample types had PFOA and PFOS values below the limit of detection (LOD) of 1.53 and 0.63 ng g^{-1} paper, respectively. Results of this study follow trends from 2005 to 2018 suggesting a reduction in PFOS and PFOA concentrations in microwave packaging.

ARTICLE HISTORY
Received 17 September 2018
Accepted 4 March 2019

KEYWORDS
Perfluorinated compounds; PFAS; PFOS; food packaging; persistent organic pollutant; perfluorooctanoic acid; perfluorooctane sulfonate

Introduction

Per- and polyfluoroalkyl substances (PFASs) are organic substances with a hydrocarbon backbone where fluorine has substituted all the hydrogens. These compounds are very stable and resistant to biological, chemical, and thermal degradation. PFASs are synthetic persistent organic pollutants (POPs) that bioaccumulate and have been detected in human blood serum (US median is equal to 4 ng/mL) (Steenland et al. 2010). Due to their stability, toxicity, bioaccumulation, and long half-lives in mammals, they have been classified as POPs (Lindstrom et al. 2011; Stahl et al. 2011; Surma et al. 2015; Schaider et al. 2017). PFASs were first produced in the 1940s and 1950s to increase grease, oil, and stain resistance on surfaces. They were added to surfactants, cookware coatings, fire-fighting foams, and food contact paper packaging products, among other applications (EFSA 2008; Sun et al. 2017). Studies have shown they are widely spread throughout the environment and in certain concentrations are detrimental to human health (EFSA 2008; Lindstrom et al. 2011; Stahl et al. 2011; Martinez-Moral and Tena 2012; OECD/UNEP Global PFC Group 2013).

PFAS compounds are all synthetic chemicals and include thousands of chemicals but some of the most common include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (Giesy and Kannan 2002). Some PFAS compounds degrade to form PFOA and PFOS resulting in many in depth research studies with these two compounds to better understand the spread in the environment and human exposure. Global research studies have attempted to understand potential human intake and health consequences, as well as their global abundance (Giesy and Kannan 2002; Lindstrom et al. 2011; Stahl et al. 2011).

PFOA and PFOS have been detected throughout the environment: water, soil, plants, and animals. PFASs bioaccumulate and have been shown to pass on through the food chain. Higher concentrations of PFASs have been found in rural and industrialised areas, but they have been detected in remote areas such as the arctic, far away from any source (Giesy and Kannan 2002; Lindstrom et al. 2011; Newton et al. 2017; Sun et al. 2017).

Significant differences in bioaccumulation and excretion have been reported between PFOA and PFOS for different mammalian species, including humans. Studies in primates and rodents have shown that PFOS and PFOA increase cancer risk, reduce childbirth weight and reduce gestational age, affect hormonal activity, metabolism, among many other health impacts that continue to be studied (Steenland et al. 2010; Geueke 2016). In humans, gender differences in PFOS and PFOA serum concentrations have been reported for Japan and the USA, being higher for males than females (Stahl et al. 2011). In

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addition, epidemiological studies in PFOS and PFOA on exposed workers are contradicting, but more recent studies show the relation between serum levels and liver, pancreatic, testicular, and breast cancer, tumour-promoting activities, immunosuppression, estrogenic and non-estrogenic hormonal disruptions, among other adverse effects to human health (Alexander et al. 2003; Lau et al. 2007; Steenland et al. 2010; Lindstrom et al. 2011; Barry et al. 2013; Vieira et al. 2013; Timmermann et al. 2017; Pierozan et al. 2018). Studies have shown increased triglycerides and other hormonal health effects, identifying PFOA as a thyroid hormone disruptor (Nelson et al. 2010; Lindstrom et al. 2011).

The Scientific Panel on Contaminants in the Food Chain (CONTAM) has established that the Tolerable Daily Intake (TDI) for PFOS is 150 ng kg^{-1} body weight day^{-1} and 1500 ng kg^{-1} body weight day^{-1} for PFOA (EFSA 2008; Geueke 2016). The major pathways of PFOA and PFOS intake by humans have been identified as dietary intake from water, animals, plants, migration into foodstuff from packaging, and other environmental sources such as indoor dust (Trudel et al. 2008). Water has been identified as a major source of contamination of all food stuff (Trudel et al. 2008; Newton et al. 2017). The distribution and actual intake mechanisms are still ambiguous and continue to be studied (Picó et al. 2011; Domingo 2012; OECD/UNEP Global PFC Group 2013).

Research has demonstrated the toxicity of PFCs and regulatory bodies in some countries have tried to legislate against their production, but other countries have picked up production to fill in the need. After the year 2000, PFAS production in Japan, Western Europe, and the USA decreased, but China, India, Poland, and Russia have increased their production levels (Geueke 2016). PFOA and PFOS are listed in the Stockholm Convention as POPs. This is one of the most important international efforts to stop production and use of these compounds (Newton et al. 2017). The Environmental Protection Agency (EPA) collaborated with 3M and DuPont to voluntarily discontinue production of PFOS and related compounds. The EPA has continued to develop new legislation to eliminate long-chain PFASs from emissions and products (Lindstrom et al. 2011). Manufacturers have started to replace the long chain PFAS with shorter chain PFAS or non-fluorinated compounds, but there is not enough information on the toxicity of these shorter chain PFASs (OECD/UNEP Global PFC Group 2013; Geueke 2016).

Historically, PFCs were used in paper to provide water, oil, and grease resistance, as well as protection from external contaminants to the food. When food comes in contact with the package, these chemicals can migrate into food, becoming a food safety issue. (Begley et al. 2008; Zafeiraki et al. 2014).

Paper packaging has been analysed for PFASs and the recovery rates have been reported. Some methods include liquid extraction with solvents, followed by liquid chromatography. Studies report using various types of ultrasound and high pressure-assisted techniques of extraction, as well as low, high and ultra-high pressure liquid chromatography (LC, HPLC, and UHPLC) coupled with different detection methods for quantitation. Some of these studies have identified PFOA and/or PFOS in their analysis; others were not able to detect either compound due to poor method sensitivity. It is an analytical challenge to quantify these compounds in food contact paper packaging. The development of liquid chromatography-tandem mass spectrometry (LC-MS/MS), triple quadrupole tandem mass spectrometry coupled to liquid chromatography (LC-(QqQ)MS/MS) and liquid chromatography quadrupole time-of-flight tandem mass spectrometry (LC-QTOF) methods has proven to be able to detect PFASs at low levels (Jogsten et al. 2009; Moreta and Tena 2013, 2014; Zafeiraki et al. 2014; Surma et al. 2015; Schaider et al. 2017).

The objective of this research study was to quantify the amount of PFOA and PFOS in popcorn bags and paper snack bags currently used in the market following the analytical method proposed and validated by Moreta and Tena (2014). Snack and sandwich paper packaging has been used by customers as an alternative to traditional microwave packaging for popping corn. The method used in this study was a focused ultrasonic liquid extraction using ethanol, with sample reconstituted in methanol and quantified using UHPLC-QTOF.

Materials and methods

Sample preparation

Seven unique unused, unfilled, single-gusseted microwave-printed popcorn bags were obtained from multiple international suppliers. Three lunch sacks were obtained from three unique retail grocery chains (Ames, IA). The lunch sacks are not printed. Sections with the adhesive were removed before sampling to avoid possible chemical interactions during extraction and chromatographic analysis. The susceptor was ground with the paper as it is in direct food contact. Eight bags of each packaging material were pulverised into uniform particle powder using an IKA A11 Analytical Mill (Wilmington, NC) with a fibre cutting blade attached. The mill and its components were cleaned completely between samples of different material to avoid cross-contamination.

Calibration standards were prepared at 1, 5, 10, 25, 50, 75, and 100 ng ml^{-1} of native, non-mass labelled, PFOA (Perfluoro-n-octanoic acid: PFOA), and PFOS (Sodium perfluoro-1-octanesulfonate:L-PFOS) standards obtained from Wellington Laboratories (Guelph, Ontario, Canada). An

initial standard solution of 100 ng ml^{-1} was prepared then diluted separately to make 75, 50, 25, and 10 ng ml^{-1} standard solutions. Standards for 5 and 1 ng ml^{-1} were prepared from separate dilutions from the 10 ng ml^{-1} obtained standard. A 20 ng ml^{-1} spike solution was prepared using a combination of the native PFOA and PFOS standards obtained from Wellington Laboratories. Isotopically labelled Perfluoro-n-[$^{13}C_8$] octanoic acid (M8PFOA) and isotopically labelled sodium perfluoro-1-[$^{13}C_8$] octanesulfonate (M8PFOS) internal standard solutions, obtained from Wellington Laboratories (Guelph, Ontario, Canada), were prepared at 300 ng ml^{-1}. Calibration standards, spike solution, and internal standard solutions were prepared in HPLC-grade methanol (Fisher Scientific; Hampton, NH) using glass volumetric flasks (20 ml, 100 ml, and 200 ml Pyrex® with glass stoppers, respectively), pipettes (Pyrex™, disposable, 10ml in 1/10), and micropipettes (Gilson pipetman, 20, 1000, and 5000 µl). Samples were stored protected from light via aluminium foil in the freezer of a conventional refrigerator (Frigidaire, FFTR1814TWO) at −16°C.

Random samples from three different popcorn bags and one snack and sandwich bag were selected for spike recovery quantification for method validation. Pulverised paper samples were suspended in ethyl acetate (Fisher Scientific; Hampton, NH) and then spiked with a 20 ng ml^{-1} solution in a 1-L glass beaker (Pyrex®, 1000 ml) to give 20 ng spike per1.5 g paper. This spike concentration was chosen because it was above the limit of quantification (LOQ) and close to the expected values in samples. The suspended and spiked samples were mixed thoroughly, then evaporated to dryness using a water bath set at 45°C, and ground again to ensure homogeneity. Spiked and non-spiked samples were stored in polyethylene bags wrapped in aluminium foil and refrigerated (Frigidaire, FFTR1814TWO) at 4°C.

Focused ultrasonic liquid extraction

Extraction of PFOS and PFOA was performed using focused ultrasonic liquid extraction (FUSLE) procedure using a Misonix S-4000 Ultrasonic Sonicator (Farmingdale, 150 NY), with a power of 600 W and an operating frequency of 20 kHz, equipped with a 3-mm titanium tip. Each packaging material was analysed in three sampling repetitions. A known amount of processed paper (~1.5 g of homogenised sample) was placed into a 50-mL (34 mm x 100 mm) glass centrifuge tube and 24 mL of ethanol was added to each sample. The weight of sample used in each extraction was recorded and used to normalise the concentration of PFAS obtained per gram of paper. Before each extraction, 100 µL of 300 ng ml^{-1} mass labelled M8PFOA and M8PFOS internal standard solution was added. The probe was inserted in the mixture to a depth of 2 cm from the bottom of the test tube. Each individual tube was then secured in an ice bath and subsequently sonicated. Samples were exposed to 30% amplitude at 50% pulsed cycle for 10 s. Extracts were filtered through a 60 mL Pyrex® Buchner funnel with fritted disc and porosity 10–15 µm using a vacuum pump at 550 in Hg vacuum. The probe, glassware, and extracted samples were washed twice with 2.5 mL of ethanol each rinse. The total amount of filtered extract with rinses was transferred to a 55 mL Pyrex® culture tube without cap and immediately dried to completion in a nitrogen evaporator with water bath at 45°C. The dry residue was reconstituted with 1-ml HPLC-grade methanol and filtered into a 2-mL LC vial using a disposable polypropylene medical sterile syringe equipped with a 0.22-µm nylon filter.

LC-MS conditions

Negative ion mode mass spectra were obtained using the Agilent (Santa Clara, CA) QTOF 6540 mass spectrometer equipped with the JetStream ESI ion source. The LC system consisted of the Agilent 1200 series binary pump and autosampler system. Sample mixtures were separated using an Agilent XDB C18, 4.6 × 150 mm, 1.8 um column at a flow rate of 700 µl min-1 at 30°C. Then, 1 µl of sample was injected. The mobile phases used were 0.1% Formic acid aqueous solution for Solvent A and 0.1% Formic acid acetonitrile solution for Solvent B. The phase composition was varied linearly from 28% to 50% Solvent B in 1.5 min, then increased to 52% Solvent B in 1.2 min. Increased again to 72% Solvent B in 0.5 min and maintained at 72% Solvent B for 1.5 min more. Then increased again to 100% solvent B in 0.1 min and then maintained at 100% Solvent B for 10.2 min. The chromatographic separations took place in 15 min, with retention times between 8 and 12 min. After each run, 100% Solvent B for 3 min was used to clean the column prior to the next sample.

The mass spectrometer was scanned from m/z 100 to 1000 and operated in the 4 GHz HRes mode. Accurate mass measurement was achieved by constantly infusing a calibrant (ions at m/z 121.0508 and 922.0098). Extracted Ion Chromatogram (EIC) peaks were displayed for native PFOA (m/z: 412.97), M8PFOA (m/z: 420.99), native PFOS (m/z: 498.92), and for M8PFOS (m/z: 506.957) standards. M8PFOA (m/z: 420.99) and M8PFOS (m/z: 506.957) were used as internal standards. Native PFOA (m/z: 412.97) and native PFOS (m/z: 498.92) peaks were observed and integrated at the same retention times of the corresponding mass labelled standards. Ratios of PFOA/M8PFOA and PFOS/M8PFOS versus concentration were plotted for accurate quantitation.

Calibration curves were run every 9 to 16 samples to check for column degradation. Blanks were run before and after calibration curves and in between samples of the same packaging material. Each paper packaging material was sampled three times, drawing paper sample from the combined ground matrix of eight bags. From each of these samples, repeated measurements from the same vial were run through the LC three non-consecutive times. The three repeated measurements were averaged to obtain the ratio for each sample. The ratios were read from the developed calibration curve to obtain the concentration for the three samples for each paper packaging. These readings were normalised by the sample weights and then averaged to provide the concentration of PFAS in each paper packaging material.

Results

PFOA and PFOS were identified in the obtained chromatograms. Native and mass labelled PFASs were identified with the peak retention time for the mass labelled PFOA or PFOS, accordingly. Three non-consecutive injections for every sample were run to account for instrument variability. The ratio between peak areas associated with PFOA and M8PFOA internal standard peak areas for each injection was used as the response reading value. The same procedure was applied for PFOS and M8PFOS readings. Calibration curves were constructed plotting the ratio against the known concentrations.

LOD and LOQ

Calibration curves do not show a pattern overtime for PFOA and PFOS; therefore, no column degradation was evident and the data were accepted. A weighted linear regression model (Ramsey and Schafer 2002) was fitted to the data from calibration curves using SAS statistical software (Statistical Analysis Systems Inc., Cary, NC, USA), as unequal variance was observed from the residuals plot. Significant values for slope and intercept were obtained. The estimated intercept and slope, with standard errors in parentheses, are 0.0267 (0.0013) and 0.03062 (0.00025) for PFOA and 0.0055 (0.00035) and 0.02737 (0.00016) for PFOS. The data obtained from the calibration curves (Figures 1 and 2) have unequal variance with respect to concentration so the Hubaux-Vos (Hubaux and Vos 1970) method for detection limits was applied to the data through an iterative process using SAS. The limit of detection (LOD) was found to be 1.53 ng PFOA g^{-1} paper and 0.63 ng PFOS g^{-1} paper. From the LOD, LOQ was calculated as 5.11 ng PFOA g^{-1} paper and 2.11 ng PFOS g^{-1} paper.

Measurement results

With the linear regression model obtained from the calibration curves and the LOD, the concentrations for the samples were obtained as shown in Table 1. Results show two packaging samples have quantifiable amounts (Limit of quantitation, LOQ = 5.11 ng g^{-1} paper) and one was detected but not quantified for PFOA (limit of detection, LOD = 1.53 ng g^{-1} paper). The concentration of PFOS in all samples measured were below the limit of detection (LOD = 0.63 ng g^{-1} paper, LOQ = 2.11 ng g^{-1} paper).

For PFOA measurements with a mean greater than 3 ng ml^{-1}, measurement uncertainty as pooled sd was 3.8 ng ml^{-1}, whereas for mean values less than 3 ng ml^{-1} it was 0.63 ng ml^{-1}. For PFOS measurements with a mean value greater than 0.6 ng ml^{-1} measurement uncertainty as pooled sd was 0.71 ng ml^{-1} and for mean values less than 0.6 ng ml^{-1} it was 0.06 ng ml^{-1}. Spike recoveries were obtained from three randomly selected different popcorn bags and one snack and sandwich paper bag. Spike recoveries for PFOA were between 71.8 and 96.4% and for PFOS were between 76.5 and 86.2%. The lowest spike recoveries were obtained in snack and sandwich bags for both PFOA and PFOS, as shown in Table 2. Previous studies of PFOA and PFOS on paper packaging report concentrations normalised to the surface area (Surma et al. 2015; Timmermann et al. 2017). In order to make these data comparable other data reported in the literature, concentrations were calculated per surface area in Table 3.

Discussion

To fully interpret the data and possible human exposure to PFOA and PFOS in paper packaging, the data were also reported in concentration per bag, as shown in Table 4. This information provides a framework to understand the maximum potential ingestion by transfer from the packaging material to the food, assuming that all of the contaminant is transferred into the food. The values for PFOA detected in popcorn bags 1 and 2 were 321.4 and 204.6 ng bag^{-1}, respectively. Correcting for the methods with the lowest of 71.8%, and assuming that all of the concentration could be transferred into the food, the maximum potential ingestion quantity would be 447.2 ng bag^{-1} and 285.0 ng bag^{-1}, respectively. Compared to the TDI of 1.5 µg kg^{-1} body weight (equivalent to 1500 ng kg^{-1} body weight per day) for PFOA (EFSA 2008), the potential contribution of the paper packaging analysed is below threshold. As an example, for a person that weighs 75 kg, the maximum TDI is 112,500 ng PFOA and the bag of popcorn with the highest concentration found could potentially contribute a maximum of

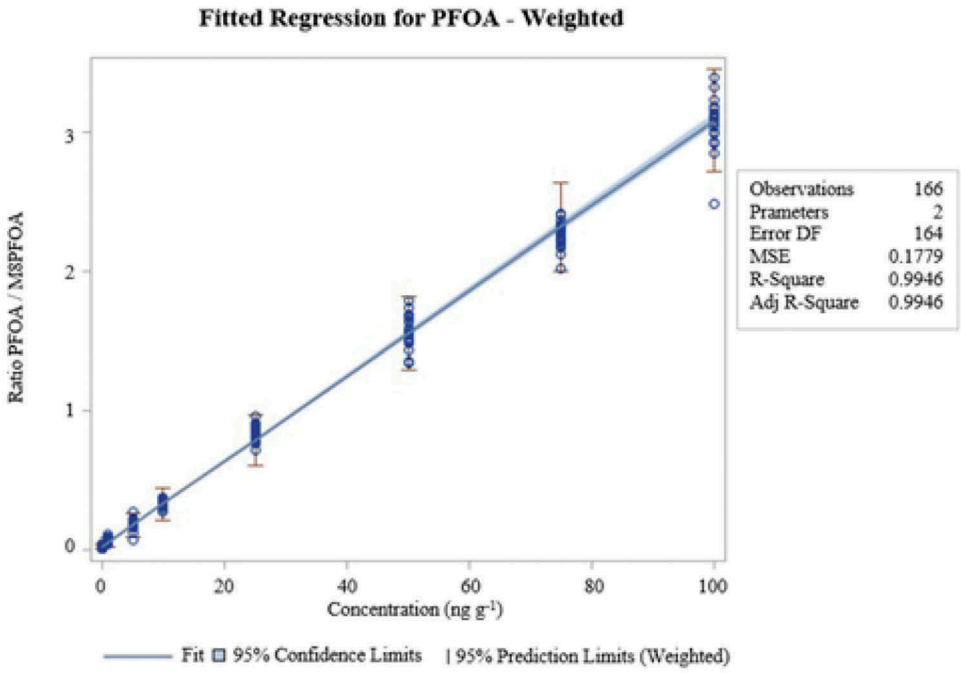

Figure 1. Calibration curve for PFOA.

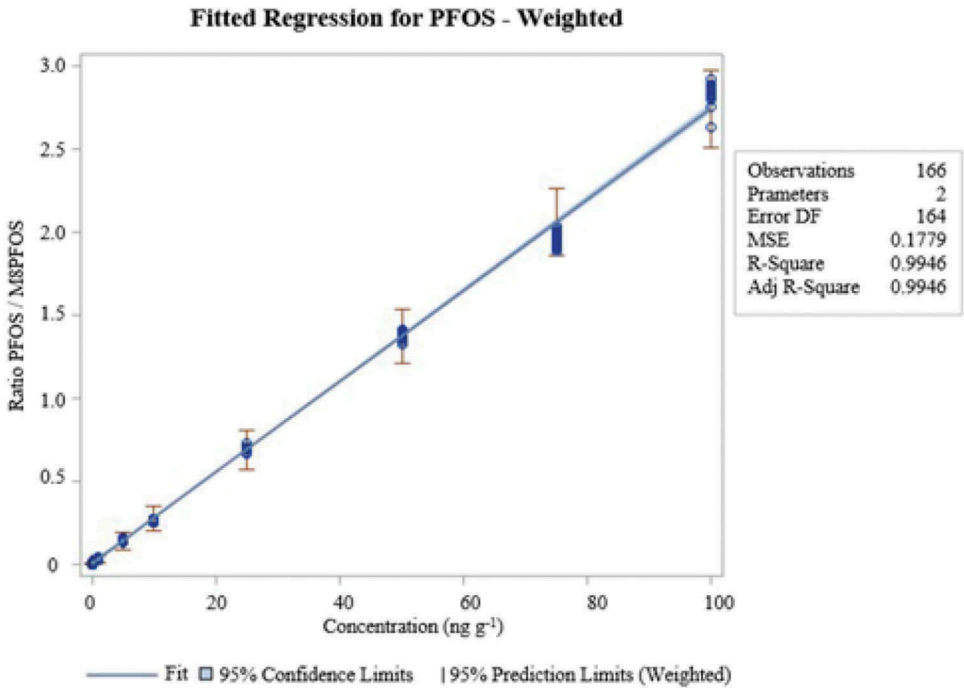

Figure 2. Calibration curve for PFOS.

447.2 ng PFOA, or 0.4%, of the maximum recommended daily intake.

In a similar comparison, all concentrations for the bags analysed were below the LOD for PFOS of 0.63 ng g^{-1} of paper packaging. One sample was above the LOD but below the LOQ. Taking a maximum content of PFOS equal to the LOQ, which is higher than the LOD, of 2.11 ng g^{-1} of paper packaging, the potential contribution of the paper packaging analysed is also below threshold. Calculating the maximum potential ingestion, utilizing the lowest

Table 1. PFC concentrations in samples; all PFOS values were below LOD.

Packaging material	Sample	PFOA (ng g^{-1})
Popcorn 1	Sample 1	28.6 ± 0.3
	Sample 2	27.0 ± 3.2
	Sample 3	30.3 ± 7.2
Popcorn 2	Sample 1	19.8 ± 2.3
	Sample 2	19.6 ± 2.1
	Sample 3	15.3 ± 3.4
Popcorn 3–7	Sample 1,2,3	< LOD
Snack & sandwich 1–3	Sample 1,2,3	< LOD

Table 2. PFC concentrations in paper packaging materials and spike recoveries; all PFOS values were below LOD.

		Spike recoveries	
Packaging material	PFOA (ng g^{-1})	PFOA (%)	PFOS (%)
Popcorn 1	28.6 ± 1.7		
Popcorn 2	18.2 ± 2.5	96.4	83.6
Popcorn 3, 4, 6	< LOD		
Popcorn 5	< LOD	81.9	86.2
Popcorn 7	< LOD	80.4	85.5
Snack and sandwich 1, 2	< LOD		
Snack and sandwich 3	< LOD	71.8	76.5

Table 3. PFC concentrations in paper packaging per surface area; all PFOS values were below LOD.

Packaging material	Paper mass (g dm^{-2})	PFOA (ng dm^{-2})
Popcorn 1	0.77	22.1
Popcorn 2	0.71	12.9
Popcorn 3, 4	0.77	< LOD
Popcorn 5	0.79	< LOD
Popcorn 6	0.82	< LOD
Popcorn 7	0.81	< LOD
Snack and Sandwich 1	0.55	< LOD
Snack and Sandwich 2	0.56	< LOD
Snack and Sandwich 3	0.45	< LOD

Table 4. PFC concentration in paper packaging per bag for samples analysed; all PFOS values were below LOD.

Packaging material	Avg. mass (g bag^{-1})	PFOA (ng bag^{-1})
Popcorn 1	11.2	321.4
Popcorn 2	11.2	204.6
Popcorn 3	11.9	< LOD
Popcorn 4	7.9	< LOD
Popcorn 5	11.7	< LOD
Popcorn 6	12.3	< LOD
Popcorn 7	12.2	< LOD
Snack and Sandwich 1	7.2	< LOD
Snack and Sandwich 2	7.3	< LOD
Snack and Sandwich 3	4.5	< LOD

recovery rate observed at 76.5% and the highest weight per bag of 12.3 g, a bag of popcorn can contribute 33.9 ng of PFOS, compared to the TDI of 150 ng PFOS kg^{-1} body weight. As an example, for a person that weighs 75 kg, the maximum TDI is 11,250 ng PFOS and a bag of popcorn with the concentration equal to the LOQ, above the observed concentrations could potentially contribute a maximum of 33.9 ng PFOS, or 0.3% of the maximum recommended daily intake.

Choi et al. (2018) evaluated 312 samples of food contact materials from the Korean market for 16 different perfluorinated compounds, including PFOA and PFOS. The 11 samples of baking paper analysed were negative for all 16 PFCs. Zafeiraki et al. (2014) also analysed 42 different samples of various paper and paperboard food contact materials in the Greek market and did not find PFOA or PFOS in any sample. These results are consistent with the results obtained in this research.

Table 5 shows compilation of data collected from different studies on PFOA and PFOS concentrations in microwave popcorn bags between 2005 and 2018, including this study. The data show a reduction overtime. Values reported in units per weight of packaging were transformed into ng dm^{-2} by assuming 0.78 g of packaging per dm^2, which was the average obtained in this study. This was done only to unify the units for comparative purposes and does not affect the trend overtime.

Ongoing research is being conducted to standardise methods and threshold limits for PFOS and PFOA in food packaging materials in the USA. Recent efforts have utilised international standards such as the Danish Ministry of Environment and Food recommended limit value of 10 µg organic fluorine per square decimetre paper (Ministry of Environment and Food of Denmark 2018). Increased sensitivity of instruments, improved extraction methods, such as the one used in this research, is now capable of detecting POPs that are not intentionally added to packaging and serve no functional purpose.

Table 5. PFOA and PFOS concentration (ng dm^{-2}) in microwave popcorn bags from studies between 2005 and 2018, including this study.

Year	Country	PFOA (ng dm^{-2})	PFOS (ng dm^{-2})	Reference
2005	U.S.	4.7*	*NA*	Begley et al. 2005
	U.S.	226.2*	*NA*	
2007	U.S.	470	*NA*	Sinclair et al. 2007
2011	Denmark	*<LOD*	*NA*	Trier et al. 2011
2011	Australia	7.1*	*<LOD*	Dolman and Pelzing 2011
2012	Spain	41.3*	*<LOQ*	Martínez-Moral and Tena 2012
	Spain	154.4*	17.9*	
2012	Thailand	0.1	*<LOD*	Poothong et al. 2012
	Thailand	1.7	2.5	
2013	Spain	*<LOD*	*<LOD*	Moreta and Tena 2013
	Spain	10.9*	4.6*	
2016	Spain	*<LOD*	*NA*	Zabaleta et al. 2016
2018	U.S.	22.1	*<LOD*	This study
	U.S.	*<LOD*	*<LOD*	

**Values reported in ng g^{-1} were converted to ng dm^{-2} using 0.78 g dm^{-2} as the average grammage of microwave bags including the susceptor.*
NA – Not analyzed
<LOD – Below the limit of detection
< LOQ – Below the limit of quantitation

Conclusions

Two of the ten samples analysed for PFAS had average concentrations of PFOA above the LOD, whereas all PFOS data remained below LOD. Both PFOA containing samples were popcorn bags. The three snack and sandwich bags analysed had average PFCs concentration below the LOD, although one of the samples of a snack and sandwich bag found detected concentrations above LOD and below LOQ. Calculating the maximum potential ingestion quantities of PFOA and PFOS from the paper packaging samples analysed, the amounts that each bag contributes are several orders of magnitude below the TDI amounts per day at 1500 ng kg^{-1} body weight per day for PFOA and 150 ng kg^{-1} body weight per day for PFOS.

PFOA and PFOS are not currently being added to paper packaging, but rather appear as environmental contaminants from the materials used in manufacturing (water, fibre sources, etc.). Removing these compounds is very difficult due to the stability of the molecules and the persistent nature of the pollutant, and previously reported global environmental contamination. Increased attention and awareness have been given to materials used in food packaging to avoid unintentional presence of PFOA and PFOS in paper packaging. This increased awareness has resulted in low-level detection of PFOA and PFOS in packaging that is an unintentional POP that does serve any functional purpose in the packaging structure.

While PFOA and PFOS were not found in some of the samples, further studies should include the identification and quantitation of other PFASs and their possible effects on human health. Consumers demand paper packaging that is water, oil, and grease resistant and paper offers a sustainable and convenient packaging material for some applications. More research is needed to develop other types of chemicals that do not harm the environment and health, but can impart oil, grease, and water resistance to paper packaging materials.

Sample_id	Analyte	Year	Country	Matrix	Value	Is_less_than	Units	Std_dev
Popcorn 1 Sample 1	PFOA	2018	US	Popcorn paper packaging	28.57		ng / g	0.3
Popcorn 1 Sample 2	PFOA	2018	US	Popcorn paper packaging	27.02		ng / g	3.2
Popcorn 1 Sample 3	PFOA	2018	US	Popcorn paper packaging	30.33		ng / g	7.2
Popcorn 2 Sample 1	PFOA	2018	US	Popcorn paper packaging	19.76		ng / g	2.3
Popcorn 2 Sample 2	PFOA	2018	US	Popcorn paper packaging	19.55		ng / g	2.1
Popcorn 2 Sample 3	PFOA	2018	US	Popcorn paper packaging	15.34		ng / g	3.4
Popcorn 3 Sample 1	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 3 Sample 2	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 3 Sample 3	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 4 Sample 1	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 4 Sample 2	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 4 Sample 3	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Snack and Sandwich 3 Sample 1	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g	
Snack and Sandwich 3 Sample 2	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g	
Snack and Sandwich 3 Sample 3	PFOA	2018	US	Paper snack and sandwich bag	5.11	<	ng / g	
Popcorn 5 Sample 1	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 5 Sample 2	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 5 Sample 3	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 6 Sample 1	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 6 Sample 2	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 6 Sample 3	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 7 Sample 1	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 7 Sample 2	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Popcorn 7 Sample 3	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g	
Snack and Sandwich 1 Sample 1	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g	
Snack and Sandwich 1 Sample 2	PFOA	2018	US	paper snack and sandwich bag	1.53	<	ng / g	
Snack and Sandwich 1 Sample 3	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g	
Snack and Sandwich 2 Sample 1	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g	
Snack and Sandwich 2 Sample 2	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g	
Snack and Sandwich 2 Sample 3	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g	
Popcorn 1 Sample 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g	
Popcorn 1 Sample 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g	
Popcorn 1 Sample 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g	
Popcorn 2 Sample 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g	
Popcorn 2 Sample 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g	
Popcorn 2 Sample 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g	
Popcorn 3 Sample 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g	

(*Continued*)

(Continued).

Sample_id	Analyte	Year	Country	Matrix	Value	Is_less_than	Units	Std_dev	
Popcorn 3 Sample 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 3 Sample 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 4 Sample 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 4 Sample 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 4 Sample 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Snack and Sandwich 3 Sample 1	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 3 Sample 2	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 3 Sample 3	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Popcorn 5 Sample 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 5 Sample 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 5 Sample 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 6 Sample 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 6 Sample 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 6 Sample 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 7 Sample 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 7 Sample 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 7 Sample 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Snack and Sandwich 1 Sample 1	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 1 Sample 2	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 1 Sample 3	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 2 Sample 1	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 2 Sample 2	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 2 Sample 3	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Sample_id Recovery	**Analyte**	**Year**	**Country**	**Matrix**	**Value**	**Is_less_than**	**Units**	**Std_dev**	**%**
Popcorn 1	PFOA	2018	US	Popcorn paper packaging	28.64		ng / g	± 1.66	
Popcorn 2	PFOA	2018	US	Popcorn paper packaging	18.22		ng / g	± 2.49	96.4%
Popcorn 3	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g		
Popcorn 4	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g		
Snack and Sandwich 3	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g		71.8%
Popcorn 5	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g		81.9%
Popcorn 6	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g		
Popcorn 7	PFOA	2018	US	Popcorn paper packaging	1.53	<	ng / g		80.4%
Snack and Sandwich 1	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g		
Snack and Sandwich 2	PFOA	2018	US	Paper snack and sandwich bag	1.53	<	ng / g		
Popcorn 1	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 2	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		83.6%
Popcorn 3	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 4	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Snack and Sandwich 3	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		76.5%
Popcorn 5	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		86.2%
Popcorn 6	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		
Popcorn 7	PFOS	2018	US	Popcorn paper packaging	0.63	<	ng / g		85.5%
Snack and Sandwich 1	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		
Snack and Sandwich 2	PFOS	2018	US	Paper snack and sandwich bag	0.63	<	ng / g		

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This study was supported by the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa and Project No. [IOW03902] by the Hatch Act and State of Iowa and the Polymer and Food Protection Consortium of Iowa State University, Ames, Iowa.

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