Wolverine Worldwide Product Testing Report: PFAS Chemicals in Shoes

In this investigation, we tested six pairs of shoes and one weather-protector spray sold by Wolverine Worldwide for total fluorine and for specific fluorinated stain and water repellent chemicals (PFASs). Total fluorine was measured by Dr. Graham Peaslee at the University of Notre Dame using Particle Induced Gamma-ray Emission (PIGE) spectroscopy. Details of the PIGE method can be found in Schaider, L.A. et al., Environ Sci Technol Lett. 4(3): 105–111 (2017). We used PIGE as a screening technique to identify samples with high levels of fluorine indicating the likely use of PFAS-containing repellents.

Samples that tested positive for fluorine were subjected to further analysis by Dr. Marta Venier at Indiana University to identify specific PFAS compounds. This was done by solvent extraction of the samples, followed by quantitative analysis using gas chromatography with mass spectrometry (GC/MS) or liquid chromatography with tandem mass spectrometry (LC/MS/MS). Dr. Venier's technique measured 43 different PFAS compounds (listed in Appendix 1), including long-chain and short-chain perfluorocarboxylates, perfluorosulfonates, and fluorotelomer-based PFAS. The technique does not, however, identify fluoropolymers likely present in shoes treated with PFAS. For that reason, as well as because PFAS compounds not included in the target list could be present, total fluorine measured by PIGE is expected to be higher than the total PFAS concentration measured by the mass spectrometric techniques.

RESULTS

Four of the six pairs of shoes contained levels of total fluorine that suggested they had been treated with PFAS. Total fluorine concentrations in the shoes that tested positive ranged between 379 and 1,219 ppm, as measured by PIGE. The long-chain fluorotelomer-based compounds 8:2 fluorotelomer alcohol (8:2 FTOH) and 10:2 fluorotelomer alcohol (10:2 FTOH) were the predominant PFAS identified in these samples by GC/MS and LC/MS/MS testing. These two chemicals made up 93-100% of the PFAS in three pairs of shoes, while a fourth pair had a lower proportion of long-chain PFAS (59%) because it contained the short-chain compound 6:2 fluorotelomer alcohol (6:2 FTOH).

The weather-protector spray contained a high concentration of total fluorine and PFAS. PIGE analysis found 14,044 ppm total fluorine in the liquid spray. Results from the GC/MS and LC/MS/MS testing showed that the spray in liquid form contained more than 46,000 ng/mL (ppb) of 6:2 FTOH and more than 65,000 ng/mL (ppb) of the related chemical 6:2 fluorotelomer methacrylate (6:2 FTACR).

ANALYTICAL RESULTS

Table 1.

Technique	PIGE[a]	LC/MS + GC/MS[b]					
Analyte / Product	**Total F, ppm**	**PFBA, ppb**	**PFOS, ppb**	**6:2 FTOH, ppb**	**8:2 FTOH, ppb**	**10:2 FTOH, ppb**	**6:2 FTACR, ppb**
Hush Puppies Rain Maker shoe	1219	2.0	0.3	6.8	3516	738	<LOD
Hush Puppies Men's Venture shoe	1170	2.3	<LOD	<LOD	160	29.8	<LOD
Ked's Women's Camp Water-Resistant Boot w/Thinsulate	1169	2.2	<LOD	<LOD	28.5	4.9	<LOD
Merrel Big Kid's Jungle Moc Frosty Waterproof	379	1.5	0.5	37.7	45.6	12.6	<LOD
Saucony Big Kid's Peregrine Shield 2 A/C sneaker	<LOD	--	--	--	--	--	--
Sperry TopSider Men's Striper II Storm Waterproof Chukka	<LOD	--	--	--	--	--	--
Hush Puppies Weather Protector Spray (liquid)	14,044	<LOD	<LOD	46,296	<LOD	<LOD	65,253

[a] Particle induced gamma emission spectroscopy

[b] Liquid chromatography / mass spectrometry and gas chromatography / mass spectrometry. PFAS in shoes reported in terms of mass per mass, while PFAS in spray is reported in terms of mass per volume. Greater than 90% of PFAS detected in all samples consisted of the six analytes shown here. Results for the other analytes not shown.

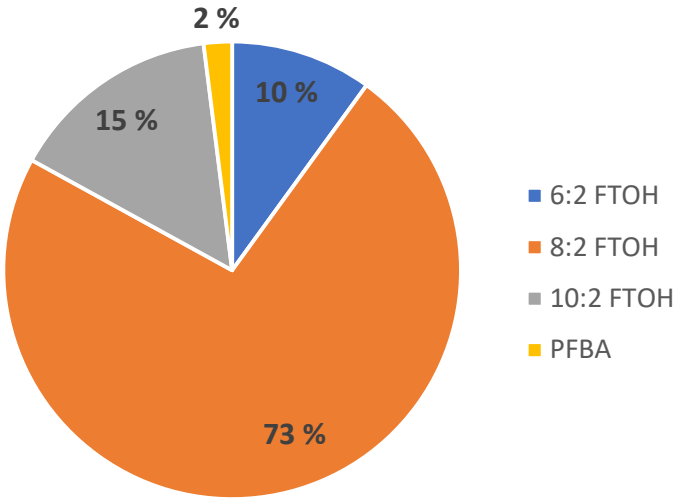

Figure 1. As measured by GC/MS and LC/MS/MS, the PFAS in the four PFAS-positive shoes consisted almost entirely of the four compounds listed here. The pie chart shows the average percentage each compound contributed to the total. Remarkably, 88% of the total consisted of long-chain PFAS (10:2 FTOH and 8:2 FTOH).

Appendix 1. Target PFAS analytes and MS parameters

PFASs analyzed on LC-MS/MS under ESI (-) mode

Abbr.	Compound Name	CAS #	Formula	Retention time (min)	Mol. Wt.	Precursor ion [M-H/D]-	Fragmentor (volts)	Product ions (m/z)	Collision energy (volts)	Structure
PFBA	Perfluorobutanoic acid	375-22-4	$C_4HF_7O_2$	2.243	214.04	213.0	64	169 \	5 \	$F_3C(CF_2)_2COOH$
PFPeA	Perfluoropentanoic acid	2706-90-3	$C_5HF_9O_2$	3.518	264.05	263.0	64	218.9 140.8	5 5	$F_3C(CF_2)_3COOH$
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	$C_6HF_{11}O_2$	5.008	314.05	313.0	73	268.9 119	5 21	$F_3C(CF_2)_4COOH$
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	$C_7HF_{13}O_2$	6.646	364.06	363.0	78	319 169	5 17	$F_3C(CF_2)_5COOH$
PFOA	Perfluoro-n-octanoic acid	335-67-1	$C_8HF_{15}O_2$	8.186	414.07	413.1	83	369 169	5 17	$F_3C(CF_2)_6COOH$
PFNA	Perfluoro-n-nonanoic acid	375-95-1	$C_9HF_{17}O_2$	9.542	464.08	463.1	83	419 218.9	5 17	$F_3C(CF_2)_7COOH$
PFDA	Perfluoro-n-decanoic acid	335-76-2	$C_{10}HF_{19}O_2$	10.712	514.08	513.0	93	468.9 269	5 17	$F_3C(CF_2)_8COOH$
PFUdA	Perfluoro-n-undecanoic acid	2058-94-8	$C_{11}HF_{21}O_2$	11.725	564.09	563.0	102	518.9 268.9	5 17	$F_3C(CF_2)_9COOH$
PFDoA	Perfluoro-n-dodecanoic acid	307-55-1	$C_{12}HF_{23}O_2$	12.601	614.10	613.0	102	569	9	$F_3C(CF_2)_{10}COOH$

Abbr.	Compound Name	CAS #	Formula	Retention time (min)	Mol. Wt.	Precursor ion [M-H/D]-	Fragmentor (volts)	Product ions (m/z)	Collision energy (volts)	Structure
								269	21	
PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	$C_{13}HF_{25}O_2$	13.347	664.11	663.1	107	619 169	9 29	$F_3C(CF_2)_{11}COOH$
PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	$C_{14}HF_{27}O_2$	13.998	714.11	713.1	112	668.9 169	13 29	$F_3C(CF_2)_{12}COOH$
PFHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5	$C_{16}HF_{31}O_2$	15.041	814.13	813.1	121	768.9 168.9	13 37	$F_3C(CF_2)_{14}COOH$
GenX	Perfluoro-2-propoxypropanoic acid	13252-13-6	$C_6HF_{11}O_3$	5.866	330.05	329.0	156	284.9 169.0	5 13	$F_3C(CF_2)_2OCF(COOH)CF_3$
PFPrS	Perfluoro-1-propanesulfonic acid	423-41-6	$C_3HF_7SO_3$	2.748	250.09	249.1	140	80 98.9	37 33	$F_3C(CF_2)_2SO_3H$
PFBS	Perfluoro-1-butanesulfonic acid	375-73-5	$C_4HF_9SO_3$	3.876	300.10	299.0	149	80 98.9	37 37	$F_3C(CF_2)_3SO_3H$
PFPeS	Perfluoro-1-pentanesulfonic acid	2706-91-4	$C_5HF_{11}SO_3$	5.336	350.11	349.0	175	80 98.9	45 37	$F_3C(CF_2)_4SO_3H$
PFHxS	Perfluoro-1-hexanesulfonic acid	355-46-4	$C_6HF_{13}SO_3$	6.885	400.11	399.0	179	80 98.9	45 41	$F_3C(CF_2)_5SO_3H$
PFHpS	Perfluoro-1-heptanesulfonic acid	375-92-8	$C_7HF_{15}SO_3$	8.357	450.12	449.0	183	80 98.9	49 45	$F_3C(CF_2)_6SO_3H$
PFOS	Perfluoro-1-octanesulfonic acid	1763-23-1	$C_8HF_{17}SO_3$	9.647	500.13	499.0	208	80 98.9	101 49	$F_3C(CF_2)_7SO_3H$

Abbr.	Compound Name	CAS #	Formula	Retention time (min)	Mol. Wt.	Precursor ion [M-H/D]-	Fragmentor (volts)	Product ions (m/z)	Collision energy (volts)	Structure
PFNS	Perfluoro-1-nonanesulfonic acid	68259-12-1	$C_9HF_{19}SO_3$	10.776	549.93	549.0	218	80 98.9	105 49	$F_3C(CF_2)_8SO_3H$
PFDS	Perfluoro-1-decanesulfonic acid	335-77-3	$C_{10}HF_{21}SO_3$	11.764	600.14	598.9	232	80 98.9	137 53	$F_3C(CF_2)_9SO_3H$
PFECHS	Perfluoro-4-ethylcyclohexanesulfonic acid	646-83-3	$C_8HF_{15}SO_3$	8.096	462.13	461.0	150	380.9 98.9	29 29	$F_5C_2(C_6F_{10})$ (*para*-) SO_3H
Cl-PFOS	8-Chloroperfluoro-1-octanesulfonic acid	777011-38-8	$C_8HF_{16}ClSO_3$	9.897	516.58	515.0	203	80 98.9	105 49	$ClF_2C(CF_2)_7SO_3H$
FOSA	Perfluoro-1-octanesulfonamide	754-91-6	$C_8H_2F_{17}NO_2S$	11.159	499.14	498.0	169	78 48.1	37 150	$F_3C(CF_2)_7SO_2NH_2$
MeFOSA	N-methylperfluoro-1-octanesulfonamide	31506-32-8	$C_9H_4F_{17}NO_2S$	12.808	513.17	512.0	160	169 218.9	29 25	$F_3C(CF_2)_7SO_2NHCH_3$
EtFOSA	N-ethylperfluoro-1-octanesulfonamide	4151-50-2	$C_{10}H_6F_{17}NO_2S$	13.375	527.20	526.0	165	169 219	29 29	$F_3C(CF_2)_7SO_2NHC_2H_5$
FHEA	2-Perfluorohexyl ethanoic acid (6:2)	53826-12-3	$C_8H_3F_{13}O_2$	7.037	378.09	377.0	185	292.9 63.1	15 3	$F_3C(CF_2)_5CH_2COOH$
FOEA	2-Perfluorooctyl ethanoic acid (8:2)	27854-31-5	$C_{10}H_3F_{17}O_2$	9.927	478.10	477.0	215	392.9 63	15 3	$F_3C(CF_2)_7CH_2COOH$
FDEA	2-Perfluorodecyl ethanoic acid (10:2)	53826-13-4	$C_{12}H_3F_{21}O_2$	12.075	578.12	577.0	245	492.9 63	15 3	$F_3C(CF_2)_9CH_2COOH$
4:2 FTS	1H,1H,2H,2H-perfluorohexane sulfonic acid (4:2)	757124-72-4	$C_6H_5F_9O_3S$	4.870	328.15	327.1	136	306.9 81	21 33	$F_3C(CF_2)_3(CH_2)_2SO_3H$

Abbr.	Compound Name	CAS #	Formula	Retention time (min)	Mol. Wt.	Precursor ion [M-H/D]-	Fragmentor (volts)	Product ions (m/z)	Collision energy (volts)	Structure
6:2 FTS	1H,1H,2H,2H-perfluorooctane sulfonic acid (6:2)	27619-97-2	$C_8H_5F_{13}O_3S$	8.091	428.17	427.0	164	406.9 81	25 41	$F_3C(CF_2)_5(CH_2)_2SO_3H$
8:2 FTS	1H,1H,2H,2H-perfluorodecane sulfonic acid (8:2)	39108-34-4	$C_{10}H_5F_{17}O_3S$	10.676	528.18	527.0	179	506.9 81	29 41	$F_3C(CF_2)_7(CH_2)_2SO_3H$

PFASs analyzed on GC-MS under PCI mode

Abbr.	Compound Name	CAS #	Formula	Mol. Wt.	Retention time (min)	Quantifier	Qualifier	Structure
FBET	2-Perfluorobutyl ethanol (4:2)	2043-47-2	$C_6H_5F_9O$	264.09	5.840	265	227	$F_3C(CF_2)_3(CH_2)_2OH$
FHET (6:2 FTOH)	2-Perfluorohexyl ethanol (6:2)	647-42-7	$C_8H_5F_{13}O$	364.10	7.569	365	327	$F_3C(CF_2)_5(CH_2)_2OH$
FOET (8:2 FTOH)	2-Perfluorooctyl ethanol (8:2)	678-39-7	$C_{10}H_5F_{17}O$	464.12	9.993	465	427	$F_3C(CF_2)_7(CH_2)_2OH$
FDET (10:2 FTOH)	2-Perfluorodecyl ethanol (10:2)	865-86-1	$C_{12}H_5F_{21}O$	564.13	12.460	565	527	$F_3C(CF_2)_9(CH_2)_2OH$
6:2 FTAcr	1H,1H,2H,2H-perfluorooctyl acrylate	17527-29-6	$C_{11}H_7F_{13}O_2$	418.15	6.450	419	399	$F_3C(CF_2)_5(CH_2)_2COOCH=CH_2$
8:2 FTAcr	1H,1H,2H,2H-Perfluorodecyl acrylate	27905-45-9	$C_{13}H_7F_{17}O_2$	518.17	9.100	519	499	$F_3C(CF_2)_7(CH_2)_2COOCH=CH_2$
10:2FTAcr	1H,1H,2H,2H-Perfluorododecyl acrylate	17741-60-5	$C_{15}H_7F_{21}O_2$	618.18	11.916	619	599	$F_3C(CF_2)_9(CH_2)_2COOCH=CH_2$
6:2 FTMAcr	1H,1H,2H,2H-perfluorooctyl methacrylate	2144-53-8	$C_{12}H_9F_{13}O_2$	432.18	7.672	433	413	$F_3C(CF_2)_5(CH_2)_2COOC(=CH_2)CH_3$
8:2 FTMAcr	1H,1H,2H,2H-heptadecafluorodecyl methacrylate	1996-88-9	$C_{14}H_9F_{17}O_2$	532.19	10.413	533	513	$F_3C(CF_2)_7(CH_2)_2COOC(=CH_2)CH_3$
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	24448-09-7	$C_{11}H_8F_{17}NO_3S$	557.22	19.068	558	540	$F_3C(CF_2)_7SO_2N(-CH_3)(CH_2)_2OH$
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	$C_{12}H_{10}F_{17}NO_3$	539.19	19.194	572	554	$F_3C(CF_2)_7SO_2N(-C_2H_5)(CH_2)_2OH$