This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.

ACS AUTHORCHOICE

Environmental Science & Technology Letters

pubs.acs.org/journal/estlcu

Letter

Field Sampling Materials Unlikely Source of Contamination for Perfluoroalkyl and Polyfluoroalkyl Substances in Field Samples

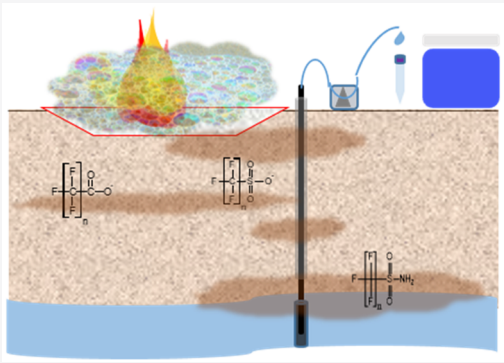
Alix E. Rodowa, Emerson Christie, Jane Sedlak, Graham F. Peaslee, Dorin Bogdan, Bill DiGuiseppi, and Jennifer A. Field*

Cite This: *Environ. Sci. Technol. Lett.* 2020, 7, 156−163

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: It is important that sample collection and shipping for monitoring perfluoroalkyl and polyfluoroalkyl substances (PFAS) in groundwater and soil do not contribute to PFAS concentrations in samples. Recommendations in state and federal PFAS sampling guidance documents are not supported by analytical data nor plausible pathways for exposure. Sixty-six materials were analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS) for 52 PFAS and total fluorine by particle-induced gamma-ray emission (PIGE) spectroscopy. Of the 22 materials with potential to come in direct contact with samples during sampling, none had quantifiable concentrations of routinely measured PFAS. Ten additional materials had quantifiable individual PFAS concentrations (<0.45−83 $\mu g/m^2$), and 15 had total fluorine (8000 to >11,000,000 μg F/m). However, no plausible pathways for contaminating samples were detected. Estimates of the quantity of PFAS-containing materials required to reach the EPA health advisory limit (70 ng/L) for a 1 L water sample demonstrates the implausibility of actually contaminating samples. Strict limitations placed on field materials without plausible contact with field samples are not supported, and future efforts should focus only on materials that come in direct contact with field samples and have a plausible pathway for impacting the concentrations of PFAS to levels of concern.



Downloaded via 207.241.229.48 on October 24, 2020 at 18:31:40 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

■ INTRODUCTION

The occurrence of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in drinking water[1] and toxicity evaluations resulted in the United States Environmental Protection Agency (EPA) drinking water lifetime health advisory level (HAL) of 70 ng/L (individual or combined concentrations) for perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA).[2] However, given that the EPA HAL concentrations are very low (ng/L), combined with the ubiquitous nature of PFAS, it is imperative to avoid creating artifacts (e.g., false positives) when collecting field samples, since detection of PFAS potentially has significant consequences for facility owners, the public, and other stakeholders. As a result, potential laboratory and instrumental contamination[3] and the impact of sample storage time and temperature on measured PFAS concentrations have received attention.[4]

Many materials associated with field sampling are listed as prohibited in PFAS sampling guidance documents published by federal and civilian organizations, including the U.S. Navy,[5] U.S. Army,[6] Australian organizations and entities including the Cooperative Research Center for Contamination Assessment and Remediation of the Environment (CRC CARE),[7] as well as private sector trade groups (e.g., the National Groundwater Association (NGWA)).[8] While avoiding materials composed of polytetrafluoroethylene (PTFE; e.g., Teflon) makes sense, because PTFE is manufactured with fluorinated polymerization aids, the rationale for many excluded materials in PFAS sampling guidance documents is not based on published data. Restricted materials including reusable ice packs, water-repellent field notebooks, indelible markers, sticky notes, and others increase the cost, time, and difficulty of sampling but with no documented benefit. There are no plausible scenarios for many of the prohibited materials to come in meaningful, direct contact with groundwater, sediment, or soil samples. It is likely that the extensive list of restrictive items listed in field sampling guidance is simply the result of information propagated from one PFAS sampling guidance document to another, without supporting analytical data.

Although there are numerous studies documenting concentrations of PFAS in consumer products (e.g., papers, textiles),[9−18] Denly et al.[19] was the first to quantify PFAS that leached into water over a 24 h period from materials including tubing, bailers, and water level tape measures, which come in direct contact with field samples. Materials also tested

Received: January 15, 2020
Revised: February 12, 2020
Accepted: February 19, 2020
Published: February 19, 2020

© 2020 American Chemical Society

https://dx.doi.org/10.1021/acs.estlett.0c00036
Environ. Sci. Technol. Lett. 2020, 7, 156−163

Table 1. Concentrations of Individual PFASs in $\mu g/m^2$ and PIGE Values in $\mu g\ F/m^2$ for Field Materials with Branched and Linear Values Separated When Applicable[a]

	Sample ID	Description	PFBA	PFHxA	PFHpA	PFOA	PFDA	PFPrS	PFBS	PFHxS	PFOS	6:2 FtS	8:2 FtS	PIGE
Group 1: Pre- staging	1	**Dryer sheet 1**	ND[d]	ND[d]	ND[d]	ND[d]	ND[d]	ND[d]	ND[d]	ND[d]	ND[d]	ND[d]	ND[d]	ND
	2	**Dryer sheet 2**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	3	**Dryer sheet3**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	4	First aid packaging (outer box)	ND	**6.0**	ND	ND	ND	ND	ND	ND	ND	ND	ND	120,000 ± 41,000
	5	First aid adhesive wrapper[b]	**0.88**	**0.68**	**0.22, 0.40**	**0.09, 3.9**	ND	ND	**1.1**	ND	**0.19, 0.32**	ND	ND	660,000 ± 83,000
Group 2: Staging	6	**PTFE tape 1**	ND	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	56,000,000 ± 11,000,000
	7	**PTFE tape 2**	ND	ND	ND	**4.4**	**<LOQ**	ND	ND	ND	**<LOQ**	ND	ND	##[c]
	8	**Aluminum foil 1 (nonstick)**	ND	ND	ND	**27**	ND	ND	**4.5**	ND	ND	ND	ND	<LOQ
	9	**Aluminum foil 2**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	10	**Aluminum foil 3**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11	Lab tissue 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	12	Lab tissue 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	13	Lab tissue 3	ND	ND	ND	ND	ND	ND	**1.7**	ND	ND	ND	ND	<LOQ
	14	Lab tissue 4	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	15	Lab tissue packaging	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	16	Label backing 1	ND	**<LOQ**	ND	ND	**<LOQ**	ND	ND	ND	ND	**2.7**	**5.7**	63,000 ± 13,000
	17	Label backing 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	18	Label 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	28,000 ± 5400
	19	Label 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	22,000 ± 5200
	20	**Paper towel adhesive**	ND	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	<LOQ
	21	**Paper towel 1**	ND	ND	ND	ND	ND	ND	ND	ND	**1.1, 3.8**	ND	ND	<LOQ
	22	**Paper towel 2**	ND	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	<LOQ
	23	**Paper towel 3**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	24	**Water-proof notepaper**	ND	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	16000 ± 3500
	25	**Lab notebook**	ND	**1.4**	**<LOQ**	**<LOQ**	ND	ND	ND	**<LOQ**	**2.2, 1.7**	ND	ND	57,000 ± 10,000
	26	**Adhesive notepad 1**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	27	**Adhesive notepad 2**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	28	**Binder plastic cover**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	29	Plastic shovel packaging	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	370,000 ± 45,000
Group 3: Sample Collection	30	Nitrile glove 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	31	Nitrile glove 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	32	Nitrile glove 3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	33	Nitrile glove 4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	34	Nitrile glove 5	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	ND
	35	Nitrile glove 6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	36	Nitrile glove 1 packaging	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	160,000 ± 33,000
	37	Nitrile glove 2 packaging	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	**<LOQ**	ND	ND	270,000 ± 95,000
	38	Putty caulk	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	39	Clear resin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

https://dx.doi.org/10.1021/acs.estlett.0c00036
Environ. Sci. Technol. Lett. 2020, 7, 156−163

Table 1. continued

	Sample ID	Description	PFBA	PFHxA	PFHpA	PFOA	PFDA	PFPrS	PFBS	PFHxS	PFOS	6:2 FtS	8:2 FtS	PIGE
	40	White glue	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	41	PVC liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10,000 ± 3300
	42	PVC liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10,000 ± 2900
	43	Core catcher	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16,000 ± 4100
	44	Vinyl end-caps	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16,000 ± 3800
	45	Core catcher liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10,000 ± 3100
	46	PVC liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16,000 ± 4200
	47	PVC screen	ND	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	28,000 ± 6200
	48	Polyethylene bladder	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	49	Core bag	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	50	**MIP Membrane**	ND	ND	ND	**<LOQ**	ND	ND	**<LOQ**	ND	ND	ND	ND	##[c]
	51	PVC liner	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	ND	ND	ND
Group 4: Shipping	52	Elastic sealing film	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	53	**Marker ink 1 (permanent)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	54	**Marker ink 2 (permanent)**	ND	ND	ND	**83**	ND	ND	ND	ND	ND	ND	ND	16,000 ± 5700
	55	**Marker ink 3 (permanent)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	56	Plastic bag 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	57	Plastic bag 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	58	Tape 1 (electrical)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10,000 ± 3300
	59	Tape 2 (duct)	ND	ND	ND	ND	ND	ND	**0.77**	ND	ND	ND	ND	ND
	60	Tape 3 (duct)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	61	Tape 4 (duct)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	62	**Cold pack 1 (outside)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	250,000 ± 33,000
	63	**Cold pack 2 (outside)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	64	**Cold pack 3 (outside)**	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	87,000 ± 13,000
	65	**Cold pack 4 (outside)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	66	**Cold pack 5 (outside)**	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	ND	81,000 ± 12,000
		LOQ	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	8000

[a]One number indicates all linear, or for PFBA, PFPeA, and PFBS a lack of analytical separation between branched/linear. Bolded field materials are listed on a field sampling guidance document.[5,6,22,24] Only the 12 PFASs that were detected greater than the limit of quantification (LOQ) out of the 52 individual PFASs analyzed appear in this table; for a full list of PFASs see the SI. [b]Material density is lower than the average material density used to calculate the LOQ; thus, the LOQ for this material is 0.22 $\mu g/m^2$. [c]##: Concentration of F was too high to measure by PIGE. [d]ND = Below the limit of detection. <LOQ = below the limit of quantification.

https://dx.doi.org/10.1021/acs.estlett.0c00036
Environ. Sci. Technol. Lett. 2020, 7, 156−163

(e.g., food packaging, bubble wrap, plastic bags, sample labels, and field notebook parts) are unlikely to have direct contact with water or soil samples. However, for the latter set of materials, leaching for 24 h is not an environmentally relevant model for determining the likelihood to contaminated field samples. As is the case when assessing the potential for human exposure to a contaminant, a pathway must exist for the contaminant (PFAS on materials at a field site) to reach and impact the receptor (field sample) in order to conclude that the source can actually contribute to measured concentrations (e.g., cross contamination).

In this study, 66 materials associated with field sampling were collected between 2016 and 2019 and analyzed for 52 individual PFAS observed in aqueous film-forming foam (AFFF)-impacted groundwater by liquid chromatography tandem mass spectrometry (LC-MS/MS)[10] and for total fluorine by particle-induced gamma-ray emission (PIGE) spectroscopy.[17] The materials tested include those representative of materials used by field personnel prior to arriving at a field site (Group 1), in the field during sampling or for staging a sampling event (Group 2), in the field for sample collection (Group 3), and in the field for shipping (Group 4). Materials were analyzed by PIGE without sample preparationn and extracted with methanol to obtain concentrations of individual PFAS by LC-MS/MS. The PFAS concentrations on materials were used to determine the area or length of a material necessary to achieve defined concentrations (method quantification limit and EPA HAL) to determine the likelihood that a material poses a realistic exposure scenario for contaminating water samples.

MATERIALS AND METHODS

Field Materials Selection, Extraction, and Analysis. Field sampling and related materials were selected as samples of convenience based upon the authors' knowledge of materials commonly used during field sampling campaigns. A total of 66 materials were collected by Oregon State University and the University of Notre Dame between 2016 and 2019 (Table 1, Table S1). During all sample handling, nitrile gloves were worn and changed between all samples. Swatches or larger sections of each material were cut from the original material using methanol-rinsed scissors and distributed into resealable PFAS-free plastic bags. For dense plastic materials (e.g., PVC screens and liners, membrane interface probe (MIP)); Sample IDs: 41−48, 50, 51), stainless steel cutters were used and methanol-rinsed between materials. For dense plastics, surface area was used as the basis for sample preparation and required to fall between 4.0 ± 0.5 cm^2. The mass range for all other materials was 0.3 ± 0.25 g, which accounted for a wide range of densities (e.g., aluminum foil, sealants, inks).[3] However, all materials were required to be entirely submerged in methanol during extraction. For permanent ink from markers, a piece of copy paper known to be nondetect (PFAS-free) for all PFAS was saturated with ink until the paper weighed an additional 0.3 ± 0.25 g. For the three sealants, a mass of 0.3 ± 0.25 g was weighed onto a piece of PFAS-free copy paper and allowed to dry before extraction.

All materials were extracted as in Robel et al. with slight modifications depending on material density (see Supporting Information).[10] Briefly, three rounds of heated methanol (60−65 °C, 10 min each) were used to extract a 0.3 ± 0.25 g swatch of each material (for methods on weighing different type of material, please see the SI). An n = 4 replicate, including at least one material from each Group 1−4, was included in every set of 10−15 samples, or 6 out of 66 samples (10%). Instrumental limits of quantification (LOQs) were set as the lowest calibration standard, 0.45 $\mu g/m^2$ for all analytes except for perfluorooctane sulfonamide (FOSA), which was 2.2 $\mu g/m^2$, unless otherwise specified. The instrumental limit of detection (ND) was set as 3 times less than the LOQ (0.15 $\mu g/m^2$ for all analytes) except for FOSA, which was 0.75 $\mu g/m^2$. Details on the LC-MS/MS operation and data quality assignments can be found in Robel et al.[10] and in the SI. Total fluorine measurements by PIGE were performed as previously described (see SI for more information) and with an LOQ of 8000 μg F/m^2.

RESULTS AND DISCUSSION

PFAS Composition and Concentration. Although the analytical method had the potential to quantify 52 PFAS (Table S1), only 12 PFAS were observed at concentrations greater than or equal to LOQ (Table 1). Overall, 11 out of 66 (17%) materials gave quantifiable (>LOQ) concentrations of individual PFAS by LC-MS/MS, while 23 (15%) had total fluorine greater than LOQ (Table 1). The higher frequency of total fluorine on materials is likely a result of the presence of fluorinated polymers on materials, which are not extracted by methanol and cannot be analyzed by LC-MS/MS[10,20,21] or additional individual PFAS not in the 52 PFAS analyte list.[10,21] Nontarget analysis by LC-high resolution mass spectrometry could potentially reveal other PFAS present in field sampling materials but was outside of the scope of this study.

Of the 11 materials with individual PFAS, only five gave quantifiable levels of total fluorine (≤ 8000 μg F/m^2) by PIGE, while six were ND or < LOQ (Table 1). The PIGE limit of quantification (8000 μg F/m^2) is equivalent to 11,600 $\mu g/m^2$ PFOA or 12,400 $\mu g/m^2$ PFOS, which is significantly higher than the LOQ for individual PFAS by LC-MS/MS (0.15 $\mu g/m^2$). Thus, materials can have concentrations of individual PFAS that are too low for detection by PIGE. Although PIGE requires no sample preparation and is less expensive, total fluorine by PIGE is not a surrogate for individual PFASs and is less sensitive than LC-MS/MS. Total fluorine measurements on papers and textiles were not significantly reduced after extraction with methanol;[10] thus, it is unlikely that total fluorine would be significantly transferred to water (e.g., leaching). More research is needed to understand the potential significance of total fluorine associated with the field materials tested in this study.

Group 1: Pre-staging. Group 1 is composed of five materials that are potentially used by field personnel prior to arriving at a field site but that do not come in direct contact with samples. The dryer sheets were of specific interest since PFAS sampling guidance documents indicate that no personal care products, including dryer sheets should be used by field personnel.[5−7,22−24] The three dryer sheets were ND for individual PFAS and total fluorine. The packaging of the first-aid bandage gave quantifiable perfluorohexanoic acid (PFHxA) and total fluorine (Table 1). In contrast, the wrapper around the first-aid bandage gave the greatest number (six) of PFAS. Four perfluoroalkyl carboxylates (PFCAs) including perfluorobutanoic acid (PFBA), PFHxA, perfluoroheptanoic acid (PFHpA), and PFOA were present as a homologous series with branched and linear isomers evident for PFHpA and PFOA (Table 1), which indicates manufacture by electrochemical fluorination (ECF).[25] In addition, PFBS and

https://dx.doi.org/10.1021/acs.estlett.0c00036
Environ. Sci. Technol. Lett. 2020, 7, 156−163

Table 2. Group Category, Material, Summed Concentration of PFOA and PFOS[a] for Materials with Detectable Levels of PFOA/PFOS and Area (cm^2) of Materials Needed to Reach the LC-MS/MS Limit of Quantification (10 ng/L) and EPA HAL (70 ng/L) in a 1 L Water Sample, Assuming All PFAS Mass Released into Water

Group No.	Material	PFOA + PFOS (ng/cm^2)	Material area to achieve 70 ng/L in (cm^2)	Material area to achieve 10 ng/L (cm^2)
1: Pre-staging	First aid adhesive wrapper	0.45	160 (4.7 wrappers[b])	22 (0.7 wrappers)
2: Staging	PTFE tape 2	0.44	160 (130 cm)	23 (19 cm)
2: Staging	Aluminum foil	2.7	26	3.7
2: Staging	Paper towel 1	0.49	140	20
2: Staging	Lab notebook cover	0.39	180	26
4: Shipping	Resusable ice pack	0.023[d]	3000 (6.7 ice packs)	430 (1.0 ice packs)

[a]US EPA HAL sums the concentration (not the molar mass) of PFOA and PFOS. [b]First aid wrapper (2.5 cm × 6.5 cm × 2 sides = 33 cm^2). [c]¥ PFTE tape 1.2 cm wide × 1 cm = 1.2 cm^2; 8.5 in. × 11 in. paper is 30 cm × 21.5 cm = 645 cm^2. [d]A concentration equivalent to one-half of the LOQ (0.23 $\mu g/m^2$ or 0.023 ng/cm^2) and the dimensions of a cold pack (15 cm × 15 cm × 2 cm or 450 cm^2) give 13 ng/ice pack. [e]Area estimation: 70 ng/L (EPA HAL) × 1 L × cm^2/# μg = cm^2 (area) or 10 ng/L × 1 L × cm^2/# μg = cm^2 (area), where # is obtained from Table 1.

branched and linear PFOS were observed, again consistent with ECF chemistry. The first-aid bandage packaging also gave measurable 660,000 μg F/m^2 total fluorine by PIGE, which is equivalent to 960,000 μg PFOA/m^2 or 1,000,000 μg PFOS/m^2.

To estimate worst-case scenarios, the summed concentration of PFOA and PFOS on the first-aid adhesive wrapper (Table 1) was used to estimate the area of wrapper needed and its associated PFOA and/or PFOS to reach the EPA HAL (70 ng/L) and the LOQ for individual PFAS by LC-MS/MS (10 ng/L) (Table 2). Nearly five first-aid bandage wrappers would be needed in 1 L of water to reach the EPA HAL of 70 ng/L (Table 2), assuming 100% transfer of the PFAS mass on the wrappers into the water sample (Table 1).

Group 2: Staging. Group 2 is composed of 24 materials that are used in the field when staging a sampling event (prior to sampling) and, thus, do not come in direct contact with samples. Materials in this group included polytetrafluoroethylene (PTFE) tape, aluminum foil, labels, various papers, adhesive note pads, and plastic shovel packaging. Sorbent materials taken into the field including lab tissues and paper towels were also evaluated. Note that the PTFE tape, which is commonly used to seal fittings on pumps or flow-through cells for water quality monitoring, when used properly would only be applied to the threads of the pipe joints, which are not in direct or prolonged contact with the flowing water. Six materials in Group 2 gave concentrations greater than LOQ for PFAS, while eight gave total fluorine greater than LOQ (Table 1).

PTFE tape 1 had very high total fluorine but no individual PFAS greater than LOQ. PTFE tape 2 gave total fluorine above the calibration range but gave measurable concentrations of PFOA greater than LOQ (4.4 $\mu g/m^2$) and was less than LOQ for perfluorodecanoic acid (PFDA) and PFOS (Table 1). Denly et al. also reported PTFE-based materials as positive for PFCAs when leached for 24 h.[19] Only the nonstick aluminum foil had detectable PFAS (e.g., 27 μg PFOA/m^2 and 4.5 μg PFBS/m^2), while all three aluminum foils were either ND or less than LOQ for total fluorine, which indicates that the PFAS concentration was too low to be quantified by PIGE. Both aluminum foil and PTFE tape can potentially be used during staging, but it would require the unlikely scenario of 23−160 cm of PTFE tape 2 or 3.7−26 cm^2 aluminum foil to completely desorb inside a 1 L water sample bottle to attain the EPA HAL for PFOS/PFOA (70 ng/L) or the LOQ for individual PFAS (10 ng/L) (Table 2).

Of the five lab tissues and packaging tested, only tissue 3 gave an individual PFAS concentration above the LOQ (1.7 $\mu g/m^2$ PFBS), and all were either ND or less than LOQ for total fluorine (Table 1). Denly et al. reported sample labels as positive for PFCAs and perfluoroalkyl sulfonates (PFSAs) in their leaching study.[19] One label backing, which is a portion of the nonstick sheet beneath the label, had the only 6:2 and 8:2 fluorotelomer sulfonates (6:2 and 8:2 FTSs) detected in this study (Table 1). In contrast, three of the four label materials were greater than LOQ for total fluorine by PIGE (Table 1). FTSs were not evaluated by Denley et al.[19] even though they occur in AFFF-impacted groundwater[26−31] and on papers and textiles.[9,10,14,32,33]

One of three paper towel materials had quantifiable PFOS only (4.9 $\mu g/m^2$; paper towel 1) and all were ND or less than LOQ for total fluorine (Table 1). All three of these paper towels were labeled as having "recycled content", which may have contributed to the PFOS in paper towel 1.[10,20] Paper towels, specifically listed as containing recycled content or that are chemically treated are listed as prohibited on one guidance document.[22] The area of paper towel required to achieve the EPA HAL of 70 ng/L is 140 cm^2 (e.g., 12 cm × 12 cm) and 20 cm^2 (4.5 cm × 4.5 cm) to achieve the individual PFAS LOQ (10 ng/L) by LC-MS/MS (Table 2). The PFOS concentrations could only be achieved if the respective areas of paper towel 1 (Table 1) completely desorbed all of the PFOS mass present into a 1 L water sample (Table 2).

Waterproof notepaper was ND or less than LOQ for PFAS, and a sheet of bound lab notebook paper had quantifiable concentrations of PFHxA (1.4 $\mu g/m^2$) and PFOS (3.8 $\mu g/m^2$). Yet both had quantifiable total fluorine by PIGE (Table 1). A field book cover and pages yielded PFBA and other PFAS above the detection limit (2 ng/L) in the Denly et al. 24 h leaching study.[19] In the case of lab notebook paper, it would take 180 and 26 cm^2 to reach the EPA HAL and individual PFAS LOQ, respectively (Table 2).

Of the remaining materials in Group 2, adhesive notepads were ND for PFAS and either ND or less than LOQ for total fluorine (Table 1). The plastic shovel packaging material was ND for PFAS but gave the highest measured concentration of total fluorine by PIGE in Group 2 (370,000 μg F/m^2) and the third highest of any material, second only to the PTFE tapes (Table 1). No estimation was performed to determine the plausibility of sample shovel packaging impacting the PFAS results of a soil sample given the lack of direct contact between that packaging and the soil to be sampled.

https://dx.doi.org/10.1021/acs.estlett.0c00036
Environ. Sci. Technol. Lett. 2020, 7, 156−163

Group 3: Sampling. Group 3 materials are used in the field and come in *direct contact* with groundwater or soil/sediment when sampling. Materials in Group 3 included nitrile gloves (and glove packaging), sealants used in well development, and soil sampling materials. Of the 22 materials tested, none had conventionally measured PFCAs or PFSAs, and only nitrile glove 6 had a quantifiable (5 $\mu g/m^2$) concentration of N-trimethylammoniopropyl perfluoropentane sulfonamide (N-TAmP-FPeSA). Denly et al. reported PFBA and PFHxS near the detection limit (2 ng/L) upon 24 h of leaching a pair of nitrile gloves in water. Because N-TAmP-FPeSA is present in both branched and linear forms, it derives from ECF chemistry. Evidence for N-TAmP-FPeSA in nitrile gloves indicates that it may be a chemical in commerce and could occur in other consumer products. While N-TAmP-FPePA has been observed in AFFF-impacted groundwater,[28] to the best of the authors' knowledge, this is the first report of N-TAmP-FPePA in a consumer product.

In contrast, 10 of the 22 materials in Group 3 had total fluorine greater than LOQ, and eight materials associated with soil and sediment sampling were positive for total fluorine. The MIP membrane, which is constructed of PTFE material, gave total fluorine that was above the calibration range (Table 1) but no quantifiable individual PFAS (Table 1). Of the materials included in Group 3, only the MIP is a prohibited material in PFAS sampling guidance documents.[4,7−9,24,25] However, none of the materials in Group 3 have concentrations for the commonly measured PFAS that are greater than LOQ. Thus, while the materials potentially come in direct contact with field samples, they are unlikely to impact measured PFAS concentrations in field samples. Additionally, a MIP is a field screening instrument that measures only volatile organic compounds that pass the gas-permeable membrane, as opposed to collecting a soil sample in contact with the membrane.

Group 4: Transport. Group 4 materials are used in the field and are externally applied to or surround sample containers and include elastic sealing film, permanent marker ink, plastic bags, various tapes, and reusable cold packs. Of the 15 materials tested, only two gave quantitative concentrations of PFAS (83 $\mu g/m^2$ PFOA in marker ink 2 and 0.77 $\mu g/m^2$ PFBS in duct tape 2; Table 1), while five materials gave quantitative concentrations of total fluorine (Table 1).

All five cold packs were either ND or less than LOQ for PFAS even though they are listed as prohibited items in PFAS sampling guidance documents.[4,7,8,24] As an exercise, a concentration equivalent to one-half of the LOQ (0.23 $\mu g/m^2$) for a cold pack (15 cm × 15 cm × 2 cm or 0.045 m^2), which was actually ND for PFOS and PFOA (Table 1), was used to estimate the number of cold packs that would have to completely desorb *inside* a 1 L sample bottle to reach the EPA HAL and the LOQ for individual PFAS. A total of 6.7 ice packs would be needed to reach the EPA HAL, and 1.0 ice packs would be needed to reach a water concentration of 10 ng/L (Table 2) if PFOA was present at one-half the LOQ. Based on this estimation, reusable cold packs (Group 4) cannot plausibly be a source of water sample contamination. Prohibition of convenient, reusable, and "green" ice packs should be reconsidered and used as alternatives to the use of nonreusable plastic bags with ice. Coolers for shipping samples were not evaluated because if ice packs are used to ship samples in coolers, there is no transfer medium (e.g., water) present. Moreover, samples in coolers are known to leak, but PFAS sampling guidance documents indicate that sample containers should be shipped in secondary containment (e.g., plastic bag) before being placed in coolers.[4,7,8,24]

Evaluation of PFAS Contamination. This study evaluated the possibility of false positive analytical results stemming from cross-contamination due to the use of PFAS-containing materials used in relation to sampling efforts at the LOQ (10 ng/L) and the U.S. EPA health advisory limit (70 ng/L). Although these values were arbitrarily selected to put the PFAS concentrations into context, lower regulatory limits (e.g., state limits) exist. However, a key evaluation criterion for this assessment was whether materials used before, during, or after sampling come into direct contact with the sampled media (e.g., water, soil). While some of the materials resulted in detectable levels of individual PFAS or total fluorine, many of these positive materials do not come into contact with the sample. Additional analysis is warranted for materials used during sampling and that come in direct contact with samples (Group 3) including bladders, bailers, passive sampling sleeves, and well construction materials. Additionally, the analysis of field sampling materials is not a substitute for equipment blanks, which are a useful tool for verifying that sample materials or the combination of materials used in the field have not impacted samples. Implementation of generally accepted sampling procedures and a common standard of care during sampling activities will avoid any contact between PFAS-containing materials and the environmental samples. Industry-standard sampling practices are well established for the purpose of preventing extraneous contaminants from entering sample containers. Use of these standard practices should prevent sample interferences from PFAS, just as they have for other potential contaminants over the past 40 years of environmental practice. Avoidance of materials that are known to contain PFAS (e.g., PTFE) is still advised; however, the actual risk of increasing the PFAS concentration of field samples is very low.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.0c00036.

Information about material selection and origins and instrumental analysis for LC-MS/MS and PIGE (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jennifer A. Field − *Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, United States;* orcid.org/0000-0002-9346-4693; Email: jennifer.field@oregonstate.edu

Authors

Alix E. Rodowa − *Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, United States;* orcid.org/0000-0002-2650-0981

Emerson Christie − *Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon 97331, United States*

Jane Sedlak − *Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States*

Graham F. Peaslee − *Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States;* orcid.org/0000-0001-6311-648X

Dorin Bogdan − *AECOM, Grand Rapids, Michigan 49546, United States*

Bill DiGuiseppi − *Jacobs, Denver, Colorado 80112, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.estlett.0c00036

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was made possible through support of the U.S. Navy (ESTCP ER-201633) and SERDP (ER19-1205) and the CH2MHill/Jacobs Innovation Grant Program.

■ REFERENCES

(1) Hu, X. D. 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 US Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ. Sci. Technol. Lett.* **2016**, *3*, 344−350.

(2) *Drinking Water Health Advisories for PFOA and PFOS*, 2017. U.S. EPA Office of Water. https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos (accessed Feb 10, 2020).

(3) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Okazawa, T.; Petrick, G.; Gamo, T. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. *Environ. Sci. Technol.* **2004**, *38*, 5522−5528.

(4) Woudneh, M. B.; Chandramouli, B.; Hamilton, C.; Grace, R. Effect of Sample Storage on the Quantitative Determination of 29 PFAS: Observation of Analyte Interconversions during Storage. *Environ. Sci. Technol.* **2019**, *53*, 12576−12585.

(5) *Interim Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) Site Guidance for NAVFAC Remedial Project Managers (RPMs)/Septmber 2017 Update*; U.S. Department of Defense, Department of the Navy, 2017.

(6) *Army Guidance for Addressing Releases of Per- and Polyfluoroalkyl Substances*; U.S. Department of Defense, Department of the Army, 2018.

(7) *Assessment, management and remediation for PFOS and PFOA Part 4: Application of HSLs and ESLs*; Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, 2017. https://www.crccare.com/publications/technical-reports (accessed Feb 10, 2020).

(8) *Groundwater and PFAS: State of Knowledge and Practice*, 2019. NGWA The Groundwater Association Press. https://www.ngwa.org/what-is-groundwater/groundwater-issues/Groundwater-and-PFAS (accessed Feb 2020).

(9) Herzke, D.; Olsson, E.; Posner, S. Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway − A pilot study. *Chemosphere* **2012**, *88*, 980−987.

(10) 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*, 9022−9032.

(11) 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.* **2019**, *6*, 38−43.

(12) Vestergren, R.; Herzke, D.; Wang, T.; Cousins, I. T. Are imported consumer products an important diffuse source of PFASs to the Norwegian environment? *Environ. Pollut.* **2015**, *198*, 223−230.

(13) Ye, F.; Zushi, Y.; Masunaga, S. Survey of perfluoroalkyl (PFAAs) and their precursors present in Japanese consumer products. *Chemosphere* **2015**, *127*, 262−268.

(14) Favreau, P.; Poncioni-Rothlisberger, C.; Place, B. J.; Bouchex-Bellomie, H.; Weber, A.; Tremp, J.; Field, J. A.; Kohler, M. Multianalyte profiling of per- and polyfluoroalkyl substances (PFASs) in liquid commercial products. *Chemosphere* **2017**, *171*, 491−501.

(15) Rewerts, J. N.; Morre, J. T.; Massey Simonich, S. L.; Field, J. A. In-Vial Extraction Large Volume Gas Chromatography Mass Spectrometry for Analysis of Volatile PFASs on Papers and Textiles. *Environ. Sci. Technol.* **2018**, *52*, 10609−10616.

(16) van der Veen, I.; Weiss, J. M.; Hanning, A. C.; de Boer, J.; Leonards, P. E. G. Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles. *Talanta* **2016**, *147*, 8−15.

(17) 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. Instrum. Methods Phys. Res., Sect. B* **2017**, *407*, 47−54.

(18) Schaider, L. A.; Balan, S. A.; Blum, A.; Andrews, D. Q.; Strynar, M. J.; Dickinson, M. E.; Lunderberg, D. M.; Lang, J. R.; Peaslee, G. F. Fluorinated Compounds in US Fast Food Packaging. *Environ. Sci. Technol. Lett.* **2017**, *4*, 105−111.

(19) Denly, L.; Occhialini, J.; Bassignani, P.; Eberle, M.; Rabah, N. Per- and polyfluoroalkyl substances in environmental sampling products: Fact or fiction? *Remediation The Journal of Environmental Cleanup Costs, Technologies, & Techniques* **2019**, *29*, 65−76.

(20) Kissa, E. *Fluorinated Surfactants and Repellants*, Second ed.; Marcel Dekker, Inc.: New York, 2001.

(21) 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*, 73−78.

(22) *For Homeowners - Private Residential Well PFAS Sampling Guidance*, 2018. Michigan Department of Environmental Quality. https://www.michigan.gov/documents/pfasresponse/Residential_Well_PFAS_Sampling_Guidance_For_Homeowners_637294_7.pdf (accessed Feb 10, 2020).

(23) Sampling for Per- and Polyfluoroakyl Substances/Perfluorinated Chemicals (PFASs/PFCs) at Contaminated Sites, 2016. New Hampshire Department of Environmental Services. https://www.des.nh.gov/organization/commissioner/pfas.htm (accessed Feb 10, 2020).

(24) Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS), 2019. California Water Boards State Water Resources Control Board. https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/PFOA_PFOS.html (accessed Feb 2020).

(25) *The Science of Organic Fluorochemistry*, 1999. 3M. http://www.fluoridealert.org/wp-content/pesticides/pfos.fr.final.docket.0006.pdf (accessed Feb 10, 2020).

(26) Backe, W. J.; Day, T. C.; Field, J. A. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from us military bases by nonaqueous large-volume injection HPLC-MS/MS. *Environ. Sci. Technol.* **2013**, *47*, 5226−5234.

(27) Baduel, C.; Mueller, J. F.; Rotander, A.; Corfield, J.; Gomez-Ramos, M. J. Discovery of novel per- and polyfluoroalkyl substances (PFASs) at a fire fighting training ground and preliminary investigation of their fate and mobility. *Chemosphere* **2017**, *185*, 1030−1038.

(28) Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; McCrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A. Discovery of 40 Classes of Per- and Polyfluoroalkyl

Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater. *Environ. Sci. Technol.* **2017**, *51*, 2047−2057.

(29) Filipovic, M.; Woldegiorgis, A.; Norstrom, K.; Bibi, M.; Lindberg, M.; Osteras, A. H. Historical usage of aqueous film forming foam: A case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish. *Chemosphere* **2015**, *129*, 39−45.

(30) Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environ. Sci. Technol.* **2013**, *47*, 8187−8195.

(31) Place, B. J.; Field, J. A. Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. *Environ. Sci. Technol.* **2012**, *46*, 7120−7127.

(32) 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-Proc. Imp.* **2018**, *20*, 1680−1690.

(33) Herzke, D.; Huber, S.; Bervoets, L.; D'Hollander, W.; Hajslova, J.; Pulkrabova, J.; Brambilla, G.; De Filippis, S. P.; Klenow, S.; Heinemeyer, G.; de Voogt, P. Perfluorinated alkylated substances in vegetables collected in four European countries; occurrence and human exposure estimations. *Environ. Sci. Pollut. Res.* **2013**, *20*, 7930−7939.

https://dx.doi.org/10.1021/acs.estlett.0c00036
Environ. Sci. Technol. Lett. 2020, 7, 156−163