Fluorinated Compounds in U.S. Fast Food Packaging

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S *Supporting Information*

ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) are highly persistent synthetic chemicals, some of which have been associated with cancer, developmental toxicity, immunotoxicity, and other health effects. PFASs in grease-resistant food packaging can leach into food and increase dietary exposure. We collected ~400 samples of food contact papers, paperboard containers, and beverage containers from fast food restaurants throughout the United States and measured total fluorine using particle-induced γ-ray emission (PIGE) spectroscopy. PIGE can rapidly and inexpensively measure total fluorine in solid-phase samples. We found that 46% of food contact papers and 20% of paperboard samples contained detectable fluorine (>16 nmol/ cm^2). Liquid chromatography/high-resolution mass spectrometry analysis of a subset of 20 samples found perfluorocarbox-

Percent with fluorine

Dessert & bread wrappers — 56%

Sandwich & burger wrappers — 38%

Paperboard — 20%

Paper cups — 0%

PIGE (total F)

PFAS treated

Untreated

counts / energy (keV)

ylates, perfluorosulfonates, and other known PFASs and/or unidentified polyfluorinated compounds (based on nontargeted analysis). The total peak area for PFASs was higher in 70% of samples (10 of 14) with a total fluorine level of >200 nmol/cm^2 compared to six samples with a total fluorine level of <16 nmol/cm^2. Samples with high total fluorine levels but low levels of measured PFASs may contain volatile PFASs, PFAS polymers, newer replacement PFASs, or other fluorinated compounds. The prevalence of fluorinated chemicals in fast food packaging demonstrates their potentially significant contribution to dietary PFAS exposure and environmental contamination during production and disposal.
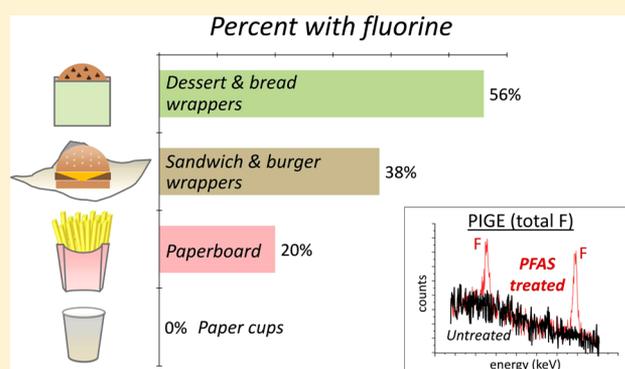
■ INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are widely used in nonstick, stain-resistant, and waterproof consumer products because of the hydrophobic and lipophobic properties of the PFASs. Their characteristic carbon–fluorine bonds make them extremely resistant to degradation, even at high temperatures. The most commonly used PFASs have been detected globally in water, soil, sediment, wildlife, and human blood samples.[1−7] Epidemiological studies have found associations between exposures to the long-chain PFASs perfluorooctanoic acid (PFOA) and/or perfluorooctanesulfonic acid (PFOS) and kidney and testicular cancer, low birth weight, thyroid disease, decreased sperm quality, pregnancy-induced hypertension, and immunotoxicity in children.[8−14] In addition, toxicological

studies in animals have linked PFOA and/or PFOS exposure to altered mammary gland development, reproductive and developmental toxicity, testicular cancer, obesity, and immune suppression.[15−19] Because of long half-lives in the human body and concerns about adverse health effects, major U.S. manufacturers have voluntarily phased out[20] production of PFOA, PFOS, and some other long-chain PFASs (defined as C6 and longer sulfonates and C7 and longer carboxylates)[21] for the majority of uses, although long-chain PFASs are still

produced globally. Common replacements include shorter-chain PFASs that have shorter human half-lives[22] and are less bioaccumulative,[23] as well as polyfluorinated polyether-based polymers.[24] Alternative PFASs are also persistent in the environment[22,25] or degrade into persistent molecules. Short-chain PFASs are harder to remove from drinking water.[26] While health effect data are limited, results from preliminary studies and structural similarities to long-chain PFASs have raised concerns about exposure to short-chain PFASs,[22,27−31] prompting efforts to support the development and use of nonfluorinated alternatives.[30,32]

PFASs have been detected in a wide range of products, including food contact materials (FCMs), carpeting and carpet cleaners, upholstery, floor waxes, and outdoor apparel.[33−35] PFASs in household products that migrate into food, indoor air, and dust can contribute to human exposure,[36−40] although these contributions are difficult to assess given the wide range of concentrations and relative abundances in exposure media.

PFAS-containing FCMs such as fast food packaging and microwave popcorn bags can contribute to indirect dietary exposure via migration into food.[36,37,41] Prior studies of fast food packaging such as wrappers, paperboard, and paper cups found a wide range of PFASs, including PFOS and other perfluoroalkyl sulfonates (PFSAs), PFOA and other perfluoroalkyl carboxylates (PFCAs), fluorotelomer alcohols (FTOHs), and polyfluoroalkyl phosphate esters (PAPs).[42−46] Relative abundances of PFASs vary among product types and studies. For instance, paper cups had relatively low PFAS concentrations compared to other types of packaging in some studies,[42,43] but relatively high concentrations in another.[46] Product formulations varied among countries, reflecting differences in production patterns. For instance, a 2016 study found that 6:2 FTOH was the most common FTOH in U.S. FCMs, whereas long-chain FTOHs were more common in samples from China, a difference attributed to the U.S. phase-out of long-chain PFASs.[43]

The extent of migration of PFASs from FCMs into food depends on the amount, type, and chain length of PFASs used, the type of food (e.g., fat- vs water-based), the contact time, and the temperature.[36,41,43] Despite brief contact times between FCMs and fast food, high temperatures and use of emulsified fats can significantly increase the extent of migration of PAPs and other PFASs into food.[36] Short-chain FTOHs and PFCAs were found to have migration efficiencies from paper bowls higher than those of long-chain analogues.[43]

Exposure to PFASs from fast food packaging is especially relevant for children, because one-third of U.S. children consume fast food daily[47] and children may be more susceptible to the adverse health effects.[13] Regulations in the United States specify which PFASs are allowed in FCMs. The U.S. Food and Drug Administration (FDA) currently approves more than 90 unique monomer and polymer PFASs for use in FCMs such as paper and paperboard,[48] including 20 PFASs approved to impart oil, grease, and/or water resistance that are listed in Table S1. Since 2008, 11 substances have been approved and registered by the FDA on the Inventory of Effective Food Contact Substance (FCS) Notifications; nine of these substances from four different chemical manufacturers are polymers that utilize a 6:2 fluorotelomer component.[48] In January 2016, in response to a petition filed by the Natural Resources Defense Council (NRDC) and other environmental organizations, the FDA rescinded approval for three families of long-chain PFASs used in FCMs, concluding there was no

longer a reasonable certainty of no harm.[49] However, this restriction is not expected to have a significant impact because the FDA had already worked with manufacturers to phase out use of these compounds in 2011.[50] While some European countries also list individual compounds approved for use in food contact materials,[51] in 2015 the Danish Ministry of Environment and Food issued a recommended limit for total organofluorine in paper and paperboard FCMs (0.35 μg of F/dm^2 or 0.18 nmol of F/cm^2).[52] The Supporting Information provides additional information about the Danish limit.

Prior studies that found PFASs in fast food packaging have been based on relatively few samples and inconsistent analytical methods. Here we applied a novel technique using particle-induced γ-ray emission (PIGE) spectroscopy as a rapid-screening method[53] to test more than 400 samples of food packaging from fast food restaurants across the United States for fluorinated chemicals. To evaluate whether samples with elevated total fluorine levels contained known PFASs and other compounds likely to be PFASs, we analyzed a subset of samples using conventional solvent extraction and liquid chromatography/high-resolution mass spectrometry analysis of PFASs. This study provides a proof-of-concept application of the PIGE method for rapidly screening a large number of packaging samples and prioritizing samples for compound-specific analyses. Our results provide the most comprehensive assessment to date of the prevalence of fluorinated compounds in U.S. fast food packaging and the availability of nonfluorinated alternatives.

■ MATERIALS AND METHODS

Sample Collection. In 2014 and 2015, we collected 407 samples of paper and paperboard food wrappers and related food packaging at U.S. fast food restaurants. The study was designed to represent a broad distribution of packaging types and geographic locations but did not necessarily reflect the overall distribution of total F concentrations in fast food packaging; 98% of samples were collected in five regions: western Washington (25%), eastern Massachusetts (24%), western Michigan (20%), northern California (17%), and metropolitan Washington, DC (12%). Three hundred ninety-five samples came from 27 large fast food chains (with ≥100 U.S. stores); each chain was sampled in up to five regions at up to three stores per region. Another 12 samples came from four individual fast food restaurants. Samples were 100−2500 cm^2 in area, and each was placed into a zip-lock bag or wrapped separately in aluminum foil to avoid fluorine transfer among samples.

Samples were divided into six categories: (1) food contact paper (e.g., sandwich wrappers and pastry bags), (2) non-contact paper (e.g., outer bags), (3) food contact paperboard (e.g., boxes for fries and pizza), (4) paper cups (for hot or cold drinks), (5) other beverages (e.g., milk and juice containers), and (6) miscellaneous (e.g., lids and applesauce containers). Food contact papers were further divided into three categories on the basis of likely uses: (1) sandwiches, burgers, and fried foods, (2) Tex-Mex food, and (3) desserts and breads.

Sample Analysis. Details of analytical methods and results of QA/QC analyses are provided in the Supporting Information. All samples were analyzed using PIGE spectroscopy at Hope College. PIGE previously has been used to measure fluorine in geological and biological samples.[54−57] An analytical method for application of PIGE to papers and textiles (Figure S1) was developed by Ritter et al.[53] and applied to

carpet and clothing samples.[58] In short, each sample was irradiated with approximately 10 nA of 3.4 MeV protons for 180 s. The characteristic γ-rays emitted from the de-excitation of ^{19}F at 110 and 197 keV had background-subtracted integrations summed for each sample irradiation. Integrated γ-ray counts in the 110 and 197 keV peaks per microcoulomb of beam on target (counts per microcoulomb) were converted to concentrations of total fluorine (in nanomoles of F per square centimeter) using PFAS standards dissolved in methanol and dried onto filter paper.[53] The limit of detection (LOD) was 16 nmol of F/cm^2, and the limit of quantification (LOQ) was 50 nmol of F/cm^2.

The ion beam typically penetrates 100−200 μm into a solid material. For wrapper samples, our analyses indicate that the beam can completely penetrate the samples, whereas the beam did not appear to completely penetrate paperboard samples that are much thicker; therefore, we analyzed thick samples on both sides and selected the higher concentration to capture the total fluorine signal associated with surface treatments.

As part of the quality assurance protocol, 10% of samples were replicated (two or three identical samples obtained simultaneously from the same restaurant and analyzed independently and blindly) to assess the reproducibility of analytical results and potential sample-to-sample variability (Table S2 and Figure S2). To assess analytical reproducibility, 5% of samples were analyzed repeatedly [two to five times per sample (Table S3)]. Results for replicates were combined prior to data analysis so that all samples were weighted identically regardless of the number of analyses.

To explore the extent to which PIGE analyses indicate the presence of PFASs, we analyzed 20 of our food packaging samples for PFASs using conventional solvent extractions followed by liquid chromatography/high-resolution mass spectrometry analysis. The identities of samples with high and low fluorine levels were unknown to the analyst conducting these measurements. We conducted methanol extractions on 14 samples with a total F concentration of >200 nmol of F/cm^2 and six samples with a total F concentration below the LOD. Extracts were analyzed for 89 PFASs with known structures and for unidentified polyfluorinated compounds using suspect screening analyses with liquid chromatography/time-of-flight mass spectrometry (LC/TOF MS) following methods described by Rager et al.[59] (see the Supporting Information for more details). Five samples (25%) were analyzed in duplicate.

■ RESULTS AND DISCUSSION

Of 407 samples, 33% had detectable total F concentrations (Table 1), ranging from 16 to 800 nmol of F/cm^2 (Figure 1). Detection frequencies varied among packaging types, from 0% for papers not in contact with food (N = 15) and paper cups (N = 30) to 46% for food contact papers (N = 248). Among food contact papers, detection frequencies ranged from 38% for sandwich/burger wrappers to ~57% for Tex-Mex food packaging and dessert/bread wrappers. Overall, fluorine was more commonly detected in grease-proof products (e.g., food contact papers) than in products holding liquids or not intended to come into contact with food. These detection frequencies indicate the presence of fluorinated food packaging currently in use but are not necessarily representative of the marketplace.

We analyzed a subset of 20 samples using LC/TOF MS methods to provide more specific identification of individual

Table 1. Percentages of Fast Food Packaging Samples with Total Fluorine above the Limit of Detection (16 nmol of F/ cm^2)

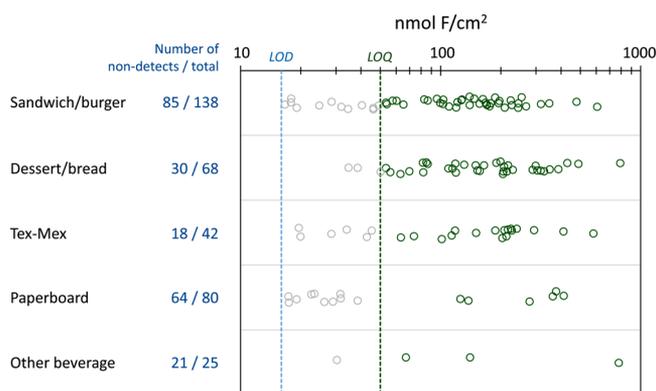|	no. of samples tested	no. of brands tested	no. of states tested	% with F
food contact paper (by category)				
sandwich/burger	138	20	5	38
dessert/bread	68	9	5	56
Tex-Mex	42	3	5	57
food contact paper (all)	248	27	5	46
food contact paperboard	80	15	5	20
noncontact paper	15	9	3	0
paper cups	30	9	4	0
other beverage containers	25	10	1	16
miscellaneous	9	7	1	0
total	407	29	5	33

Figure 1. Total F concentrations (in nanomoles of F per square centimeter) based on PIGE analyses of fast food packaging samples. Only samples with concentrations of total F above the LOD (16 nmol of F/cm^2) are plotted; detection frequencies are listed in Table 1. Concentrations between the LOD and LOQ (50 nmol of F/cm^2) are considered estimated.

PFASs and to validate the results of the PIGE analyses. The most commonly detected types of PFASs were PFCAs (e.g., PFOA and PFHxA), PFSAs (e.g., PFBS), and fluorotelomer sulfonates (e.g., 6:2 FTS) (Table S5). Six of the 20 samples (collected in 2014 and 2015) contained detectable levels of PFOA, even though U.S. manufacturers voluntarily agreed to stop distributing products containing C8 perfluorinated compounds for food contact purposes in interstate commerce in 2011 through a U.S. FDA initiative.[60] Unknown polyfluorinated compounds were indicated by a homologous series of compounds whose molecular weight differed by 49.9968 (accurate mass of the $-CF_2$ group) and/or had a negative mass defect. Total peak areas for known and unknown PFASs varied by more than 3 orders of magnitude. For many samples, the signal for unknown polyfluorinated compounds was similar to, and sometimes much larger than, the signal for known PFAS compounds, suggesting that a substantial portion of organofluorine in these samples cannot be ascribed to known PFASs.

In general, the LC/MS analyses supported the PIGE results, because total peak areas associated with known and unknown

PFASs in 70% of samples (10 of 14) that had a PIGE total F concentration of >200 nmol/cm^2 were greater than peak areas in six samples with a total F concentration below the LOD (Figures S3 and S4 and Table S4). However, some samples with high levels of total fluorine according to PIGE did not contain elevated levels of PFASs according to LC/MS analyses. Four samples with a total F concentration of >200 nmol/cm^2 contained peak areas for known and/or unknown PFASs that were at or below levels detected in six samples with a total F concentration below the LOD. One explanation for these findings is that much of the total fluorine in these samples was present as inorganic fluorine or non-PFAS organofluorine compounds. Another explanation is that our extraction and LC/TOF MS analyses failed to capture a substantial portion of the PFASs present in the samples. For instance, FTOHs have been among the most frequently detected PFASs in FCMs,[43] but they are volatile and form adducts with LC modifiers, making their measurement erratic as determined by LC/MS. We screened for but did not find detectable FTOH-acetate or formate adduct ions (4:2 through 10:2), which are expected to form if FTOHs were present, although FTOHs may have been lost during sample preparation. Food packaging also can contain newer replacement compounds, such as polyfluorinated polyether-based (PFPEs) polymers,[24] which were not among our target analytes because of a lack of authentic standards and difficulties in their analysis. We found evidence that PFPEs were present in some of our sample extracts via the detection of repeating units consistent with -C_2F_4O- (115.989 units). Paper and paperboard may also contain other fluorinated polymers (Table S1) that may not be readily extractable in methanol.

Among regions, detection frequencies for total F ranged from 38 to 55% for food contact papers and from 10 to 33% for paperboard containers (Table S6). A logistic regression for the presence of fluorinated chemicals did not find significant differences among regions (Table S7), using region and product type as categorical independent variables. Dessert/bread wrappers and Tex-Mex food packaging had a percentage of fluorinated samples higher than those of all other categories of food contact samples (Table 1 and Table S7). To evaluate short-term temporal variability, we collected nine sets ($N = 2-6$) of identical samples from the same locations over the course of 1–8 weeks. We observed little variation in fluorine detection on this time scale. Five sets all contained quantifiable fluorine (above the LOQ); three sets all were below the LOD, and in one set, one sample was below the LOD and the other between the LOD and LOQ.

We attempted to investigate the fast food chains' knowledge of their use of fluorinated food packaging. For each of the fast food chains that we sampled, we submitted questions through Web sites and by phone regarding company use, sourcing, and general policies on fluorinated products. Only two companies provided a substantive response: one stated that they believed none of their food packaging contained fluorinated chemicals, and the other stated that they verified with their suppliers that their food packaging did not contain PFASs. However, we found a substantial portion of fluorinated food contact papers from these two chains. While it is difficult to draw conclusions on the basis of so few responses, this suggests a lack of knowledge in the fast food industry about the use of fluorinated packaging.

Study Implications. We found that fluorinated compounds are common in food contact papers and other fast food packaging in the United States; 33% of samples we tested had

total fluorine concentrations above the LOD for PIGE of 16 nmol of F/cm^2 (∼60 μg/g in wrappers, ∼14 μg/g in paperboard). This LOD, which is equivalent to 30 μg of F/dm^2 (or 44 μg of PFOA/dm^2), is well above the Danish Ministry of Environment and Food's guideline of 0.35 μg of F/dm^2 for total organic fluorine,[52] which may include both intentionally added and background PFASs. Samples with detectable total fluorine based on the PIGE method were likely treated with PFASs or other fluorinated compounds; according to the Danish Ministry of Environment and Food, diPAP concentrations of 600−9000 μg of F/g in food packaging (∼360−5400 μg of F/g of paper) were attributed to intentional additions to paper pulp, and diPAP concentrations of 1−100 μg of F/g (∼0.6−60 μg of F/g of paper) were hypothesized to be associated with surface coatings.[61,62] However, the PIGE method may not be sufficiently sensitive to identify all samples with intentionally added PFASs. We detected PFASs in all of our samples with a total F concentration below the LOD using a more sensitive LC/MS method, which may capture both PFASs that are intentionally added to packaging materials and background levels, for instance, from recycled paper or unintentional cross contamination. At this point, there is no clear distinction between PFAS or total F concentrations associated with intentional addition to food contact materials and unintentional background levels. Thus, while we found that the concentration of total F in many samples was below the LOD for the PIGE method (54% of papers and 80% of paperboard), we cannot determine the proportion of these samples that are free of the addition of PFAS-containing grease-proofing additives.

It is difficult to assess exposure and risk associated with PFASs in fast food packaging because the extent of exposure from FCMs and the toxicity of most fluorinated chemicals in FCMs are poorly characterized. While much of the U.S. production of PFOS and PFOA was phased out between 2000 and 2015, these compounds are still produced in other regions of the world. Some food packaging approved by the U.S. FDA is labeled "PFOA-free" but contains shorter-chain C6 PFASs[63] or long compounds with perfluorinated subunits linked by ether groups.[25] PFHxA, the C_6 homologue of PFOA, has a much shorter human half-life (32 days compared to 3.5 years),[64] but preliminary toxicity testing suggests it has some of the same adverse effects.[29,31] In general, very little information about human half-lives and potential health effects of other replacement PFASs is available, despite widespread exposures and documented toxicity of related long-chain PFASs.[28,30]

Fluorinated FCMs are also a source of PFASs to the environment. Manufacturing facilities for PFAS-containing paper products may release PFASs into air and wastewater.[51] PFASs in consumer products that end up as municipal solid waste can be transported to groundwater through landfill leachate.[65] Because of their environmental persistence, PFASs should be considered incompatible with compostable food packaging.[66] However, ASTM compostability standards D6400 and D6868 do not consider PFASs, so they are currently allowed in compostable foodware.[67,68] Direct land application of compost with PFAS-containing food packaging may result in elevated soil concentrations and enhanced phytoaccumulation. PFASs in land-applied biosolids have been shown to accumulate in crop plants.[69−72] PFASs are mobile in groundwater systems and have been detected in drinking water wells globally.[73−76]

Our study demonstrates the utility of the PIGE spectroscopic method for measuring total fluorine concentrations in food packaging and identifying samples most likely to contain high levels of PFASs. In addition to consumer products, PIGE also can be used to analyze environmental samples for the presence of PFASs and delineate impacted areas. Because sample preparation and analysis take only a few minutes, we were able to rapidly screen more than 400 packaging samples for PFASs. The PIGE method is nondestructive and can be used as an inexpensive screening technique to prioritize samples for more time- and labor-intensive chemical analyses to identify individual PFASs and characterize their migration into food. In addition, because PIGE measures total fluorine, it can detect unidentified PFASs that are not included in conventional mass spectrometry-based analyses. This technique can be applied to provide information to food packaging distributors, restaurants, and consumers who prefer truly compostable products and wish to avoid PFAS-containing FCMs because of concerns about potential adverse human and ecological health effects.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00435.

A list of PFASs approved by the U.S. FDA for food contact materials, additional information about analytical methods, QA/QC results, regional comparisons of PIGE detection frequencies, and LC/MS results (PDF)

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Notes

This article was reviewed in accordance with the policy of the National Exposure Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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■ ACKNOWLEDGMENTS

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