Environmental Science & Technology

pubs.acs.org/est

Article

Organic Fluorine as an Indicator of Per- and Polyfluoroalkyl Substances in Dust from Buildings with Healthier versus Conventional Materials

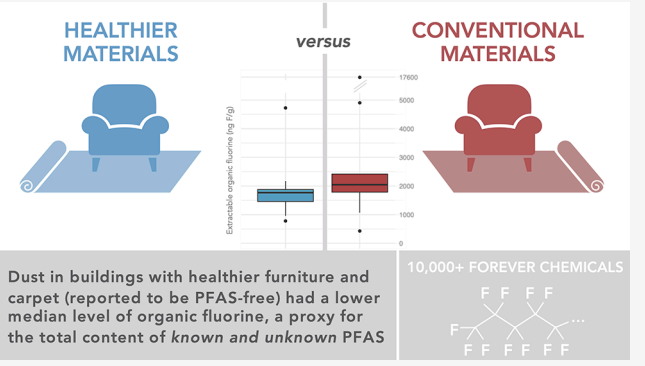
Anna S. Young,* Heidi M. Pickard, Elsie M. Sunderland, and Joseph G. Allen

Cite This: *Environ. Sci. Technol.* 2022, 56, 17090−17099

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Per- and polyfluoroalkyl substances (PFAS) are a class of thousands of persistent, organic fluorinated chemicals added to materials and products mainly to repel stains and water. PFAS have been associated with many adverse human health effects. We aimed to determine whether buildings with "healthier" materials—defined here as reportedly free of all PFAS—exhibit lower PFAS in dust. In addition to analyzing targeted PFAS with available commercial standards, we measured extractable organic fluorine (EOF) as a novel proxy that includes both known and unknown types of PFAS. We measured at least 15 targeted PFAS (n = 24), EOF (n = 24), and total fluorine (TF; n = 14) in dust collected from university common spaces and classrooms, half of which had "healthier" furniture and carpet. We observed lower PFAS contamination in buildings with "healthier" materials: "healthier" rooms had a 66% lower median summed PFAS and a 49% lower Kaplan−Meier estimated mean EOF level in dust in comparison to conventional rooms. The summed targeted PFAS were significantly correlated with EOF but accounted for up to only 9% of EOF, indicating the likely presence of unidentified PFAS. EOF levels explained less than 1% of TF in dust. We emphasize the need to use chemical class-based methods (e.g., EOF) for evaluating class-based solutions and to expand non-PFAS solutions for other building materials.



KEYWORDS: *EOF, PFAS, chemical classes, intervention, furniture, carpet, healthy buildings*

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a class of highly fluorinated, anthropogenic chemicals added to products for their surfactant, stain-resistant, and water-resistant properties.[1] To date, over 12,000 different PFAS structures have been identified.[2] Because of concerns about the toxicity and persistence of this class of thousands of chemicals, scientists have called for PFAS to be addressed as a chemical class instead of as one chemical at a time.[3−5] This class-based approach seeks to avoid the common issue of well-known types of PFAS being eliminated in favor of a less-known substitute PFAS with similar concerns for health and the environment. Addressing the prevalent use of PFAS in over 200 different consumer and industrial categories[6] is critical because PFAS have contaminated drinking water and environments on every continent;[7−10] have been detected in the blood of over 98% of Americans;[11] and have been associated with human risk of thyroid disease, stunted development, weakened immune system, high cholesterol, cancer, obesity, and diabetes.[1,12−18]

In recent years, the "healthier" materials movement has advanced alternative building materials that are reported by manufacturers to be free of all types of PFAS, flame retardants, and other chemicals, although these materials are not common yet. One university implemented some of the first interventions to refurnish interiors of certain buildings with "healthier" furniture and carpet that reportedly did not contain any added PFAS (or certain other chemicals), as specified by manufacturers in product purchasing agreements with the university. In our previous study, we scientifically evaluated the effectiveness of the completed interventions at that university. We found that rooms with so-called "healthier" furniture and carpet had 78% significantly lower total levels of 15 measured PFAS in dust compared to rooms with conventional materials, indicating a substantial benefit of "healthier" materials interventions.[19] To our knowledge, no other study has yet been published that evaluates a real-world intervention to reduce exposure to this ubiquitous group of chemicals. In addition, the advancement of class-based analytical methods is

Received: July 19, 2022
Revised: October 19, 2022
Accepted: October 20, 2022
Published: November 4, 2022

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099

needed to fully evaluate the extent of unknown PFAS contamination and the effectiveness of chemical class-based interventions.

Organic fluorine has recently emerged as a novel indicator that encompasses the total content of both known and unknown types of PFAS, unlike traditional targeted analyses that can reliably quantify only a few dozen known PFAS that have commercially available analytical standards. Measurement of total fluorine (TF) is inexpensive, but it is not as reliable of a proxy for PFAS because it includes inorganic fluoride in addition to organic fluorine. By contrast, extractable organic fluorine (EOF) measurements exclude interference from any inorganic fluoride by removal of the inorganic fraction via extraction.[20−23] In the past decade, several studies have measured TF and/or EOF in food packaging, paper, cosmetics, textiles, and firefighter gear. These studies found potentially large quantities of unknown PFAS in the products, with specific measured PFAS usually accounting for up to only about 2% of EOF or TF levels.[22,24−27] Scarce research has been done on EOF or TF in indoor dust, which is a major route of human exposure to PFAS. Because PFAS are noncovalently bound additives, they readily migrate out of materials and accumulate in the dust in buildings.[27−29]

In this study, we investigated the impact of a "healthier" materials intervention in university buildings on levels of targeted PFAS, extractable organic fluorine, and total fluorine in indoor dust. Specifically, our objectives were to (1) compare concentrations of EOF and targeted PFAS in indoor dust samples collected from 12 indoor spaces with "healthier" furnishings versus 12 spaces with conventional furnishings, (2) determine the fraction of EOF and TF that cannot be explained by the known targeted PFAS, and (3) evaluate the strength of correlation between EOF concentrations and TF measurements within a small subset of 14 samples.

METHODS

Study Design. We investigated PFAS and EOF in dust samples collected from 24 rooms in buildings at a university in the United States. These samples were collected in 2019 as part of our previous study of 48 rooms.[19] The study included as many buildings as possible that had undergone a "healthier" carpet and furniture renovation by the university. The "healthier" carpet and furniture were defined here as being reported by manufacturers to be free of all types of PFAS (down to a certain reporting threshold such as 100 ppm), based on product purchasing agreements with the university. The materials were also reported to be free of chemical flame retardants, as investigated in our previous study. "Furniture" referred to furnishings that were generally not fixed within the rooms, except for electronics. We confirmed with the university teams which campus building rooms had undergone the full "healthier" materials intervention and which did not have any intervention on the furniture or carpet (i.e., conventional materials). We selected and categorized rooms as "healthier" or conventional before we collected any dust samples in the selected rooms.

We attempted to choose conventional rooms that were otherwise as similar as possible to "healthier" rooms—among the buildings available to sample—in terms of room characteristics, size, recentness of last renovation, and construction year. The median year of building construction was 1965 for the conventional rooms in this study and 1972 for "healthier" rooms. The median year of last refurnishing was 2016 for conventional rooms (refurnished with conventional materials) and was 2018 for "healthier" rooms (refurnished with "healthier" materials), based on product procurement records or on furniture tags in the rooms. All sampled rooms were carpeted (by study selection criteria), never had stain-repellant coatings applied to carpets (according to the university), and were vacuumed at least two times per week.

For our current substudy, we included 14 common areas and 10 classrooms across 14 unique buildings. This subset of rooms (n = 24) from the parent study (n = 48) was selected randomly to achieve equal numbers of conventional and "healthier" rooms among common areas and classrooms in the parent study with sufficient masses of dust. For secondary analysis of TF in the same dust samples, we analyzed a total of 14 samples (from eight common areas and six classrooms), which were randomly selected for equal numbers across conventional versus "healthier" materials type.

Dust Collection. Each room area was split into thirds, and a separate dust sample was collected within each third of the room for different laboratory analyses (one dust sample for targeted chemicals; one for EOF and TF analysis; and one for cell assays for a different study) (Figure S1). Dust samples were collected by vacuuming floor dust for 10 min into a cellulose extraction thimble secured with a nitrile rubber O-ring inside a crevice tool attached to a vacuum cleaner (Dyson CY18). In this way, the only reused equipment the dust contacted was the crevice tool, which was cleaned with isopropyl alcohol and tap water between uses. After collection, the samples were stored in polypropylene centrifuge tubes in a freezer at −13 °C. Blank thimbles in centrifuge tubes were used as field blanks (n = 4) that were transported to and from each sampling location but never opened. Further details on the sampling protocol are available in our previous contribution.[19]

Sample Extraction and Targeted PFAS Analysis from Previous Study. As part of this study, we included chemical data collected in our previous study of the concentrations of 15 PFAS analytes in the dust samples.[19] These included: perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), perfluorohexanoate (PFHxA), perfluorohexanesulfonate (PFHxS), perfluorooctane sulfonamide (FOSA), perfluoroheptanoate (PFHpA), perfluoropentanoate (PFPeA), perfluorononanoate (PFNA), perfluorobutanesulfonate (PFBS), perfluorodecanesulfonate (PFDS), perfluorobutanoate (PFBA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), and n-methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA).

The 15 targeted PFAS were quantified using high-performance liquid chromatography (HPLC) coupled with electrospray triple quadrupole tandem mass spectrometry (ESI-MS/MS) and monitored by multiple reaction monitoring mode under negative ionization. Prior to extraction, the dust samples were sieved through a 150 μm stainless steel mesh (sample masses: 0.2−0.5 g) and spiked with internal standards (30 ng). They were extracted with 30 mL of methanol, mechanically oscillated for 1 hr, ultrasonicated for 30 min, centrifuged for 10 min (3500g), and transferred into new polypropylene tubes. The extraction was repeated twice with 3 mL of acetonitrile and 3 mL of ethyl acetate, and the extracts were combined and evaporated to 3 mL under nitrogen. The extracts were reconstituted with 200 μL of methanol and filtered through a 0.2 μm nylon filter into glass vials for HPLC analysis. The

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099

concentrations of the 15 targeted PFAS were corrected for extraction losses and matrix interferences, because internal standards were added prior to extraction in the methods for the quantification of the 15 targeted PFAS. Additional details are provided in the previous publication.[19]

Sample Extraction for Current Study. For the current study, we analyzed concentrations of EOF in dust samples at the Biogeochemistry of Global Contaminants Laboratory at Harvard University. We analyzed replicate dust samples that had been collected in a different one-third split of each room at the same time as the other dust samples for analysis of 15 targeted PFAS (see diagram in Figure S1). To determine the fraction of EOF explained by measured PFAS, dust samples extracted for EOF analysis included an additional measurement of 37 known PFAS using this laboratory's targeted analysis method, for direct comparison between measured PFAS and EOF. The targeted analysis method is described in detail in prior publications.[30,31] Since EOF measurements are not recovery-corrected, comparison of PFAS to EOF requires additional analysis of targeted PFAS in which internal standards (ISs) are added after extraction to avoid recovery correction. Concentrations of these 37 nonrecovery-corrected PFAS may be underestimated compared to the 15 PFAS that were measured with ISs added before extraction due to recovery correction based on extraction losses and matrix interferences. Thus, the resulting concentrations from the 37 measured PFAS are used only to calculate the organic fluorine equivalents from measured PFAS in order to evaluate the unknown fraction of EOF. The recovery-corrected concentrations of 15 targeted PFAS measured in the previous study are used to discuss specific PFAS contamination in dust in the buildings and how that varied by intervention type.

For the analysis of EOF (alongside 37 measured PFAS), replicate dust samples (~200 mg) were left unsieved, extracted with 5 mL of methanol (MeOH) in a 15 mL polypropylene tube, vortexed, and sonicated in a 40 °C water bath for 20 min. Samples were then centrifuged for 5 min at 5000 rpm, and the MeOH extract was decanted to a new tube. This process was repeated two more times, and the extracts were combined. The final 15 mL extract was evaporated to 1 mL using an N-EVAP nitrogen evaporator. The 1 mL sample extracts were loaded onto preconditioned Supelco Envi-carb cartridges (250 mg, 6 mL) and eluted with 3 mL of MeOH. The eluted extract was evaporated to 0.5 mL on the N-EVAP.

To remove inorganic fluoride from the extracts for EOF analysis,[32−34] the 0.5 mL sample extract was diluted with 10 mL of Milli-Q (MQ) water and loaded onto preconditioned Oasis WAX cartridges (150 mg, 30 μm). Following sample loading, cartridges were washed with 20 mL of 0.01% ammonium hydroxide in MQ water and 10 mL of MQ water. Cartridges were dried under vacuum for 30 min and eluted with 4 mL of MeOH and 4 mL of 0.1% ammonium hydroxide in MeOH. Sample extracts were evaporated to dryness, reconstituted in 1 mL of MeOH, and split in half for analysis on the liquid chromatograph-tandem mass spectrometer (LC-MS/MS) for measured PFAS and the combustion ion chromatograph (CIC) for EOF. Isotopically labeled ISs were added to the LC-MS/MS fraction after splitting and combined in 50:50 MQ water−MeOH for analysis.

Analysis of EOF, TF, and PFAS Fluorine Equivalents. Split sample extracts were analyzed at Harvard University for EOF on a Metrohm CIC with combustion unit from Analytik Jena (Jena, Germany), 920 Absorber Module, and 930 Compact IC Flex ion chromatograph from Metrohm (Herisau, Switzerland). Sample extracts (100 μL) were injected into the combustion unit at 1050 °C, and the anions were separated with an ion exchange column (Metrosep A Supp 5-150/4) operated at 30 °C, with sodium carbonate−bicarbonate buffer as eluent and isocratic elution. The fluorine (F^-) concentration was measured via ion conductivity.

To determine the fraction of EOF in the extracts explained by organic fluorine equivalents calculated from measured PFAS, 37 targeted analytes were measured using splits of the same sample extracts for EOF determination. Postextraction IS-spiked sample extracts were analyzed on an Agilent (Santa Clara, CA, U.S.A.) 6460 triple quadrupole LC-MS/MS equipped with an Agilent 1290 Infinity Flex Cube online SPE, following previously published methods, with slight modifications.[35] Method detection limits (MDLs) ranged from 0.016 to 4.5 ng/g for the 37 PFAS analyzed (Table S1). Further information on the laboratory methods can be found in the Supporting Information (SI), and mass spectrometry acquisition parameters are detailed in Table S2. The 37 measured PFAS included the same analytes as the previous study plus perfluorotridecanoate (PFTrDA), perfluorotetradecanoate (PFTeDA), perfluoropentanesulfonate (PFPeS), perfluoroheptanesulfonate (PFHpS), perfluorononanesulfonate (PFNS), perfluoro-1-hexanesulfonamide (FHxSA), perfluorodecanesulfonamide (FDSA), perfluoro-1-butanesulfonamide (FBSA), 4:2 fluorotelomer sulfonate (FTSA), 6:2 FTSA, 8:2 FTSA, 10:2 FTSA, 3:3 fluorotelomer carboxylate (FTCA), 5:3 FTCA, 7:3 FTCA, N-ethyl perfluorooctane sulfonamidoacetic acid (N-EtFOSAA), perfluorooctane sulfonamidoacetic acid (FOSAA), *N*-methyl perfluorooctane sulfonamide (N-MeFOSA), N-ethyl perfluorooctane sulfonamide (N-EtFOSA), *N*-methyl perfluorooctane sulfonamido ethanol (N-MeFOSE), N-ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE), and dodecafluoro-3H-4,8-dioxanonanoate (ADONA).

TF measurements were carried out using the same Metrohm CIC. Dust material (4.6−10 mg) was weighed directly into a quartz sample boat with quartz insert to keep the sample in place. Quartz sample boats were baked prior to sample combustion to minimize background contamination. The samples were combusted at 1050 °C for approximately 4.5 min. Combustion gases were absorbed in Milli-Q water during the entire length of the combustion process using the 920 Absorber Module, and an aliquot of the absorption solution was injected onto the ion chromatograph. The fluorine (F^-) concentrations were measured via ion conductivity.

Quality Assurance and Quality Control. For the primary data on 15 targeted PFAS from the previous study, field blank levels were almost all below the limit of detection (LOD) or well below sample concentrations. More details on the quality assurance/quality control are provided in the previous publication.[19] Information on the quality assurance/quality control of the current analysis of 37 measured PFAS (which were interpreted only in the context of the EOF fraction due to the sample extraction procedure) can be found in the SI.

For EOF analysis, a quartz boat without sample (boat blank) was analyzed twice between each set of duplicate sample injections to determine background fluorine (F^-) levels between sample injections. Samples were blank-corrected using the peak areas of the boat blanks run before and after each set of injections. Methanol blanks were run during calibration and after every ten samples to account for any

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099

Table 1. Medians, Ranges, and Kaplan−Meier (KM) Estimated Means for Concentrations of Total Fluorine (TF), Extractable Organic Fluorine (EOF), and the Sum of 15 Targeted PFAS in up to 24 Samples of Indoor Dust from University Spaces with Either Conventional Materials or "Healthier" Materials Reported to Be Free of All PFAS[a]

			all rooms		conventional rooms			"healthier" rooms		
parameter	units	n	median	range	median	KM mean	range	median	KM mean	range
total fluorine (organic + inorganic)	ng F/g	14	2190000	[<MDL−17800000]	2330000		[<MDL−17800000]	1810000		[657000−13800000]
extractable organic fluorine	ng F/g	24	1830	[<MDL−17600]	2050	3390	[<MDL−17600]	1770	1720	[<MDL−4730]
sum of 15 targeted PFAS (recovery-corrected)	ng/g	24	274	[19.5−1750]	403		[226−1750]	136		[19.5−422]

[a]Reverse Kaplan−Meier (KM) estimation was used as an alternative, nonparametric approach for summarizing mean EOF concentrations because of the multiple, relatively high detection limits in these left-censored data; by contrast, the median and range of EOF levels were based on simple nondetect substitution. Sample sizes were split equally between conventional rooms and "healthier" rooms (n = 12 of each category for EOF and PFAS measurements; n = 7 each for TF measurements).

source of contamination from the solvents used in the analysis. Extraction blanks were used to determine the LOD, which was calculated as the average plus three times the standard deviation of duplicate injections of extraction blanks. The extraction LOD was determined to be 514 ng F/mL, and individual sample MDLs were calculated based on the extraction LOD multiplied by each sample's dilution factor based on sample mass extracted. Sample MDLs ranged from 2177 to 3132 ng F/g. All four field blank samples were less than the MDL. Sample concentrations were determined from the average peak areas of duplicate injections using a nine-point calibration curve (R^2 > 0.999) of a custom anion mix in LC-MS grade methanol from 100 to 10,000 μg F/L. Concentrations above the MDL were adjusted for the dilution factor and corrected by subtracting the average field blank concentration. Quality control points were included after every 12 samples and had a variance of <12%. Samples (n = 3) were spiked with inorganic fluoride (IF) to assess removal efficiency with the extraction procedure and were all less than the MDL. The percent recovery (96−105%, n = 3) was calculated from the concentration of organic fluorine measured by the CIC divided by the concentration of organic fluorine measured by the LC-MS/MS using a 1065 μg F/L PFOS spike in extracted MeOH.

For TF analysis, quantification was carried out using a quadratic 13-point calibration curve of single 100 μL injections of a custom anion mix in MQ water ranging from 50 to 80,000 ng F/sample (R^2 > 0.999). Quality control calibration checks were included throughout the analysis and had a variance of <6%. The LOD for TF measurements was calculated from the average area obtained from boat blanks run throughout the analysis plus three times the standard deviation of the blanks which resulted in an LOD of 26 ng F/sample. A TF blank of Milli-Q water was tested and yielded a concentration less than the LOD. Dust sample concentrations were blank-corrected using the field blank (cellulose extraction thimble used to collect dust) due to detectable levels of F^- in the field blanks that accounted for up to 3% of the fluorine concentration measured in the dust samples. A 15,030 ng F/sample sodium fluoride spike in Milli-Q water was included to assess combustion efficiency and recovery (109% recovery). TF concentrations were converted to ng F/g based on the sample mass combusted.

Statistical Analysis. All EOF, TF, and PFAS concentrations were blank-corrected by subtracting the average value of the field blanks. We calculated the sum of targeted PFAS levels by summing the individual concentrations of the analytes, where values less than MDL were treated as the MDL divided by the square root of two.

For statistical analyses of EOF, we substituted concentrations of EOF less than the MDL with the MDL divided by the square root of two. However, we also performed alternative statistical analyses of EOF using nonparametric reverse Kaplan−Meier (KM) estimation, which is often preferred over simple substitution methods because it accounts for left censored data with multiple different—and comparatively high—detection limits for EOF in the samples, which is less of an issue in targeted PFAS analysis. The lowest observed EOF concentrations were not censored nondetects, so no correction method was needed for KM estimation, and 33% of the EOF data were censored. The KM estimation does not make distributional assumptions.[36,37] This approach was not needed for the PFAS concentrations due to lower, more sensitive detection limits.

Significant differences in the levels of PFAS and EOF between conventional versus "healthier" rooms were assessed using nonparametric Wilcoxon rank sum tests or using Peto−Prentice tests for Kaplan−Meier estimates. Correlations were calculated as nonparametric Spearman coefficients. Statistical significance was evaluated at α = 0.05 with suggestive evidence at α = 0.10.

To investigate the fraction of EOF or TF not accounted for by measured PFAS, we converted the levels of each PFAS to organic fluorine equivalents using the following equation[25] and then summed them for each sample:

$$C_F = C_{PFAS}\frac{n_F \cdot AW_F}{MW_{PFAS}}$$

where C_F is the calculated fluorine concentration (ng F/g) in the dust from that PFAS, C_{PFAS} the concentration (ng/g) of each PFAS in the dust, n_F the number of fluorine atoms on each PFAS, AW_F the atomic weight of fluorine (18.998 g/mol), and MW_{PFAS} the molecular weight of each PFAS (g/mol). For each sample, we calculated the sum of the organic fluorine equivalents for all PFAS and divided this by the actual measured EOF or TF concentration as an indicator of the percent of EOF or TF accounted for by these targeted analytes. All analyses were conducted in R (version 4.1.2).

RESULTS

Targeted PFAS. In the samples of dust from 24 common areas or classrooms at a university, the summed concentrations

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099

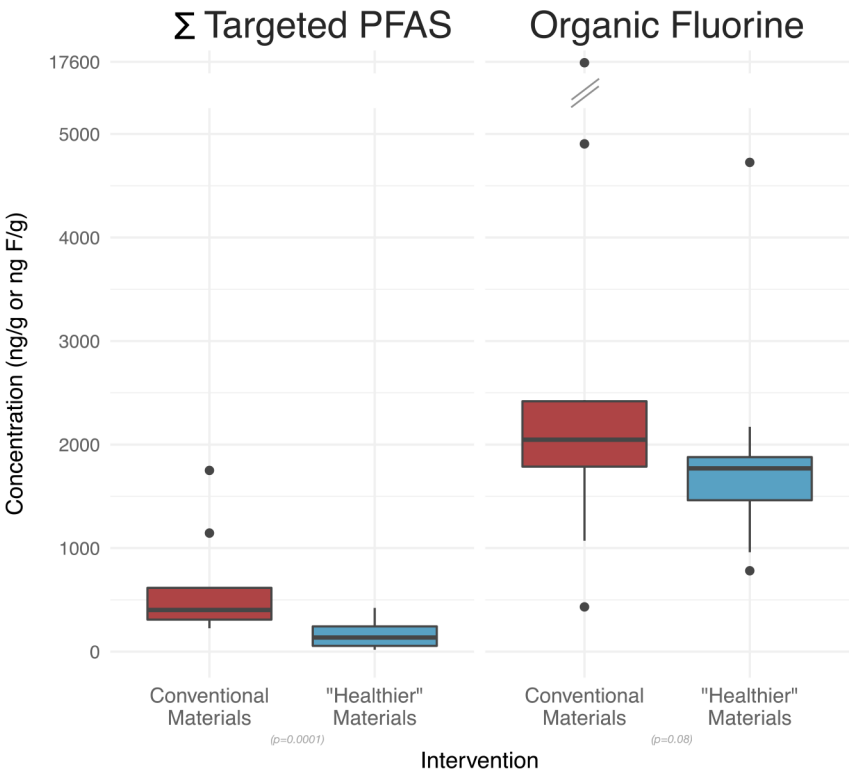


Figure 1. Concentrations of the sum of 15 targeted PFAS (ng/g) (left panel) and extractable organic fluorine (EOF) (ng F/g) (right panel) in 24 dust samples from rooms with conventional or "healthier" building materials.

of targeted PFAS were significantly lower in the rooms with "healthier" materials specified to be free of all PFAS in comparison to the rooms with conventional materials. Specifically, the median sum of 15 targeted PFAS in the dust samples was 66% lower in the 12 rooms with "healthier" materials compared to the 12 conventional rooms. The differences were statistically significant with $p = 0.0001$. The median [range] was 403 [226−1750] ng/g for conventional rooms and 136 [19.5−422] ng/g for "healthier" rooms (Table 1).

Organic Fluorine. Across all 24 conventional and "healthier" rooms, there was a median 1,830 ng F/g of extractable organic fluorine and maximum 17,600 ng F/g (Table 1). Levels of EOF were above the method detection limit in 67% of dust samples (16 of 24). Samples with levels less than the MDL were collected from 5 "healthier" rooms and 3 conventional rooms.

The summarized concentrations of extractable organic fluorine were lower in dust from the rooms with "healthier" materials compared to rooms with conventional materials (Figure 1). The median EOF was 14% lower in "healthier" rooms (1,770 ng F/g [range: <MDL−4,730 ng F/g]) than in conventional rooms (2,050 ng F/g [<MDL−17,600 ng F/g]; $p = 0.083$) (Table 1) with suggestive evidence (defined as $p \leq 0.1$). Based on reverse Kaplan−Meier estimation, which better accounts for the relatively high detection limits compared to targeted PFAS analysis, the mean EOF levels in dust were 49% lower in rooms with "healthier" materials (1,720 ng F/g) compared to rooms with conventional materials (3,390 ng F/g) (Table 1). Differences between EOF concentrations in "healthier" rooms and conventional rooms were more pronounced using reverse Kaplan−Meier mean estimation, although this difference did not reach statistical significance due to small sample numbers (suggestive evidence at $p = 0.1$). The 95% confidence intervals (CIs) for the KM means of EOF were 1,720 ng F/g (95% CI: 1,020−2,420 ng F/g) for "healthier" rooms and 3,390 ng F/g (727−6,050 ng F/g) for conventional rooms.

The calculated organic fluorine equivalents based on 37 measured PFAS from the EOF extraction also had a 53% lower median concentration in rooms with "healthier" materials (25.4 ng F/g [range: 15.0−51.5 ng F/g]) compared to conventional materials (54.5 ng F/g [24.5−597 ng F/g]), and this difference was statistically significant ($p = 0.0045$) (Table 1). These 37 measured PFAS were not recovery-corrected during laboratory analysis in this study (unlike the 15 targeted PFAS from our previous analysis) in order to have direct comparison to EOF levels, as described in detail in Methods.

Figure 2 demonstrates the substantial difference in magnitudes between levels of measured EOF and organic fluorine equivalents calculated from the 37 measured PFAS, even while both indicators had medians that were lower in "healthier" rooms compared to conventional rooms (Figure 2). Across all samples, the EOF concentrations had a median of 1,830 and maximum of 17,600 ng F/g, whereas the calculated concentrations of organic fluorine equivalents based on the measured PFAS had a median of 39.5 and maximum of 597 ng F/g (Table 1). The measured PFAS only accounted for between 1.0 and 9.2% (median 2.6%) of the EOF concentrations among the 16 samples with detectable EOF. There were significant positive correlations between the EOF levels and the organic fluorine equivalents of 37 measured PFAS (Spearman $r = 0.47$, $p = 0.020$) and the sum of recovery-corrected concentrations of 15 targeted PFAS from the previous study ($r = 0.43$, $p = 0.034$).

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099

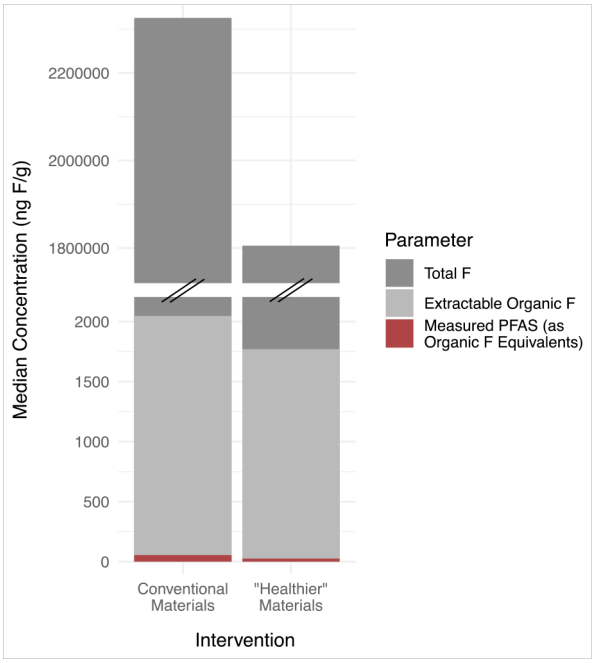


Figure 2. Median concentrations (ng F/g) of total fluorine, extractable organic fluorine (EOF), and calculated organic fluorine equivalents based on measured PFAS in dust samples from n = 24 rooms with conventional or "healthier" materials.

Total Fluorine. All but one sample had levels of total fluorine above detection limits. The concentrations of TF, which includes both organic and inorganic fluorine, were orders of magnitude higher than the measured concentrations of extractable organic fluorine (Table 1). In fact, the percent of TF explained by EOF was <1% in all samples with detectable levels of both TF and EOF (range: 0.014−0.61%). Similarly, among the samples with measured and detectable levels of TF, only up to 0.021% (min: 0.00028%) of TF was accounted for by the organic fluorine equivalents calculated from the 37 measured PFAS. Although TF was only moderately correlated with EOF (Spearman r = 0.45, p = 0.11) and had a small sample size (n = 14), we did observe a nonsignificant 22% lower median concentration of TF in dust from the rooms with "healthier" materials (1,810,000 ng F/g [range: 657,000−13,800,000 ng F/g]) compared to conventional rooms (2,330,000 ng F/g [<MDL−17,800,000 ng F/g]) (p = 0.53) (Figure 2 and Table 1).

DISCUSSION

In a novel intervention, buildings with reportedly "healthier" furniture and carpet had lower summarized levels of both known PFAS and organic fluorine in dust compared to buildings with conventional materials at a university. The "healthier" materials in this study were specified by manufacturers (in agreements with the university) to be free of the entire chemical class of PFAS. While our laboratory analysis quantified only up to 37 specific PFAS in the dust for comparison to EOF, our measurement of EOF acts as a novel proxy that may encompass the *total* fluorinated content of thousands of variants of PFAS that are often substituted for each other in products.[2,23] Thus, this study was able to demonstrate suggestive evidence that the rooms with "healthier" materials did have nearly half the mean dust levels of EOF (based on KM estimation), in addition to significantly lower levels of the small subset of widely known PFAS. Even without being able to intervene on building structural materials or the consumer products that people bring into buildings, the interior furnishing renovations were associated with lower PFAS contamination. The expected reduction in PFAS and EOF concentrations in dust in buildings with "healthier" carpet and furniture is supported by previous evidence of high levels of PFAS and fluorine on carpets and upholstery at a U.S. university campus.[27] Our study highlights the importance of employing chemical class-based analytical methods for the evaluation of chemical class-based "healthier" material solutions. Because of the prevalent and repeated substitution of less-known PFAS for well-known PFAS over time,[3] we must motivate long-term solutions that are shown to be effective at eliminating the whole PFAS class.

There were some nuances in the difference in reduction level between EOF and targeted PFAS for the conventional versus "healthier" rooms. The reduction in the total levels of targeted PFAS in dust had strong statistical significance while the reduction in EOF had suggestive evidence. This may be influenced by a combination of several possible reasons. First and perhaps most important, our small sample size for this analysis (n = 24) did limit the statistical power of our significance tests. Second, EOF measurements are well-established to have limitations of lower sensitivity (higher detection limits) compared to targeted PFAS analysis,[23] so statistical analyses have to make stronger assumptions when substituting nondetect EOF values. Third, it is possible that any other organic fluorinated chemicals captured by EOF (e.g., some refrigerants, pharmaceuticals, or pesticides),[38,39] even if at low levels and similar between conventional and "healthier" rooms, could slightly dilute the observable reductions in PFAS. Fourth, a large prevalence of unknown PFAS (which would be picked up by EOF but not targeted PFAS analysis) could be brought in from many other building material or product categories besides interior furniture and carpet.[6] The "healthier" rooms may have had slightly newer ages of other building materials that could not be intervened on and thus potentially more unknown, emerging PFAS substitutes used in those additional sources. The median year of building construction for the conventional rooms was 1965 [1925−2016] compared to 1972 [1966−2018] for "healthier" rooms. Fifth, the reported elimination of all PFAS, including unknown types, by manufacturers was not verified in these early (often custom-designed) "healthier" materials and may not have applied to trace concentrations of PFAS (e.g., <100 ppm) or unintentional contamination in the supply chain and production process. Nonetheless, these early "healthier" materials interventions on carpet and furniture did provide notable benefits for reducing content of these chemicals in buildings. Our results build scientific evidence for an expansion of chemical class-based solutions to more product categories that could further reduce PFAS contamination in buildings (e.g., structural building materials, flooring, sealants, adhesives, paints, coatings, electronics, glass, and pipes).[6] To grow the "healthier" materials movement, there needs to be sufficient guidance for manufacturers and capital project teams on a definition of PFAS that is clear and nonambiguous[40] and that ensures the elimination of PFAS variants that have not been formally identified yet.

The relatively low fraction (up to 9%) of extractable organic fluorine accounted for by 37 PFAS simultaneously measured in the dust indicates a potentially large contribution of other

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099

unidentified PFAS and demonstrates the importance of addressing PFAS as a class. The PFAS measured in this study did not include some known types of PFAS such as fluorotelomer alcohols (FTOHs) and polyfluoroalkyl phosphoric acid diesters (diPAPs), which are commonly found in indoor dust.[41,42] However, even if we estimate the potential fluorine contribution of these chemicals based on the geometric means of the commonly detected 8:2 and 10:2 FTOHs in dust from office buildings in Boston (most similar to our study)[43] and the median of the frequently detected 6:2 diPAP in dust from homes in North Carolina,[42] over half of the EOF levels in our study would still be left unaccounted for in all but two of our samples. Other non-PFAS types of organic fluorinated compounds (including refrigerants, pharmaceuticals, or pesticides)[38,39] could have been tracked into the buildings at low levels but are also unlikely to constitute a major proportion of EOF or to explain away the intervention results; any contamination would have been similar between the conventional and "healthier" rooms within the same university, and we did discern reductions in EOF with the "PFAS-free" materials intervention.

The low explained fraction of EOF aligns with most previous studies of fluorine in other types of samples. In one study, 44 measured PFAS (including diPAPs) accounted for up to only 0.3% of the EOF levels in nine samples of disposable food packaging.[22] In another study, 39 measured PFAS (including diPAPs) explained less than 1.3% of EOF in 28 of the cosmetics samples (up to 28% in three other samples with the highest levels).[25] To our knowledge, there is only one other online report (by an environmental institute) of EOF levels in indoor dust.[44] The authors found that 20 measured anionic PFAS (including FTOHs) explained between 10% and over 100% of the EOF levels measured in duplicates of the dust samples. However, in this study they compared recovery-corrected PFAS concentrations from the targeted analysis to nonrecovery-corrected (likely underestimated) EOF concentrations. Since different extraction and cleanup methodologies with internal standard addition were used for these two analyses (as the authors acknowledge), these PFAS and EOF results should not be directly compared.[44] This prior result is not comparable to the current study because we directly compared EOF and PFAS measurements using equivalent methods and because we measured orders of magnitude higher EOF and summed PFAS concentrations in building dust in our study (max EOF: 17,600 ng F/g; max PFAS: 1,750 ng/g) compared to their study (max EOF: 96 ng F/g; max PFAS: 79 ng/g).

A very low percent of total fluorine (less than 1%) was accounted for by extractable organic fluorine levels in our dust samples, suggesting that EOF is a more relevant proxy for total PFAS in dust matrices. Previous studies also observed low explained fractions of TF by EOF, although with consumer products. For example, EOF accounted for up to 5.5% of TF levels in disposable food packaging samples[22] and an average of 9% of TF levels in cosmetic samples.[25] The orders of magnitude difference between EOF and TF in our dust samples is likely influenced by inorganic fluoride from natural soil in the dust samples.[45] Because of the potentially large contribution to TF from inorganic fluoride, measurements of EOF in dust are more specific and useful as proxies for total PFAS content. Future studies should advance methods to directly measure levels of inorganic fluoride in indoor dust and other solid matrices to determine how much of the TF is explained by inorganic fluoride as opposed to unextractable PFAS or other fluorinated chemicals.[25] In any future research, the choice of methods should consider the sample matrix type (e.g., dust, water, soil, consumer products), which can have varying interference from inorganic fluoride or fluorinated pharmaceuticals/pesticides; the feasibility of sample treatment (e.g., nondestructive direct analysis versus extraction); the need for low limits of detection; the preference of either surface fluorine measurements or average full-sample measurements; and any need for high-throughput screening of many samples.[23,46] An ideal workflow recently described by Koch et al. (2020) suggests analysis of organic fluorine in samples followed by the measurement of targeted PFAS in at least a subset of samples; if unquantifiable/unknown organic fluorine is substantial, it can then be identified via other approaches (e.g., nontargeted analysis, suspect screening, or total oxidizable precursor [TOP] assays).[46]

There were several strengths of our study. This study, along with our previous publication about the same buildings, were the first to evaluate the benefits of a real-world intervention to reduce exposure to the concerning, ubiquitous group of PFAS at the source. Furthermore, our study focused on chemical class-based solutions that are intended to prevent common issues with regrettable substitution of one type of PFAS for another. In addition, to our knowledge this is the first research study of extractable organic fluorine in indoor dust samples, which represent real-world mixtures that are a major route of human exposure, and EOF measurements have the advantage over total fluorine measurements of excluding irrelevant contributions from inorganic fluoride. The pairing of EOF analysis with novel "healthier" materials interventions enabled us to quantify the potential reduction in PFAS as an entire class in dust due to "healthier" furniture choices. In addition, in comparing rooms that had similar characteristics except for the use of conventional versus "healthier" materials, any other non-PFAS organic fluorinated chemicals interfering with EOF levels in the dust would have been similar between the two room categories. In that way, we were able to pinpoint differences in EOF that were mostly driven by PFAS. Furthermore, because we collected multiple dust samples within different splits of each room, we were able to conduct several analyses on the dust samples, including TF, EOF, targeted PFAS (recovery-corrected), and nonrecovery-corrected PFAS for comparison to the fluorine measurements.

Limitations of this study included the small sample size (n = 24), especially for the subset analyzed for total fluorine (n = 14), which limited the statistical power of our analyses. The detection limits for EOF in the dust samples were relatively high, which is a well-established limitation across sample matrices due to the lower sensitivity compared to targeted analysis.[23] As a result, summary statistics based on EOF levels where nondetects were substituted with MDL $\div \sqrt{2}$ may have overestimated the levels in especially "healthier" rooms. Another limitation is the possibility that hair could have been captured in the dust extracts analyzed for EOF, but the EOF and the PFAS measured alongside EOF were still significantly correlated with the PFAS measured in our previous study in dust duplicates that had been sieved down to 150 μm to exclude hair and any other materials.[19] Furthermore, our targeted PFAS analytes did not include all common types of PFAS in indoor dust, such as diPAPs and FTOHs, as discussed previously. EOF measurements would serve as much simpler and more comprehensive proxies of

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099

total PFAS content than attempting to measure as many targeted PFAS as feasible. In terms of study design, we attempted to sample conventional rooms that were refurnished as recently as possible (with conventional materials), but they still had a slightly older median year of last refurnishing compared to "healthier" rooms. However, these spaces are all vacuumed very frequently by professional maintenance, so any old dust is minimized; before our sampling, we asked that rooms be left unvacuumed for 2−3 days to ensure there was sufficient recent dust buildup in all the sampled rooms. Finally, we could not analyze the "healthier" materials themselves to verify the absence of PFAS.

In conclusion, compared to university classrooms and common spaces with conventional materials, the equivalent rooms with "healthier" PFAS-free furniture and carpet had lower median dust concentrations of both known PFAS and extractable organic fluorine, which is a proxy that accounts for the total content of all known and unknown types of PFAS. Thus, the "healthier" materials solutions were beneficial for reducing the accumulation of PFAS inside buildings. The organic fluorine measurements demonstrated the importance of chemical class-based analytical methods for investigating the effectiveness of class-based materials solutions. Such "healthier" furniture and carpet materials free of all types of PFAS still need to become more widely available options (or preferably, defaults) and should provide fully disclosed, third-party-verified chemical ingredient lists from manufacturers. Furthermore, "healthier" alternatives need to be developed for other categories of products to further reduce PFAS exposure in buildings.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c05198.

Detailed description and tables of methods for analysis of 37 measured PFAS following the EOF extraction protocol (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Anna S. Young − *Harvard, T. H. Chan School of Public Health, Boston, Massachusetts 02115, United States;* orcid.org/0000-0002-6047-4406; Email: ayoung@mail.harvard.edu

Authors

Heidi M. Pickard − *Harvard, John A. Paulson School of Engineering and Applied Sciences, Boston, Massachusetts 02134, United States;* orcid.org/0000-0001-8312-7522

Elsie M. Sunderland − *Harvard, T. H. Chan School of Public Health, Boston, Massachusetts 02115, United States; Harvard, John A. Paulson School of Engineering and Applied Sciences, Boston, Massachusetts 02134, United States;* orcid.org/0000-0003-0386-9548

Joseph G. Allen − *Harvard, T. H. Chan School of Public Health, Boston, Massachusetts 02115, United States;* orcid.org/0000-0003-2702-5550

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.2c05198

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to thank Heather Henriksen for her support of this study. We would like to acknowledge Dr. Kannan Kurunthachalam and Dr. Hong Kai Zhu for their prior collaboration on the measurement of targeted chemicals in the dust samples. We also thank Dr. Aaron Specht for his help with dust analysis. This research was made possible by NIEHS Grant T32 ES007069, NIOSH Grant T42 OH008416, NIH Grant P30ES000002, and the Harvard Campus Sustainability Innovation Fund. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the funders.

■ REFERENCES

(1) Sunderland, E. M.; Hu, X. C.; Dassuncao, C.; Tokranov, A. K.; Wagner, C. C.; Allen, J. G. A Review of the Pathways of Human Exposure to Poly- and Perfluoroalkyl Substances (PFASs) and Present Understanding of Health Effects. *J. Expo. Sci. Environ. Epidemiol* **2018**, 131.

(2) US Environmental Protection Agency. *PFAS Master List of PFAS Substances*. https://comptox.epa.gov/dashboard/chemical-lists/pfasmaster (accessed 2022-05-25).

(3) Wang, Z.; Dewitt, J. C.; Higgins, C. P.; Cousins, I. T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environ. Sci. Technol.* **2017**, *51* (5), 2508−2518.

(4) Cousins, I. T.; DeWitt, J. C.; Glüge, J.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Scheringer, M.; Wang, Z. The High Persistence of PFAS Is Sufficient for Their Management as a Chemical Class. *Environ. Sci. Process. Impacts* **2020**, *22* (12), 2307−2312.

(5) Kwiatkowski, C. F.; Andrews, D. Q.; Birnbaum, L. S.; Bruton, T. A.; DeWitt, J. C.; Knappe, D. R. U.; Maffini, M. V.; Miller, M. F.; Pelch, K. E.; Reade, A.; Soehl, A.; Trier, X.; Venier, M.; Wagner, C. C.; Wang, Z.; Blum, A. Scientific Basis for Managing PFAS as a Chemical Class. *Environ. Sci. Technol. Lett.* **2020**, *7* (8), 532−543.

(6) Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. An Overview of the Uses of Per- and Polyfluoroalkyl Substances (PFAS). *Environ. Sci. Process. Impacts* **2020**, *22* (12), 2345−2373.

(7) Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaider, L. A.; Grandjean, P.; Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; Higgins, C. P.; Sunderland, E. M. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ. Sci. Technol. Lett.* **2016**, *3* (10), 344−350.

(8) Pickard, H. M.; Criscitiello, A. S.; Spencer, C.; Sharp, M. J.; Muir, D. C. G.; De Silva, A. O.; Young, C. J. Continuous Non-Marine Inputs of per- and Polyfluoroalkyl Substances to the High Arctic: A Multi-Decadal Temporal Record. *Atmos. Chem. Phys.* **2018**, *18* (7), 5045−5058.

(9) Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P. K. S.; Kannan, K. Perfluorinated Acids as Novel Chemical Tracers of Global Circulation of Ocean Waters. *Chemosphere* **2008**, *70* (7), 1247−1255.

(10) Giesy, J. P.; Kannan, K. Global Distribution of Perfluorooctane Sulfonate in Wildlife. *Environ. Sci. Technol.* **2001**, *35* (7), 1339−1342.

(11) Calafat, A. M.; Wong, L. Y.; Kuklenyik, Z.; Reidy, J. A.; Needham, L. L. Polyfluoroalkyl Chemicals in the U.S. Population: Data from the National Health and Nutrition Examination Survey (NHANES) 2003−2004 and Comparisons with NHANES 1999−2000. *Environ. Health Perspect* **2007**, *115* (11), 1596−1602.

(12) Fenton, S. E.; Ducatman, A.; Boobis, A.; DeWitt, J. C.; Lau, C.; Ng, C.; Smith, J. S.; Roberts, S. M. Per- and Polyfluoroalkyl Substance

Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environ. Toxicol. Chem.* **2021**, *40* (3), 606−630.
(13) Rappazzo, K. M.; Coffman, E.; Hines, E. P. Exposure to Perfluorinated Alkyl Substances and Health Outcomes in Children: A Systematic Review of the Epidemiologic Literature. *Int. J. Environ. Res. Public Health* **2017**, *14* (7), 691 DOI: 10.3390/ijerph14070691.
(14) Xiao, C.; Grandjean, P.; Valvi, D.; Nielsen, F.; Jensen, T. K.; Weihe, P.; Oulhote, Y. Associations of Exposure to Perfluoroalkyl Substances with Thyroid Hormone Concentrations and Birth Size. *J. Clin. Endocrinol. Metab* **2019**, 735 DOI: 10.1210/clinem/dgz147.
(15) Lin, P.-I. D.; Cardenas, A.; Hauser, R.; Gold, D. R.; Kleinman, K. P.; Hivert, M.-F.; Fleisch, A. F.; Calafat, A. M.; Webster, T. F.; Horton, E. S.; Oken, E. Per- and Polyfluoroalkyl Substances and Blood Lipid Levels in Pre-Diabetic Adults-Longitudinal Analysis of the Diabetes Prevention Program Outcomes Study. *Environ. Int.* **2019**, *129*, 343−353.
(16) Liew, Z.; Goudarzi, H.; Oulhote, Y. Developmental Exposures to Perfluoroalkyl Substances (PFASs): An Update of Associated Health Outcomes. *Curr. Environ. Heal. reports* **2018**, *5* (1), 1−19.
(17) Barry, V.; Winquist, A.; Steenland, K. Perfluorooctanoic Acid (PFOA) Exposures and Incident Cancers among Adults Living near a Chemical Plant. *Environ. Health Perspect* **2013**, *121* (11−12), 1313−1318.
(18) Stanifer, J. W.; Stapleton, H. M.; Souma, T.; Wittmer, A.; Zhao, X.; Boulware, L. E. Perfluorinated Chemicals as Emerging Environmental Threats to Kidney Health: A Scoping Review. *Clin. J. Am. Soc. Nephrol* **2018**, *13* (10), 1479−1492.
(19) Young, A. S.; Hauser, R.; James-Todd, T. M.; Coull, B. A.; Zhu, H.; Kannan, K.; Specht, A. J.; Bliss, M. S.; Allen, J. G. Impact of "Healthier" Materials Interventions on Dust Concentrations of per- and Polyfluoroalkyl Substances, Polybrominated Diphenyl Ethers, and Organophosphate Esters. *Environ. Int.* **2021**, *150*, 106151.
(20) Miyake, Y.; Yamashita, N.; So, M. K.; Rostkowski, P.; Taniyasu, S.; Lam, P. K. S.; Kannan, K. Trace Analysis of Total Fluorine in Human Blood Using Combustion Ion Chromatography for Fluorine: A Mass Balance Approach for the Determination of Known and Unknown Organofluorine Compounds. *J. Chromatogr. A* **2007**, *1154* (1−2), 214−221.
(21) Ritter, E. E.; Dickinson, M. E.; Harron, J. P.; Lunderberg, D. M.; DeYoung, P. A.; Robel, A. E.; Field, J. A.; Peaslee, G. F. PIGE as a Screening Tool for Per- and Polyfluorinated Substances in Papers and Textiles. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **2017**, *407*, 47−54.
(22) Schultes, L.; Peaslee, G. F.; Brockman, J. D.; Majumdar, A.; McGuinness, S. R.; Wilkinson, J. T.; Sandblom, O.; Ngwenyama, R. A.; Benskin, J. P. Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform? *Environ. Sci. Technol. Lett.* **2019**, *6* (2), 73−78.
(23) De Silva, A. O.; Armitage, J. M.; Bruton, T. A.; Dassuncao, C.; Heiger-Bernays, W.; Hu, X. C.; Kärrman, A.; Kelly, B.; Ng, C.; Robuck, A.; Sun, M.; Webster, T. F.; Sunderland, E. M. PFAS Exposure Pathways for Humans and Wildlife: A Synthesis of Current Knowledge and Key Gaps in Understanding. *Environ. Toxicol. Chem.* **2021**, *40* (3), 631−657.
(24) Robel, A. E.; Marshall, K.; Dickinson, M.; Lunderberg, D.; Butt, C.; Peaslee, G.; Stapleton, H. M.; Field, J. A. Closing the Mass Balance on Fluorine on Papers and Textiles. *Environ. Sci. Technol.* **2017**, *51* (16), 9022−9032.
(25) Schultes, L.; Vestergren, R.; Volkova, K.; Westberg, E.; Jacobson, T.; Benskin, J. P. Per- and Polyfluoroalkyl Substances and Fluorine Mass Balance in Cosmetic Products from the Swedish Market: Implications for Environmental Emissions and Human Exposure. *Environ. Sci. Process. Impacts* **2018**, *20* (12), 1680−1690.
(26) Peaslee, G. F.; Wilkinson, J. T.; McGuinness, S. R.; Tighe, M.; Caterisano, N.; Lee, S.; Gonzales, A.; Roddy, M.; Mills, S.; Mitchell, K. Another Pathway for Firefighter Exposure to Per- and Polyfluoroalkyl Substances: Firefighter Textiles. *Environ. Sci. Technol. Lett.* **2020**, *7* (8), 594−599.
(27) Tokranov, A. K.; Nishizawa, N.; Amadei, C. A.; Zenobio, J. E.; Pickard, H. M.; Allen, J. G.; Vecitis, C. D.; Sunderland, E. M. How Do We Measure Poly- and Perfluoroalkyl Substances (PFASs) at the Surface of Consumer Products? *Environ. Sci. Technol. Lett.* **2018**, *6*, 38 DOI: 10.1021/acs.estlett.8b00600.
(28) Poothong, S.; Papadopoulou, E.; Padilla-Sánchez, J. A.; Thomsen, C.; Haug, L. S. Multiple Pathways of Human Exposure to Poly- and Perfluoroalkyl Substances (PFASs): From External Exposure to Human Blood. *Environ. Int.* **2020**, *134*, 105244.
(29) Mitro, S. D.; Dodson, R. E.; Singla, V.; Adamkiewicz, G.; Elmi, A. F.; Tilly, M. K.; Zota, A. R. Consumer Product Chemicals in Indoor Dust: A Quantitative Meta-Analysis of U.S. Studies. *Environ. Sci. Technol.* **2016**, *50* (19), 10661−10672.
(30) Ruyle, B. J.; Pickard, H. M.; LeBlanc, D. R.; Tokranov, A. K.; Thackray, C. P.; Hu, X. C.; Vecitis, C. D.; Sunderland, E. M. Isolating the AFFF Signature in Coastal Watersheds Using Oxidizable PFAS Precursors and Unexplained Organofluorine. *Environ. Sci. Technol.* **2021**, *55* (6), 3686−3695.
(31) Young, A. S.; Sparer-Fine, E. H.; Pickard, H. M.; Sunderland, E. M.; Peaslee, G. F.; Allen, J. G. Per- and Polyfluoroalkyl Substances (PFAS) and Total Fluorine in Fire Station Dust. *J. Expo. Sci. Environ. Epidemiol* **2021**, 930 DOI: 10.1038/s41370-021-00288-7.
(32) Aro, R.; Carlsson, P.; Vogelsang, C.; Kärrman, A.; Yeung, L. W. Y. Fluorine Mass Balance Analysis of Selected Environmental Samples from Norway. *Chemosphere* **2021**, *283*, 131200.
(33) Yeung, L. W. Y.; Miyake, Y.; Li, P.; Taniyasu, S.; Kannan, K.; Guruge, K. S.; Lam, P. K. S.; Yamashita, N. Comparison of Total Fluorine, Extractable Organic Fluorine and Perfluorinated Compounds in the Blood of Wild and Pefluorooctanoate (PFOA)-Exposed Rats: Evidence for the Presence of Other Organofluorine Compounds. *Anal. Chim. Acta* **2009**, *635* (1), 108−114.
(34) Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M. K.; Taniyasu, S.; Lam, P. K. S.; Kannan, K. Determination of Trace Levels of Total Fluorine in Water Using Combustion Ion Chromatography for Fluorine: A Mass Balance Approach to Determine Individual Perfluorinated Chemicals in Water. *J. Chromatogr. A* **2007**, *1143* (1−2), 98−104.
(35) Weber, A. K.; Barber, L. B.; LeBlanc, D. R.; Sunderland, E. M.; Vecitis, C. D. Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts. *Environ. Sci. Technol.* **2017**, *51* (8), 4269−4279.
(36) Shoari, N.; Dubé, J.-S. Toward Improved Analysis of Concentration Data: Embracing Nondetects. *Environ. Toxicol. Chem.* **2018**, *37* (3), 643−656.
(37) Johnson, N.; Shelton, B. J.; Hopenhayn, C.; Tucker, T. T.; Unrine, J. M.; Huang, B.; Christian, W.; Zhang, Z.; Shi, X.; Li, L. Concentrations of Arsenic, Chromium, and Nickel in Toenail Samples from Appalachian Kentucky Residents. *J. Environ. Pathol. Toxicol. Oncol. Off. organ Int. Soc. Environ. Toxicol. Cancer* **2011**, *30* (3), 213−223.
(38) Ogawa, Y.; Tokunaga, E.; Kobayashi, O.; Hirai, K.; Shibata, N. Current Contributions of Organofluorine Compounds to the Agrochemical Industry. *iScience* **2020**, *23* (9), 101467.
(39) Sandford, G. Organofluorine Chemistry. *Philos. Trans. R. Soc. LONDON Ser. A-MATHEMATICAL Phys. Eng. Sci.* **2000**, *358* (1766), 455−471.
(40) Hammel, E.; Webster, T. F.; Gurney, R.; Heiger-Bernays, W. Implications of PFAS Definitions Using Fluorinated Pharmaceuticals. *iScience* **2022**, *25* (4), 104020.
(41) Eriksson, U.; Karrman, A. World-Wide Indoor Exposure to Polyfluoroalkyl Phosphate Esters (PAPs) and Other PFASs in Household Dust. *Environ. Sci. Technol.* **2015**, *49* (24), 14503−14511.
(42) Hall, S. M.; Patton, S.; Petreas, M.; Zhang, S.; Phillips, A. L.; Hoffman, K.; Stapleton, H. M. Per- and Polyfluoroalkyl Substances in Dust Collected from Residential Homes and Fire Stations in North America. *Environ. Sci. Technol.* **2020**, *54* (22), 14558−14567.
(43) Fraser, A. J.; Webster, T. F.; Watkins, D. J.; Strynar, M. J.; Kato, K.; Calafat, A. M.; Vieira, V. M.; McClean, M. D. Polyfluorinated Compounds in Dust from Homes, Offices, and Vehicles as Predictors

of Concentrations in Office Workers' Serum. *Environ. Int.* **2013**, *60*, 128−136.
(44) Bohlin-Nizzetto, P.; Hanssen, L.; Herzke, D.*PFASs in House Dust*; NILU − Norwegian Institute for Air Research, 2015.
(45) Jha, S. K.; Mishra, V. K.; Sharma, D. K.; Damodaran, T.; Whitacre, D. M. Fluoride in the Environment and Its Metabolism in Humans. *Reviews of Environmental Contamination and Toxicology* **2011**, *211*, 121−142, DOI: 10.1007/978-1-4419-8011-3_4.
(46) Koch, A.; Aro, R.; Wang, T.; Yeung, L. W. Y. Towards a Comprehensive Analytical Workflow for the Chemical Characterisation of Organofluorine in Consumer Products and Environmental Samples. *TrAC Trends Anal. Chem.* **2020**, *123*, 115423.

https://doi.org/10.1021/acs.est.2c05198
Environ. Sci. Technol. 2022, 56, 17090−17099