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January 14, 2020

Submitted online via CalSAFER

Re: Safer Consumer Products Product-Chemical Profile for Treatments Containing Perfluoroalkyl and Polyfluoroalkyl Substances for Use on Converted Textiles or Leathers

On behalf of the undersigned organizations, thank you for the opportunity to comment on the Department of Toxic Substance Control's (Department) Product-Chemical Profile on treatments containing PFAS. We have no financial interest in any of the products or chemicals which may be the subject of these comments.

We urge the Department to promulgate a regulation listing this product-chemical combination as a priority product. The product-chemical profile provides strong support for listing of this product-chemical combination as a priority product, as both potential adverse effects and potential exposure are well documented.[1] The potential adverse waste and end-of-life effects documented in the profile also support listing.[2] These potential exposures and adverse effects are substantiated by strong and high quality information in the profile.[3] Furthermore, no other regulatory programs adequately protect against the potential adverse impacts, potential exposure pathways, and adverse waste and end-of-life effects under consideration.[4]

Based on the information provided in the profile, it is critical that California address the harmful impacts of PFAS chemicals in textile and leather treatments and seek safer alternatives.

Our comments are summarized here and more details are provided below.

1. **The standards for listing as a Priority Product are met because PFAS have the potential to cause adverse health and environmental impacts, particularly for sensitive subpopulations such as children and pregnant women.** A strong body of science links the PFAS class of chemicals to adverse health and environmental effects as the profile amply documents.[5] The 2014 Helsingør[6] and 2015[7] Madrid Statements, founded on extensive reviews of the scientific literature, provided consensus from more than 200 scientists on the potential for harm associated with the entire class of PFAS. This includes long-chain PFAS (like perfluorooctanoic acid, or PFOA, and perfluorooctanesulfonic acid, or PFOS) as well as their short-chain per- and poly-fluorinated replacements. The profile

appropriately describes the adverse impacts associated with members of the PFAS class of chemicals found in textile and leather treatments, those PFAS chemicals found in dust and air and linked to the use of PFAS-containing treatments, and the harms associated with their break-down products.[8] The fact that the presence of PFAS in textile and leather treatments have the potential to contribute to adverse impacts for sensitive subpopulations also supports listing, given the mandate for the Department to give "special consideration" to such potential impacts.[9]

2. **The standards for listing as a Priority Product are met because there is a large potential for widespread public exposure to the chemicals.** The profile extensively documents evidence that PFAS-containing textile and leather treatments contribute to widespread environmental contamination and exposures throughout the product's lifecycle. PFAS treatments contribute to exposures in workplace and household dust and indoor air resulting in the potential for widespread public exposure.[10] In particular, the profile highlights the increased exposures to young children and workers. Children's play activities and hand-to-mouth behavior result in increased exposure to PFAS chemicals in household dust. In addition, workers also face the potential for increased exposure, for instance in retail settings where upholstered furniture and other treated textiles and leathers are sold, at carpet and upholstery cleaners, at drycleaners which weatherize clothing, at auto dealership and detailing businesses, and at recycling and waste operations. Furthermore, inhalation during product use is a particularly concerning exposure route, due to the aerosolization of the product during application; therefore, we recommend more detailed discussion of this unique exposure route and risk to product users.

3. **These potential adverse impacts and exposures are exacerbated by adverse waste and end-of-life effects.** The continued release of PFAS into the environment via disposal of products treated with PFAS to landfills and other waste streams and discharges to storm drains and sewers can continue to expose more people and environments to PFAS, as the profile demonstrates.[11] It can also lead to additional costs for treatment and cleanup. Of note, incineration of PFAS treated textiles and leathers, which produces air toxicants, often occurs at incinerators located in low-income communities already overburdened with environmental exposures. These additional impacts also support listing of PFAS-containing treatments as a Priority Product.

4. **No other regulatory programs provide adequate protection against these potential hazards and exposures.** As the profile discusses, no existing state or federal regulatory programs restrict, or eliminate, the presence of the class of PFAS chemicals in textile and leather treatments in the United States or adequately prevent the resulting exposures described in the profile.[12] The listing of PFAS in textile and leather treatments as a Priority Product would "meaningfully enhance protection of public health and/or the environment"[13] by identifying and shifting the market towards the adoption of safer alternatives.

5. **The goal of the Safer Consumer Products Program is "to create safer substitutes for hazardous ingredients in consumer products sold in California" which includes avoiding regrettable substitution.** As the profiles discusses, including the entire class of PFAS is essential to avoid replacement with other members of the PFAS class that have the potential for exposure and adverse impacts.

6. **To protect consumers and workers from the exposures outlined in the profile, DTSC should expand the product category both to industrial uses of PFAS treatments in California and to products treated with PFAS treatments.** The same risks posed by consumer PFAS treatment

products are potentially even more marked for workers in industrial facilities which use PFAS treatments. Similarly, products with pre-market PFAS treatments expose consumers and retail workers to risks similar to after-market PFAS treatments. We therefore recommend expanding the product scope to include industrial uses of PFAS treatments and to products with pre-market PFAS treatments.

DETAILED COMMENTS

1. The standards for listing as a Priority Product are met because PFAS have the potential to cause adverse health and environmental impacts, particularly for sensitive subpopulations such as children and pregnant women.

As the Department's profile notes, PFAS have the potential to cause adverse health and environmental impacts due to:

- (a) Physicochemical properties that result in environmental persistence, high mobility leading to long-range transport and extensive distribution in multiple environmental media, bioaccumulation, or lactational and transplacental transfer.
- (b) Potential to degrade into other members of the PFAS class.
- (c) Human toxicity including, but not limited to, carcinogenicity, developmental toxicity, reproductive toxicity, cardiovascular toxicity, endocrine toxicity, hematotoxicity, hepatotoxicity and digestive system toxicity, and immunotoxicity.
- (d) Additive or multiplicative impacts associated with mixtures of individual PFAS chemicals.

Although, each chemical in the PFAS class may not have documented evidence for all of these characteristics, all of the sub-classes are known to exhibit at least one of these characteristics. As the Department's profile notes, there is sufficient evidence documenting PFAAs' potential to cause widespread adverse impacts. And although PFAAs constitute a small subset of PFASs, "they are terminal degradation products, manufacturing aids/feedstocks, or impurities of other PFAS class members. This makes their hazard traits relevant to the entire class." Furthermore, claims of reduced toxicity for shorter-chain PFAAs used to replace PFOA and PFOS have not been substantiated and, as the profile documents, toxicity testing has raised numerous concerns about these compounds as well. The Department appropriately followed the regulations when considering, "the adverse impacts associated with structurally or mechanistically similar chemicals" in identifying concern for the entire class of PFAS.[14] The profile identifies structural similarities between chemicals to categorize chemicals with similar physicochemical properties that are indicative of hazard traits, such as persistence and mobility in the environment, and the potential for the creation of intermediate break-down and degradation products of high toxicity.

Physicochemical properties of PFAS leading to transplacental and lactational transfer put pregnant and nursing women, children, and the developing fetus at increased risk of harm. In addition, evidence of developmental and reproductive toxicity from PFAS increase the vulnerability of these sensitive subpopulations to harmful effects of these chemicals, to which the Department must give special regulatory consideration.[15]

California's consideration of all PFAS compounds is consistent with recommendations made by scientific experts[16] and recent actions taken by several states and the European Union. For example, Washington, Colorado, New York, and New Hampshire have passed legislation to limit use of PFAS-containing firefighting foam.[17] Washington has passed legislation to ban the use of PFAS in food packaging.[18] Vermont passed legislation directing the state to consider regulating PFAS as a class or subclasses.[19] Finally, in December 2019, the European Commission proposed setting a drinking water standard for the entire class.[20] In addition, Sweden, the Netherlands, Germany, and Denmark have proposed a plan to the European Commission to phase out most uses of PFAS compounds by 2030.[21]

2. **The standards for listing as a Priority Product are met because there is a large potential for widespread public exposure to the chemicals.**

The Department appropriately demonstrates the potential human exposures to PFAS both from direct exposure to products treated with PFAS and from indirect exposures resulting from the manufacture, use, and disposal of PFAS treatments and the products on which the treatments have been used. The profile describes studies showing that examples from each of the sub-classes of PFAS are linked to exposures via one or more of these pathways, thereby demonstrating the potential for widespread exposure to the entire class of chemicals. However, direct inhalation due to the aerosolization of the product during application is a particularly acute and concerning exposure route for this product. Although the Department acknowledges this route of exposure, we recommend that it expand upon this unique exposure route and risk. Please see Dr. Gina Solomon's comment #12305 and associated documents for multiple examples of acute respiratory toxicity resulting from the use of PFAS-containing treatment sprays.

Additionally, we would like to bring to your attention a recent study by the Ecology Center that is not reflected in the profile. [22] The study tested six pairs of shoes and one weather-protector spray sold by Wolverine Worldwide for total fluorine and for specific PFAS. The weather-protector spray contained a high concentration of total fluorine and PFAS. Particle Induced Gamma-ray Emission (PIGE) analysis found 14,044 ppm total fluorine and GC/MS and LC/MS/MS testing showed that the spray contained more than 46,000 ppb of 6:2 FTOH and more than 65,000 ppb of 6:2 fluorotelomer methacrylate (6:2 FTACR). (please see attached)

In addition to direct contact with textile products treated with PFAS, PFAS migrate and collect in the air and dust of homes and workplaces. The profile documents studies showing both PFAAs and PFAA precursor chemicals in PFAS treated textiles. In addition, multiple studies link levels of PFAAs and PFAA precursors in dust and air to the presence of PFAS-treated textiles such as carpets and rugs. The manufacture of PFAS has been linked to extensive contamination of the local environment surrounding the manufacturing facility as well as contribution to global contamination. Because wastewater treatment plants are largely incapable of removing PFAS, effluent testing shows the presence of multiple PFAAs. The profile identifies both manufacturing, use, and disposal of the product as potential sources. As noted in the profile, these discharges are major point sources for PFAS contamination of aquatic environments.

Children have been shown to have higher levels of PFAS in their bodies which is likely due, in part, to increased exposures and higher contact with contaminated dust because they crawl, play on the floor, and put their hands in their mouths.[23,24] This increased exposure increases the vulnerability of children to this product-chemical combination, and the potential for adverse impacts on sensitive subpopulations like children is something to which the Department must give special consideration.[25]

Among the adult population, monitoring in workplaces has found higher amounts of PFAS in carpets used in institutional settings and higher PFAAs in the air in carpet stores. These findings suggest the potential for increased exposures among workers with a high degree of contact with carpets and rugs. In addition, workers in retail where upholstered furniture and other treated textiles and leathers are sold, carpet and upholstery cleaners, dry cleaners, auto dealership and detailing workers, and workers engaged in recycling and waste activities are also likely to be at increased risk.

3. **These potential adverse impacts and exposures are exacerbated by adverse waste and end-of-life effects.**

The profile highlights numerous pathways by which the disposal of PFAS-treated textiles and leathers contribute to human and environmental exposures including leaching from landfills, accumulation in recycled products, and emissions from incineration. In particular, the profile describes studies identifying high levels of multiple PFAS in landfill leachate and studies linking landfills as sources for nearby environmental contamination. Additionally, the profile describes how the fluorinated polymers and fluorotelomers used to treat textiles degrade in landfills to release PFAA precursors which can continue to be a long-term (years to centuries) source of environmental contamination. Finally, disposal of PFAS waste often presents an environmental justice concern. Incineration of PFAS under normal incineration conditions does not result in the defluorination of PFAS, but instead in the formation of hazardous substances, ozone depleting substances, and potent greenhouse gases. As the Department notes, "incinerators [are] often located in low-income communities, where emissions burden people already impacted by aggregate chemical exposures from other sources, creating environmental justice concerns." In addition, a large amount of PFAS-contaminated dust is produced near recycling and waste facilities, leading to higher exposures for surrounding communities.

4. **No other regulatory programs provide adequate protection against these potential hazards and exposures.**

As the profile documents, no state programs address the presence of PFAS in textile and leather treatments.[26] Federal EPA has initiated voluntary agreements to phase out PFOA in certain companies' emissions and products, and has begun reviewing substitutes for PFOA, PFOS, and other longer-chain PFAS.[27] However, the voluntary agreements do not apply to all manufacturers and the review of substitutes has not led to further action on PFAS or their substitutes. Finally, the applicable international treaties cover only PFOA and PFOS at this time; PFHxS is currently being considered for inclusion, but other PFAS are not covered.[28]

5. **The goal of the Safer Consumer Products Program is "to create safer substitutes for hazardous ingredients in consumer products sold in California" which includes avoiding regrettable substitution.**

The substitution of short-chain PFAS for PFOA/PFOS clearly demonstrate the potential for regrettable substitution from related compounds within the PFAS class of chemicals. For example, GenX is a replacement technology for PFOA and PFBS is a replacement for PFOS. The US Environmental Protection Agency (EPA) released draft toxicity assessments in November of 2018 on two GenX chemicals (hexafluoropropylene oxide (HFPO) dimer acid and its ammonium salt) and PFBS. The assessment shows that GenX chemicals are associated with liver and pancreatic cancers and adverse effects on the kidneys, blood, liver, immune system, and development.[29] PFBS is also associated with health impacts, specifically thyroid and kidney effects and reproductive and developmental toxicity.[30] Additionally, as noted earlier, PFAAs are either terminal degradation products, manufacturing aids or feedstocks, and/or impurities of other PFAS class members and therefore their hazard traits can be applied to the entire class. Therefore, the profile correctly identifies inclusion of the entire class of compounds is needed to prevent regrettable substitution and meet the goals of the Safer Consumer Products program.

6. **To protect consumers and workers from the exposures outlined in the profile, DTSC should expand the product category both to industrial uses of PFAS treatments in California and to products with PFAS treatments.**

The current product scope would result in continued high exposures to workers involved in the production of textiles and leathers treated with PFAS in California. Finishing agents are usually applied to textiles and leathers before assembly, which means that workers in the textile dyeing and finishing mills and cut and sew facilities are and will continue to receive high levels of exposure where PFAS is used on textiles. It is important to note that workers at cut-and-sew facilities, who are in close contact with PFAS treated fabrics as well as its scrap and dust, are predominately female. Many of them are also at childbearing ages and will continue working even when they are pregnant.

Furthermore, products with pre-market PFAS treatments expose consumers and retail workers to risks similar to after-market PFAS treatments. The current product scope would not affect the use of PFAS in the textiles and leather products manufacturing process. As current estimates of the PFAS market show that 36% of PFAS is used in textiles,[31] this could result in significant continued exposures and releases of PFAS from textile and leather products. PFAS, whether used during manufacturing or after, once produced and used will inevitably be released into the environment and will, as the Department points out, “become part of a virtually closed cycle leading to chronic human and ecological exposures.”

We therefore recommend expanding the product scope to include industrial uses of PFAS treatments in California and to products with pre-market PFAS treatments.

ADDITIONAL MINOR COMMENTS

1. On page 36 of the profile, (DeWitt 2015) is referenced three times in a row, this is likely a typo as there are not three DeWitt listings in the references.
2. In the “Aggregate effects” section on page 45, in support of the statement, “This can result in exposure to complex PFAS mixtures…,” many biomonitoring studies show that people often have multiple different PFAS in their bodies, including studies performed by the California Biomonitoring program. Alternative methods for detecting PFAS in blood serum are showing an increasing trend of unidentified organofluorine in blood serum samples, which suggest that people are being exposed to new and unidentified PFAS.[32,33]
3. On page 57, Hu et al. estimated that approximately 6 million people were served drinking water above 70 ppt not 16.5 million. They found 16.5 million people were served water above the UCMR MRLs.
4. On page 59, it is also notable that most of the sites where the SWRCB found PFAS in drinking water sources had multiple PFAS.
5. On page 67, in addition to PFBS, PFHxA and PFBA, GenX is also a short-chain PFAA that also shows evidence for hazard traits, including liver and pancreatic cancers and adverse effects on the kidneys, blood, liver, immune system, and development.[34]
6. On page 82, EPA’s PFAS Action Plan only commits the EPA to proposing a regulatory determination, not to set a MCL for PFOA and PFOS by the end of 2019.

7. On page 83, Vermont's combined health advisory for 5 PFAS at 20 ppt is now enforced. New Jersey only adopted a MCL for PFNA first in 2017, but has since proposed MCLs for PFOA and PFOS. New Hampshire set MCLs for 4 PFAS in 2019.[35]
8. On page 84, to add to activity around cleanup at military sites, the National Defense Authorization act passed in December of 2019 contains multiple PFAS-related amendments, including phase out of PFAS-containing firefighting foam, addition of multiple PFAS to the Toxics Release Inventory, and Requiring DoD to enter into cooperative agreements with communities for testing, monitoring, and clean-up of PFAS where DOD has contaminated the environment, among others.[36]

Conclusion

The Safer Consumer Products Program, while focused on California, has the potential to have national and even international impacts on how chemicals are used in consumer products and the resulting impact on human health and the environment, particularly the impacts on vulnerable subpopulations for which the regulations require special consideration. This is particularly true for persistent chemicals like PFAS, which remain in the environment and are transported through air and water across wide areas of the globe. By motivating industry to develop and switch to safer alternatives, the Program will be fulfilling its mandate in California and helping to reduce national and international exposure to these toxic chemicals. We commend the Department's well-substantiated profile of treatments containing PFAS for converted textiles and leathers and urge swift and decisive action to list PFAS treatments as a Priority Product.

Thank you for your consideration of these comments. We look forward to working with the Department to improve environmental and public health protections from chemicals in consumer products.

Sincerely,

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[1] 22 CCR §§ 69503.2(a), 69503.3; *see also* § 69504.1(b)(3)(B).

[2] *See* 22 CCR § 69503.2(b)(1)(B).

[3] *See* 22 CCR § 69503.2(b)(1)(C).

[4] *See* 22 CCR § 69503.2(b)(2).

[5] DTSC, Product-Chemical Profile for Treatments Containing Perfluoroalkyl and Polyfluoroalkyl Substances for use on Converted Textiles or Leathers 32-38 (addressing potential adverse effects across a range of regulatory factors: physicochemical properties; environmental fate; potential to degrade, form reaction products or metabolize into another chemical with hazard traits; toxicological and environmental hazard traits/endpoints; cumulative effects; sensitive subpopulations, and other factors) (hereafter, "DTSC, Profile").

[6] Scheringer M, Trier X, Cousins IT, de Voogt P, Fletcher T, Wang Z, Webster TF. Helsingør statement on poly- and perfluorinated alkyl substances (PFASs). *Chemosphere*. 2014;114:337-9.

[7] Blum A, Balan SA, Scheringer M, Trier X, Goldenman G, Cousins IT, Diamond M, Fletcher T, Higgins C, Lindeman AE, Peaslee G, de Voogt P, Wang Z, Weber R. The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs). *Environ Health Perspect*. 2015;123(5):A107-A111.

[8] *See* 22 CCR § 69503.3(a)(3) (authorizing consideration of adverse effects of "structurally or mechanistically similar chemicals for which there is a known toxicity profile").

[9] 22 CCR § 69503.3(a)(2).

[10] DTSC, Profile at 39-64 (documenting potential exposure across a range of regulatory factors: market presence of the product; household and workplace presence of the product; the occurrence, and potential occurrence, of exposures to the Candidate Chemical in the product; potential exposures to the Candidate Chemical in the product; and other factors).

[11] DTSC, Profile at 70-72.

[12] DTSC, Profile at 78-79.

[13] 22 CCR § 69503.2(b)(2).

[14] 22 CCR § 69503.3(a)(3).

[15] 22 CCR § 69503.3 (a)(2)(A); see also 22 CCR § 69501.1(a)(64): " 'Sensitive subpopulations' means subgroups that comprise a meaningful portion of the general population that are identifiable as being at greater risk of adverse health effects when exposed to one or more chemicals that exhibit a hazard trait and/or toxicological endpoint, including, but not limited to, infants, children, pregnant women, and elderly individuals. 'Sensitive subpopulations' also include individuals at greater risk of adverse health effects when exposed to chemicals because they are either individuals with a history of serious illness or greater exposures to chemicals, or workers with greater exposures to chemicals due to the nature of their occupation."

[16] Krowech G, Hoover S, Plummer L, Sandy M, Zeise L, Solomon G. Identifying Chemical Groups for Biomonitoring. *Environ Health Perspect.* 2016; 124(12):A219-A226.

[17] Washington (State). Senate Bill 6413. 2018 Regular Session. Accessed at: http://lawfilesext.leg.wa.gov/biennium/2017-18/Pdf/Bills/Senate%20Passed%20Legislature/6413-S.PL.pdf;
Colorado. House Bill 1279. 2019 Regular Session Accessed at: https://leg.colorado.gov/bills/hb19-1279;
New York. Assembly Bill 445A. 2019 Regular Session. Accessed at: https://assembly.state.ny.us/leg/?bn=A00445&term=&Summary=Y&Actions=Y&Votes=Y&Memo=Y&Text=Y&leg_video=1;
New Hampshire. Senate Bill 257. 2019 Regular Session. Accessed at: https://legiscan.com/NH/text/SB257/id/1872612.

[18] Washington (State). House Bill 2658. 2018 Regular Session. Accessed at: http://lawfilesext.leg.wa.gov/biennium/2017-18/Pdf/Bills/House%20Passed%20Legislature/2658-S.PL.pdf;

[19] Vermont. Senate Bill 49. 2019 Regular Session. Accessed at: https://legislature.vermont.gov/Documents/2020/Docs/ACTS/ACT021/ACT021%20As%20Enacted.pdf.

[20] The Greens/EFA in the European Parliament. Media Briefing, December 19, 2019. Accessed at: https://sven-giegold.de/wp-content/uploads/2019/12/Media-briefing-Drinking-water-19.12.2019.pdf.

[21] European Commission. Elements for a EU-strategy for PFAS. December 2019. Accessed at: https://www.documentcloud.org/documents/6586418-EU-Strategy-for-PFASs-FINAL-VERSION-December-19.html.

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[22] Ecology Center. Wolverine Worldwide Product Testing Report, November 26, 2019. Accessed at: https://drive.google.com/file/d/1bvPJ_pL5VtWQQW0_8w7Bng2-Tkh9mXwL/view?usp=sharing

[23] DTSC, Profile at 60

[24] Wu XM, Bennett DH, Calafat AM, et al 2015. Serum concentrations of perfluorinated compounds (PFC) among selected populations of children and adults in California. Environ Res 136:264-73.

[25] 22 CCR § 69503.3 (a)(2)(A); see also 22 CCR § 69501.1(a)(64).

[26] DTSC, Profile at 78.

[27] DTSC, Profile at 78-79.

[28] DTSC, Profile at 86.

[29] U.S. Environmental Protection Agency, 2018b. Toxicity Assessment: Human Health Toxicity Values for Hexafluoropropylene Oxide (HFPO) Dimer Acid and Its Ammonium Salt (CASRN 13252-13-6 and CASRN 62037-80-3). November 2018. EPA 823-P-18-001. U.S. Environmental Protection Agency, Office of Water. Washington, DC.

[30] U.S. Environmental Protection Agency, 2018c. Toxicity Assessment: Human Health Toxicity Values for Perfluorobutane Sulfonic Acid (CASRN 375-73-5) and Related Compound Potassium Perfluorobutane Sulfonate (CASRN 29420-49-3). November 2018. EPA 823-R-18-0307. U.S. Environmental Protection Agency, Office of Water. Washington, DC.

[31] Global Market Insights. Fluorotelomers Market Size by Product (Fluorotelomer Iodide, Fluorotelomer Acrylate, Fluorotelomer Alcohols), By Application (Textiles, Stain resistant, Food packaging, Fire fighting foams), Industry Analysis Report, Regional Outlook, Application Potential, Price Trends, Competitive Market Share & Forecast, 2016 – 2023. Accessed at: https://www.gminsights.com/industry-analysis/fluorotelomers-market

[32] Yeung LWY, et al., 2008. Perfluorinated compounds and total and extractable organic fluorine in human blood samples from China. Environ. Sci. Technol 42(21): 8140-8145.

[33] Yeung LW and Mabury SA, 2016. Are humans exposed to increasing amounts of unidentified organofluorine. *Environ. Chem*, *13*(1), 102-110.

[34] U.S. Environmental Protection Agency, 2018b. Toxicity Assessment: Human Health Toxicity Values for Hexafluoropropylene Oxide (HFPO) Dimer Acid and Its Ammonium Salt (CASRN 13252-13-6 and CASRN 62037-80-3). November 2018. EPA 823-P-18-001. U.S. Environmental Protection Agency, Office of Water. Washington, DC.

[35] Vermont. Senate Bill 49. 2019 Regular Session. Accessed at: https://legislature.vermont.gov/Documents/2020/Docs/ACTS/ACT021/ACT021%20As%20Enacted.pdf;
New Jersey Department of Environmental Protection. Site Remediation Program. Accessed at: https://www.nj.gov/dep/srp/emerging-contaminants/;
New Hampshire Department of Environmental Services: Press Release, June 28, 2019. Accessed at: https://www.des.nh.gov/media/pr/2019/20190628-pfas-standards.htm

[36] U.S. Congress. National Defense Authorization Act Fiscal Year 2020. Accessed at: https://www.congress.gov/bill/116th-congress/senate-bill/1790/text

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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.

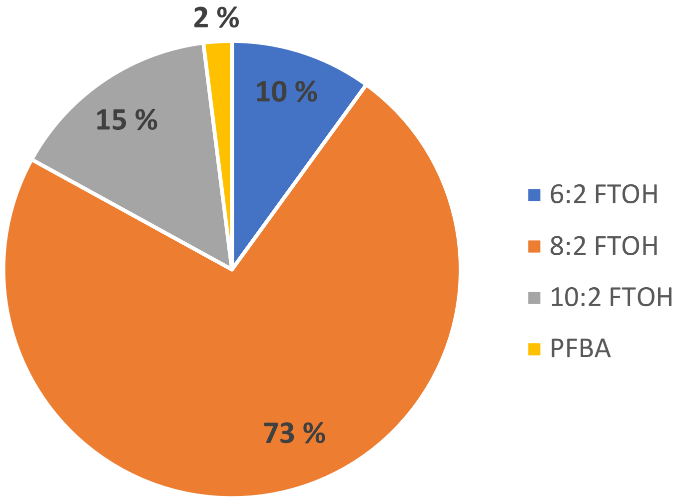

Figure 1. As measured by GC/MS and LC/MS/MS, the PFAS in the four PFAS-positive shoes consisted almost entirely of the four compounds listed here. The pie chart shows the average percentage each compound contributed to the total. Remarkably, 88% of the total consisted of long-chain PFAS (10:2 FTOH and 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	$F_3C(CF_2)_7SO_2N(-C_2H_5)(CH_2)_2OH$