PFAS Exposure in Textiles: Knowns, Unknowns, and Relevance to Human Exposure

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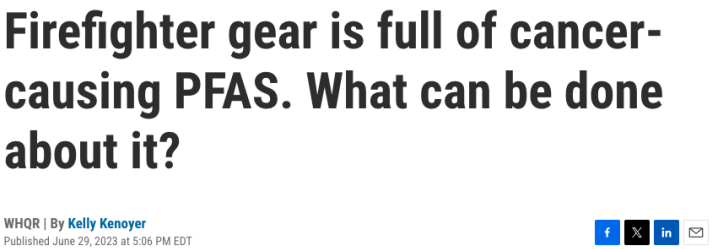
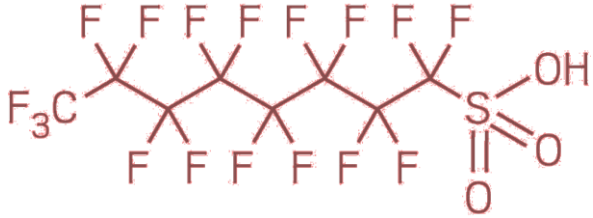
PFAS in the News

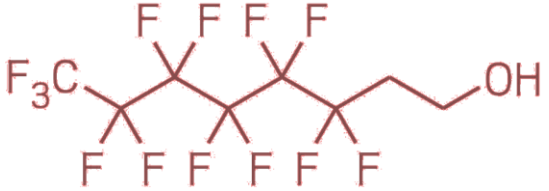


What are PFAS?

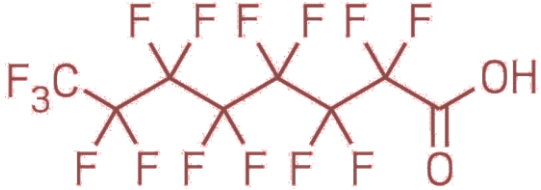
- Per- and Polyfluoroalkyl Substances (PFAS)
- Per = Fully Poly = Many



Perfluorooctane Sulfonic Acid (PFOS)



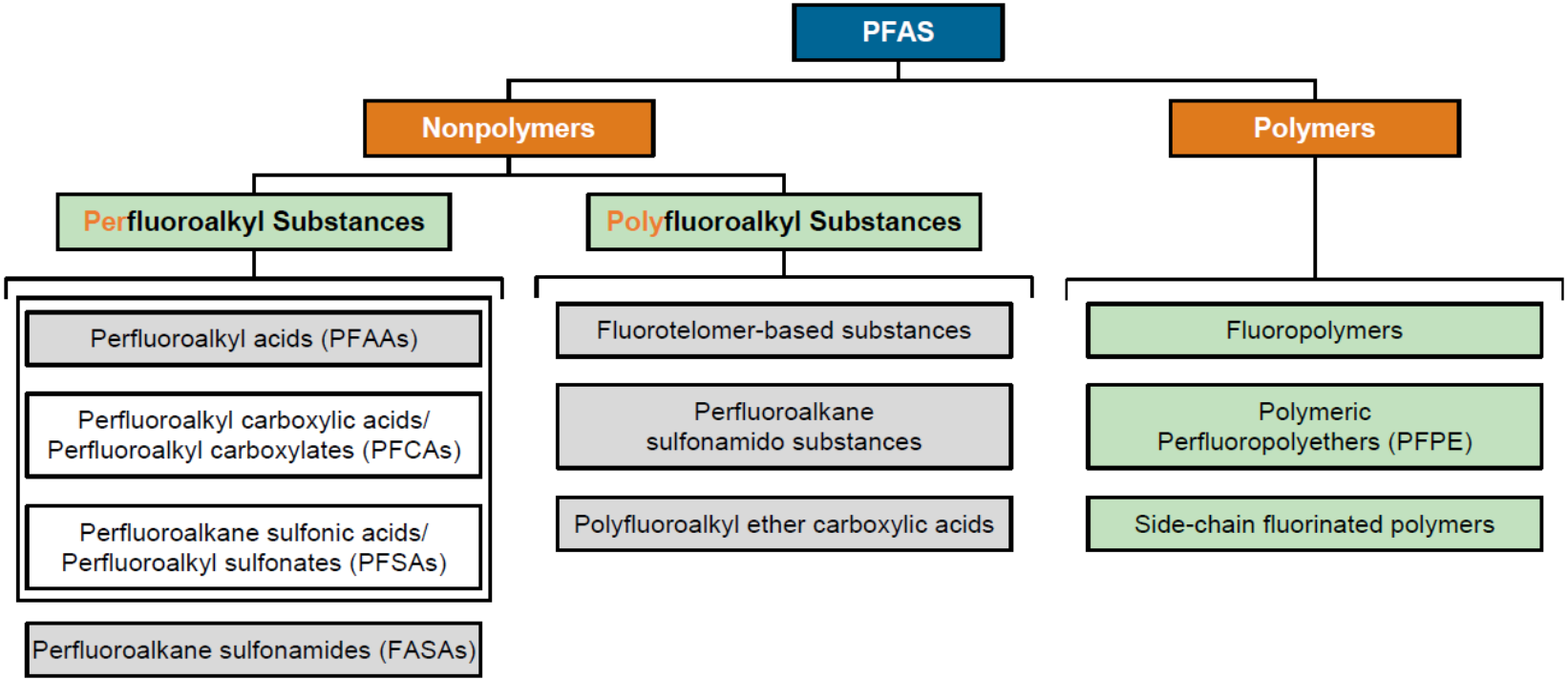
6:2 Fluorotelomer Alcohol (6:2 FTOH)



Perfluorooctanoic Acid (PFOA)

8:2 Fluorotelomer Alcohol (8:2 FTOH)

PFAS Terminology



ITRC, Naming Conventions and Physical and Chemical Properties of Per-and Polyfluoroalkyl Substances (PFAS), https://pfas-1.itrcweb.org/fact-sheets/

PFAS Chemical Properties

- Surface Active Agents
  - Same type of compounds as detergent and soaps
  - Hydrophilic (water-loving) and Hydrophobic (water-hating)

Perfluorooctane sulfonate (PFOS)

Tail $F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2$ — SO_3^- Head

Perfluorooctane carboxylate (PFOA)

Tail $F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2$ — CO_2^- Head

- Water and Oil Repellency
  - All oil repellents also repel water
  - Not all water repellents repel oils
  - Harder to repel oil

PFAS Uses

- **Many PFAS are thermally and chemically stable**
  - **Resistance to degradation -> “Forever Chemicals”**
  - **Can be difficult to tell if a chemical is treated with PFAS**

RIVERSIDE PUBLIC UTILITIES VS.
POLYFLUOROALKYL SUBSTANCES (PFAS)

PFAS Release to the Environment

- Exposure sources vary regionally
  - Industrial inputs
  - Land application of sewage sludge
  - Consumer products
    - **Carpeting, upholstery**
    - Cosmetics
    - Food packaging

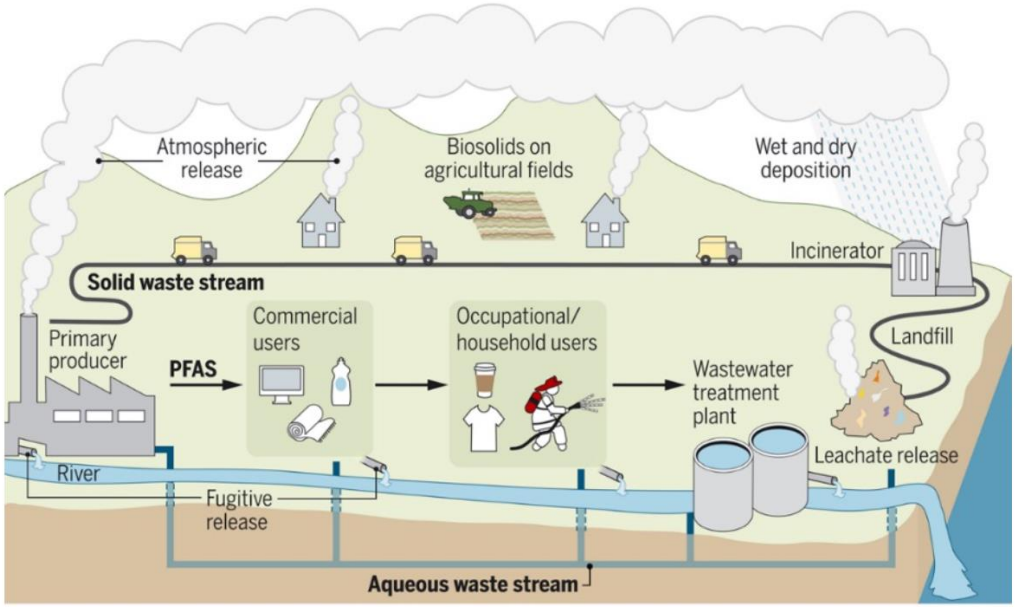
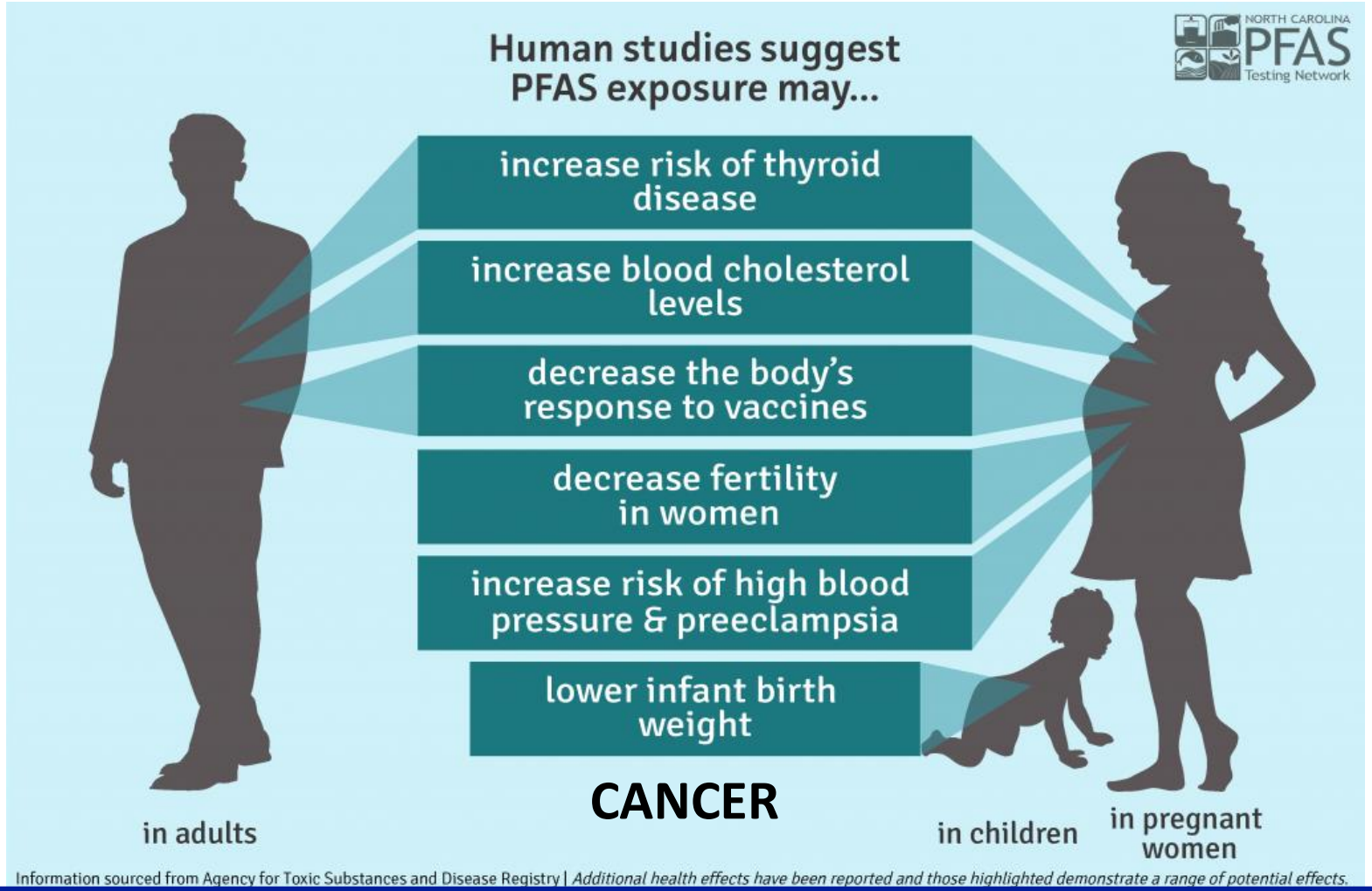


Figure. PFAS contamination can be found where PFAS is made, used, disposed of, or spilled. PFAS contamination is likely near facilities that use or have used fluorochemicals, commercial airports, military bases, wastewater treatment plants, farms where sewage sludge may have been used, or landfills or incinerators that have received PFAS-containing waste.

Human Exposure to PFAS

Fact: >99% of the US population has PFAS in their blood

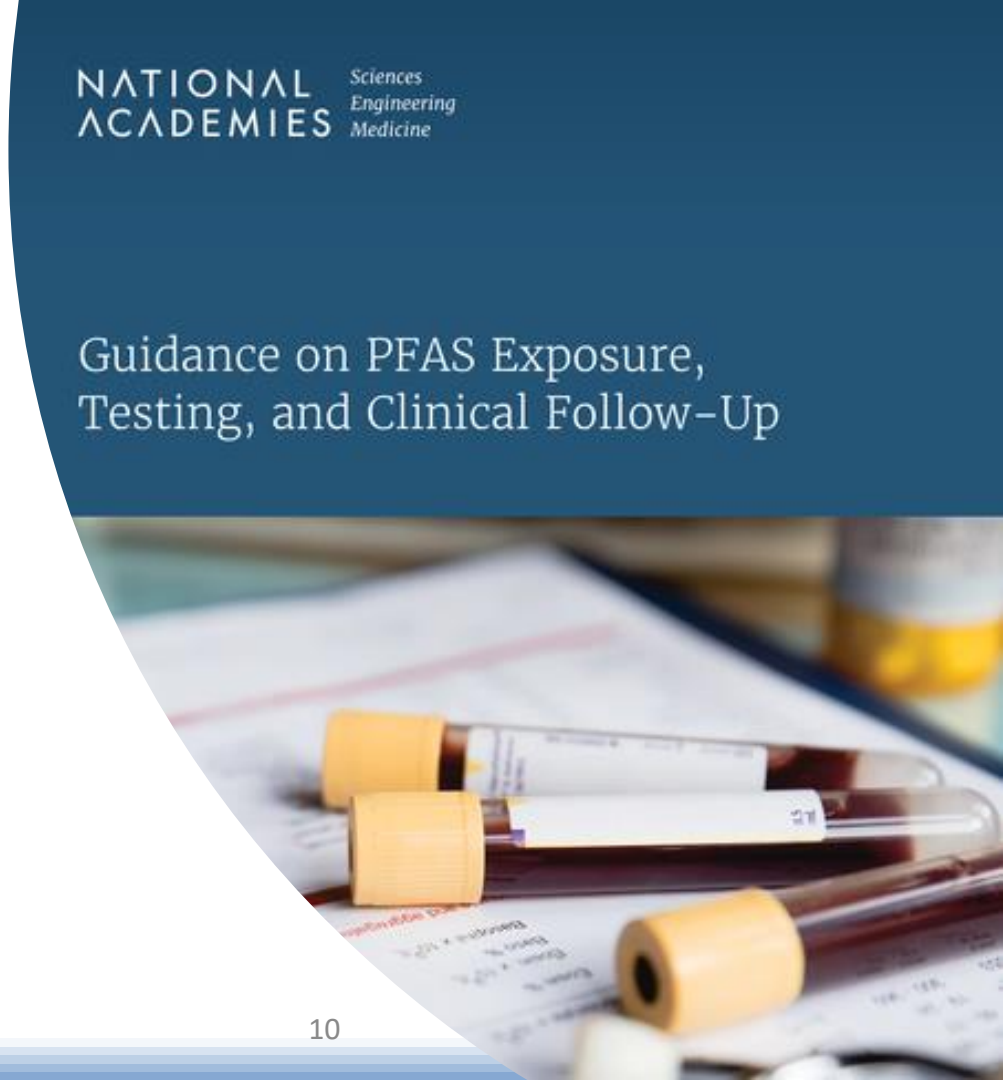
- Inhalation (gas-phase & particle)
- Inadvertent ingestion of dust
- Transfer across placenta in utero
- Ingestion of contaminated food, & ***drinking water***


Human studies suggest
PFAS exposure may...
NORTH CAROLINA PFAS Testing Network
increase risk of thyroid disease
increase blood cholesterol levels
decrease the body's response to vaccines
decrease fertility in women
increase risk of high blood pressure & preeclampsia
lower infant birth weight
CANCER
in adults
in children
in pregnant women
Information sourced from Agency for Toxic Substances and Disease Registry | Additional health effects have been reported and those highlighted demonstrate a range of potential effects.

PFAS Clinical Guidance

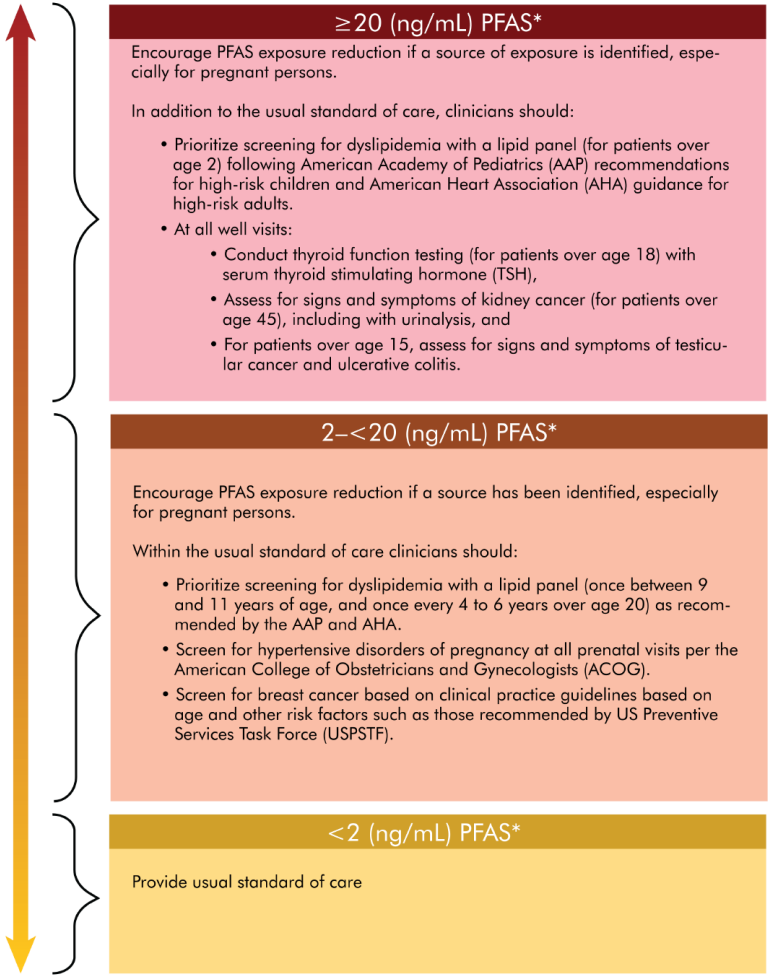
Report released online July 28, 2022

- Scientists and medical doctors evaluated the scientific literature
- Looked for epidemiological evidence
- Developed clinical guidelines and cancer screening recommendations based on blood levels



PFAS & Clinical Care

- Calculate the sum of these 7 PFAS:
  - PFOA
  - PFOS
  - PFHxS
  - PFNA
  - PFDA
  - PFUndA
  - MeFOSAA
- If >20 ng/mL, recommended medical screenings for high cholesterol, thyroid disease and some cancers
- Note: not all PFAS are measured in blood

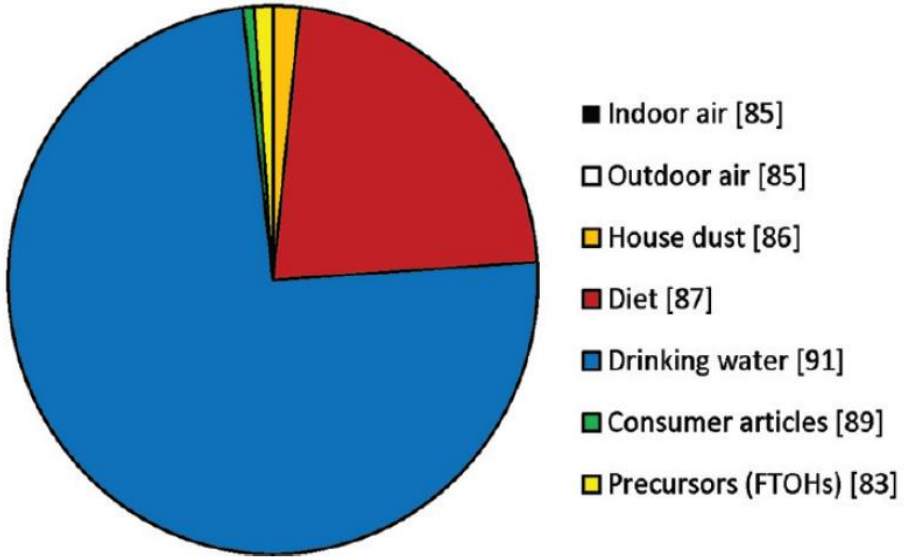


What are the Primary Sources of Exposure to PFAS?

PFOA Exposure in the General Population

- On average, >90% of our exposure to PFAAs is from our ***drinking water & food***
  - Drinking water dominates exposure when levels are above 100 pptr
  - PFAS exposure in food still important
  - Indoor exposure is minor contribution in these situations

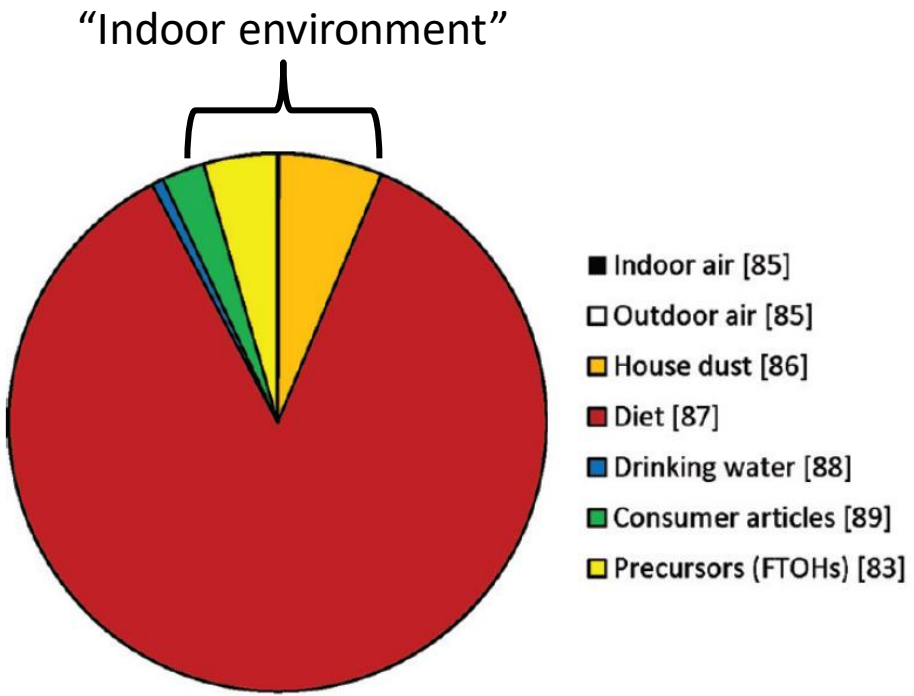
"High" Levels in Drinking Water (~500 pptr)



Source: Vestergren et al. 2009

PFOA Exposure in the General Population

- On average, 75-80% of our exposure to PFAAs is from our ***diet*** when
  - Low levels of PFAS in drinking water (<5 pptr)
- Greater percentage of exposure coming from indoor air/dust and precursors



Source: Vestergren et al. 2009

Question: Are PFAS Treated Furnishings Contributing to Human PFAS Exposure?

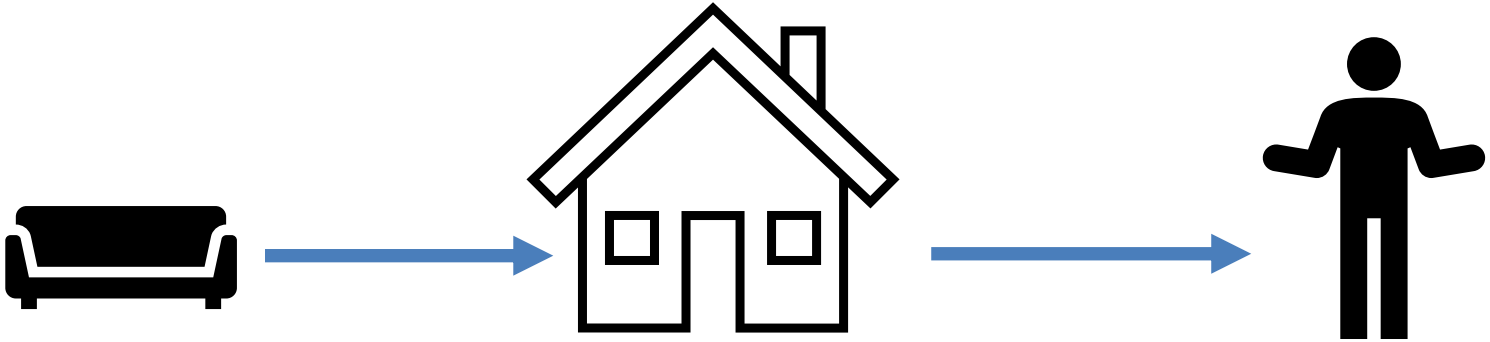
PFAS Treated Furnishings

Stain repellent treated carpets

Stain repellent treated furniture

From Source to Dose

(knowns and unknowns)



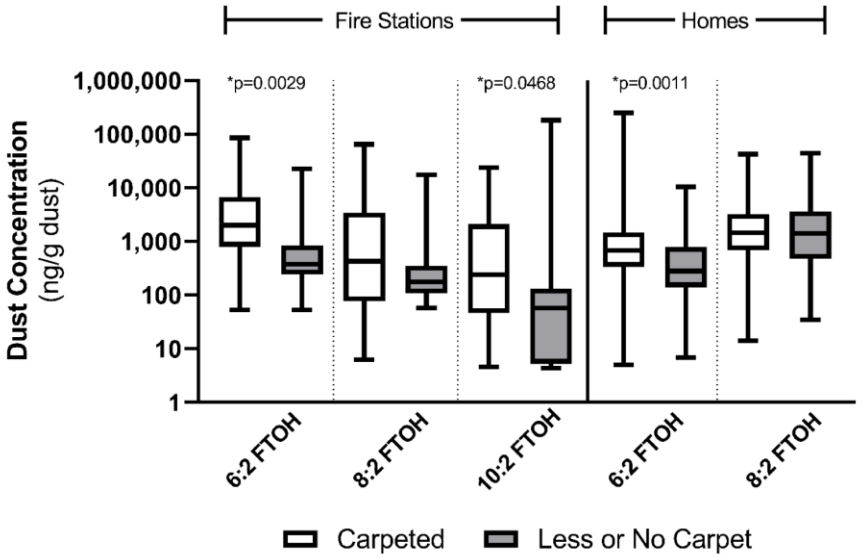
Treated Products

Exposure Media (air, dust)

Internal Dose (blood levels)

PFAS Levels in Dust Associated with Carpeting

- Dust was collected in NC homes and in the living quarters of fire stations
- Some PFAS (FTOHs) were higher in homes with more carpeting, suggesting carpeting was a source



Hall et al. 2020

PFAS Levels in Dust Associated with Carpeting

- Paired samples of dust and snips of the carpet fibers were collected in child care centers

- PFAS levels in the carpet fibers were significantly correlated with levels measured in dust

Chemosphere 251 (2020) 126771

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Per- and polyfluoroalkyl substances in paired dust and carpets from childcare centers

Yan Wu [a], Kevin Romanak [a], Tom Bruton [b], Arlene Blum [b], Marta Venier [a, *]

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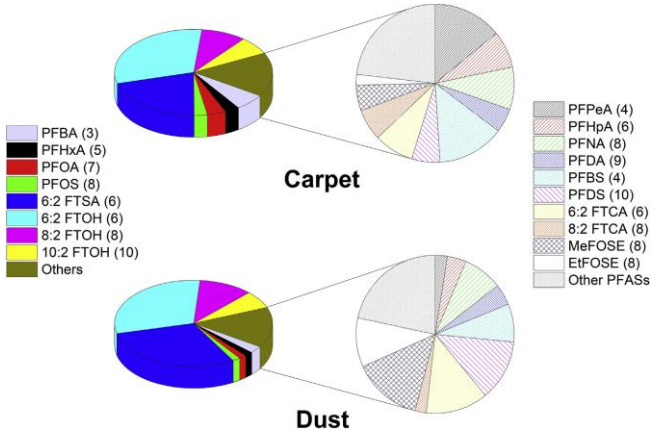
[b] Green Science Policy Institute, Berkeley, CA, 94709, United States



PFAS Levels in Blood Associated with Carpeting

- Analyzed PFAS blood levels reported in NHANES dataset based on survey characteristics of the home

- Two PFAS in blood (PFHxS and MeFOSAA) were significantly higher in individuals living in homes with low pile carpeting compared to individuals in homes with smooth surfaces

- 19-24% higher in blood when living in home with low pile carpeting

Environmental Research 195 (2021) 110758

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Household low pile carpet usage was associated with increased serum PFAS concentrations in 2005–2006

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[a] Program in Public Health, University of California, Irvine, CA, 92697-3957, USA
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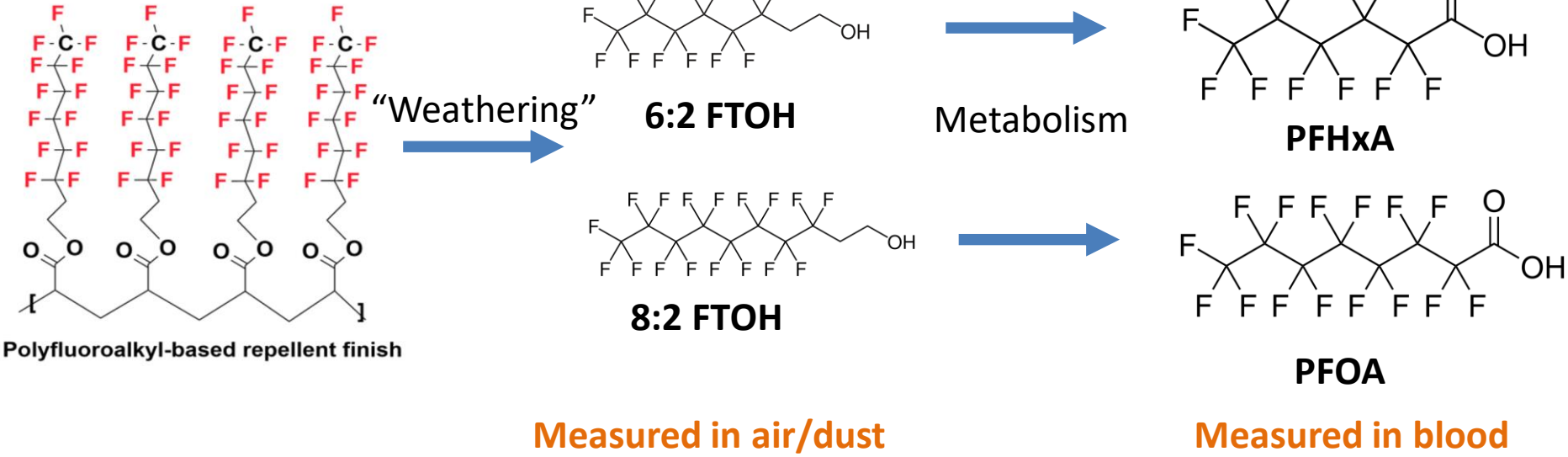
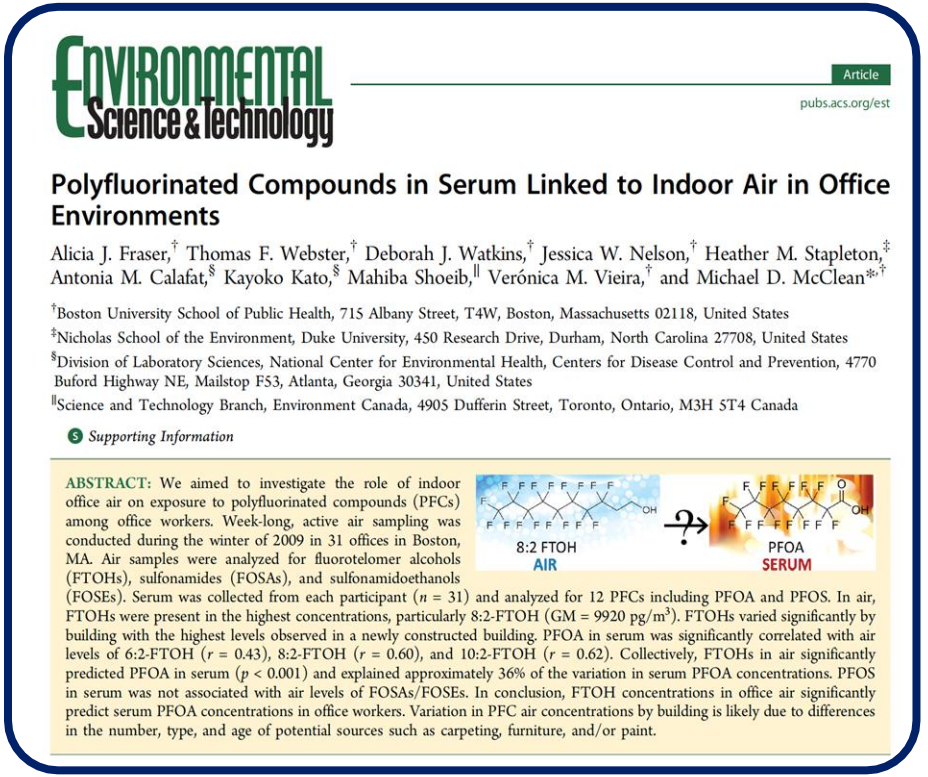
PFAS Precursor Degradation in Textiles

- PFAS treatments on textiles can break down over time to form volatile PFAS. See example below



"Precursors" can form harmful PFAS

- Air sampled in office buildings (both new and old)
- Blood collected from office workers
- 8:2 FTOH levels in air were significantly correlated with PFOA levels in blood



Environmental Science & Technology

Article

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Polyfluorinated Compounds in Serum Linked to Indoor Air in Office Environments

Alicia J. Fraser,[†] Thomas F. Webster,[†] Deborah J. Watkins,[†] Jessica W. Nelson,[†] Heather M. Stapleton,[‡] Antonia M. Calafat,[§] Kayoko Kato,[§] Mahiba Shoeib,[∥] Verónica M. Vieira,[†] and Michael D. McClean*[,†]

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Supporting Information

ABSTRACT: We aimed to investigate the role of indoor office air on exposure to polyfluorinated compounds (PFCs) among office workers. Week-long, active air sampling was conducted during the winter of 2009 in 31 offices in Boston, MA. Air samples were analyzed for fluorotelomer alcohols (FTOHs), sulfonamides (FOSAs), and sulfonamidoethanols (FOSEs). Serum was collected from each participant (n = 31) and analyzed for 12 PFCs including PFOA and PFOS. In air, FTOHs were present in the highest concentrations, particularly 8:2-FTOH (GM = 9920 pg/m^3). FTOHs varied significantly by building with the highest levels observed in a newly constructed building. PFOA in serum was significantly correlated with air levels of 6:2-FTOH (r = 0.43), 8:2-FTOH (r = 0.60), and 10:2-FTOH (r = 0.62). Collectively, FTOHs in air significantly predicted PFOA in serum (p < 0.001) and explained approximately 36% of the variation in serum PFOA concentrations. PFOS in serum was not associated with air levels of FOSAs/FOSEs. In conclusion, FTOH concentrations in office air significantly predict serum PFOA concentrations in office workers. Variation in PFC air concentrations by building is likely due to differences in the number, type, and age of potential sources such as carpeting, furniture, and/or paint.

Ongoing Research Study

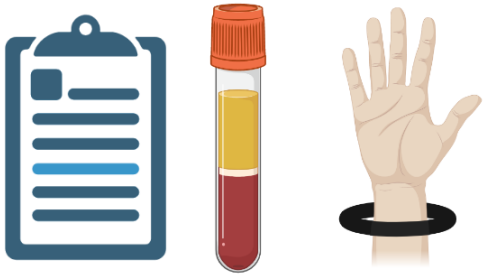
Dr. Courtney Carignan
Michigan State Univ.

Recruitment:

- Flyers
- Local Newspaper Ads
- Facebook Ads

Samples collected: June – November 2021

N = 87 individuals



- Questionnaire
- Blood serum collected
- Wristband worn for 1 week

N = 32 homes

- Passive air sampler
- Investigator collected dust

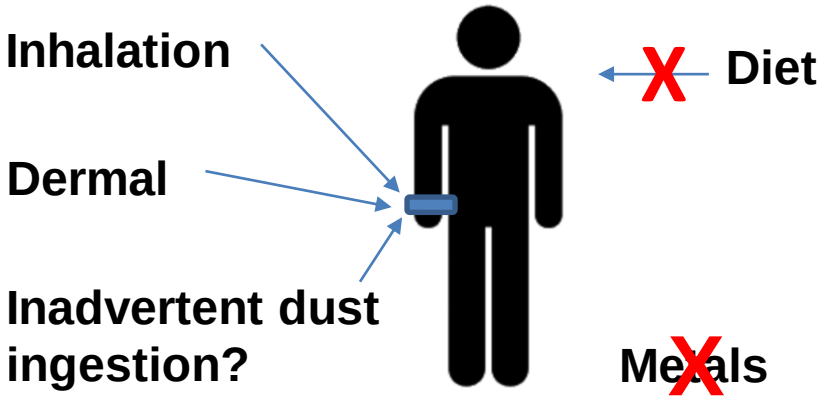
Inclusion Criteria:

- Living in or former resident of drinking water impacted Michigan community
- Children or adults
- Consumed city water or had a private well from 2005-2018

Wearable Samplers:
The Silicone Wristband

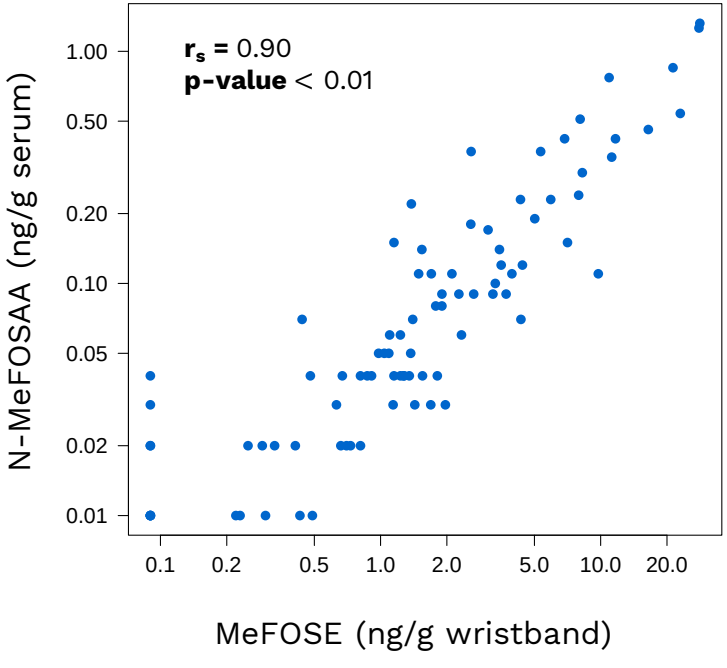
- **Wristbands first introduced as a wearable personal passive sampler to measure ambient exposure in occupational settings and in the general population (O'Connell et al., 2014)**

Exposure Routes



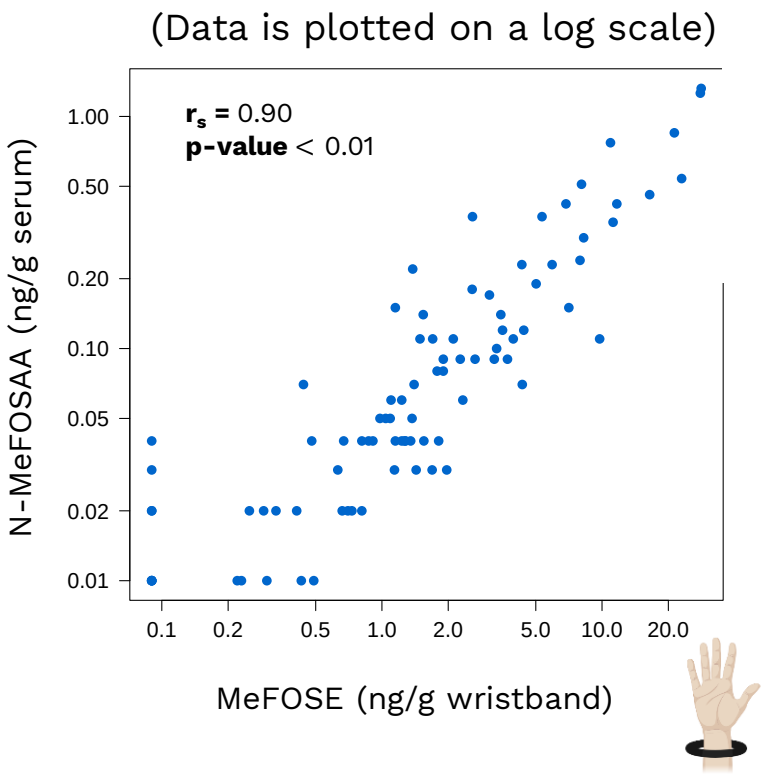
PFAS in Wristbands Predict Blood PFAS

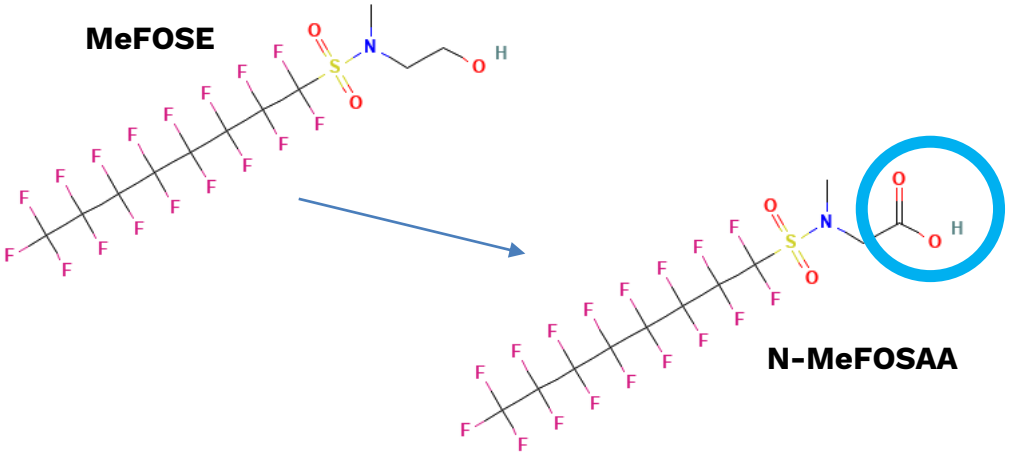
(Note: Data is plotted on a log scale)



Hoxie et al., Under Review

PFAS in Wristbands Predict Blood PFAS



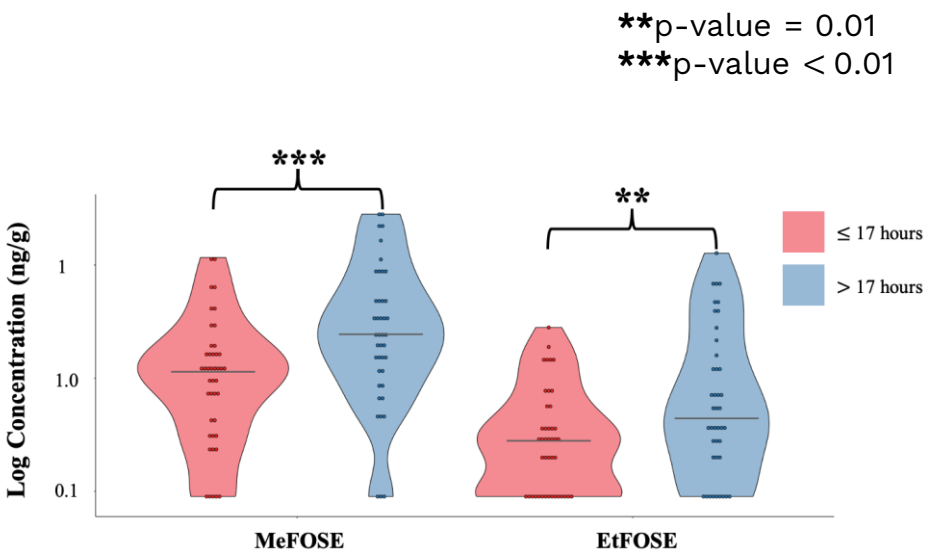


- Suggests that >80% of exposure is from indoor air or dust

Hoxie et al., Under Review

More Time Indoors = More PFAS Exposure

- Participants completed a survey and reported on average time spent in the home per day
- Wristband MeFOSE levels were ~2X higher if spent more than 17hrs in the home per day
- MeFOSE levels also higher with age of participant



Hoxie et al., Under Review

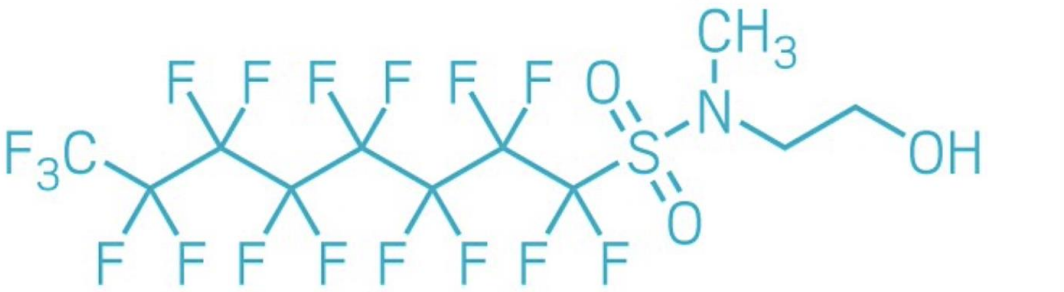
PERSISTENT POLLUTANTS

The EPA asks for more PFAS toxicity tests

3M, Wacker Chemical need to fill in data holes for *N*-MeFOSE

by ***Leigh Krietsch Boerner***

March 27, 2024 | A version of this story appeared in **Volume 102, Issue 10**



***N*-MeFOSE**

MOST POPULAR IN

Changes in the Carpet Industry

Results:

Home Depot to phase out some products containing PFAS chemicals

The home improvement company will stop purchasing and selling any carpets or rugs containing the toxics by the end of the year

- The carpet industry had recently shifted from the older long-chain C8 to short-chain C6 PFAS treatments and came into the workshop believing the chemical industry claim that C6 was not problematic. After learning that C6 and likely the whole class of PFAS were also harmful during our workshop, the companies all agreed at the end of the day to phase out all PFAS including C6 and other short chains substitutes.
- Several leading carpet manufacturers have told us our workshop and follow-up meetings were a catalyst for their moving away from all PFAS to better chemistries.
- Manufacturers that have completely phased out PFAS include Engineered Floors, Interface, Shaw, and Tarkett.
- As of January 2020, retailers The Home Depot and Lowe's have stopped selling any carpets and rugs treated with PFAS.
- In March 2021, major carpet manufacturer Shaw Industries gave our Institute a leadership award for our work supporting "the wellbeing of people and the planet amid the unprecedented challenges of 2020."
- On July 1, 2021, the California Department of Toxic Substance Control, who had participated in our 2018 workshop, designated carpets and rugs containing PFAS as a Priority Product for regulation.

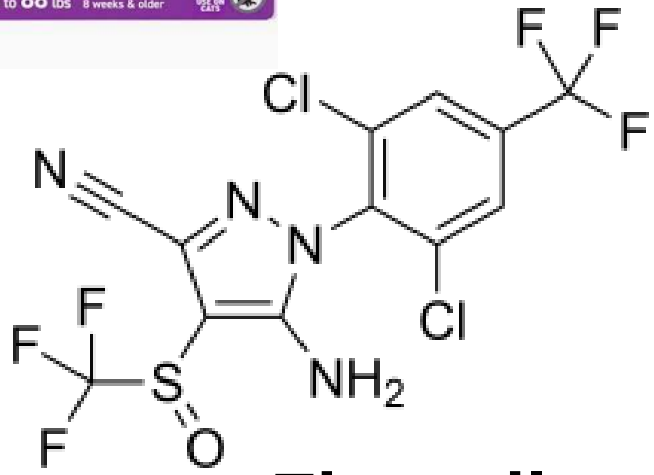
Challenges in the EPA Reporting Rule

There are a lot of unknown uses of PFAS – tracking in the supply chain can be difficult

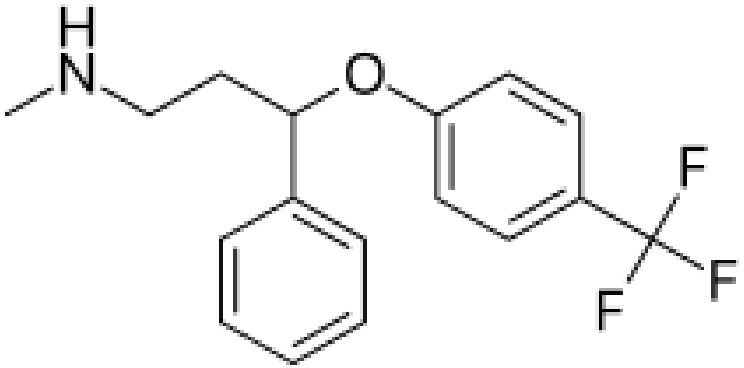
How do you define PFAS?

How do you measure PFAS?

Is it a PFAS?

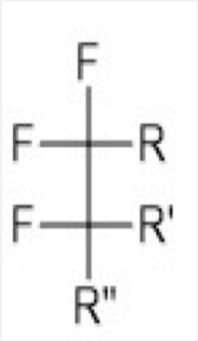


Fipronil



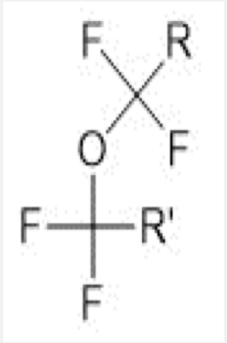
Prozac

EPA PFAS Reporting Rule: Is it a PFAS?



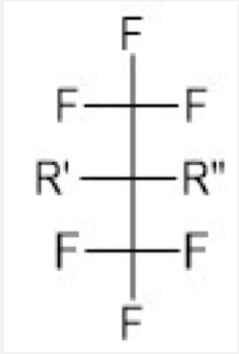
where R, R', R'' = any substituent

Structure 1



where R, R' = F, O, or $CR_1R_2R_3$

Structure 2



where R', R'' = F, or $CR_1R_2R_3$

Structure 3

Analyzing Materials for PFAS

- **Qualitative**
  - Total Oxidizable Precursor (TOP) assay – measures the mass of PFAS precursors that can break down into the PFAAs (more toxic forms)
  - Particle-induced gamma-ray emissions (PIGE) spectroscopy – measures elemental fluorine on thin surfaces
  - Adsorbable organic fluorine (AOF) or extractable organic fluorine (EOF)- measures the organofluorine content of a sample as fluoride using combustion ion chromatography.

- **Quantitative**
  - Mass Spectrometry
    - Do you want to measure neutral/volatile PFAS or ionic/aqueous PFAS?
    - Targeted or untargeted

Thermo Scientific™ Q Exactive™ GC Orbitrap™ GC-MS/MS

Closing Points

- PFAS exposure is ubiquitous
- Identifying which products/uses contributes most to human exposure is incredibly difficult due to unknown applications/uses in the home
- Diet is a dominant exposure route for some PFAS; however, exposure to N-MeFOSAA appears to be primarily via inhalation indoors
- More transparency in PFAS use can help identify where there are risks for exposure and where there is no/minimal risk

Acknowledgements

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- Lee Ferguson, PhD

collaboratory
science. policy. solutions.

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- Bryan Ormond

Colorado School of Mines

- Chris Higgins

Michigan State University

- Courtney Carignan

FIRE DEPARTMENT DURHAM N.C. 1872

V FOUNDATION
Victory Over Cancer

ThermoFisher SCIENTIFIC

NIH National Institute of Environmental Health Sciences
Your Environment. Your Health.

Duke Cancer Institute

ENTECH INSTRUMENTS

EPA United States Environmental Protection Agency

R01 ES016099
P42 ES010356

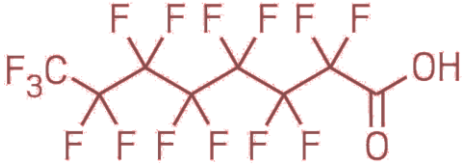
CR-83948201

HHEAR Human Health Exposure Analysis Resource

U2C ES030851

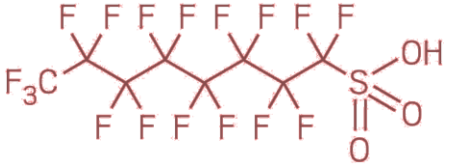
Michael & Annie Falk Foundation

High PFAS Exposure and Cancer



Perfluorooctanoic Acid (PFOA)

Group 1 Carcinogen



Perfluorooctane Sulfonic Acid (PFOS)

Group 2B Possible Carcinogen

- Kidney cancer – sufficient evidence for association with PFOA
- Testicular cancer - suggestive evidence for association with PFOA
- Breast cancer – limited and inconsistent evidence

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Article

An Outdoor Aging Study to Investigate the Release of Per- And Polyfluoroalkyl Substances (PFAS) from Functional Textiles

Steffen Schellenberger, Ioannis Liagkouridis, Raed Awad, Stuart Khan, Merle Plassmann, Gregory Peters, Jonathan P. Benskin, and Ian T. Cousins*

Cite This: *Environ. Sci. Technol.* 2022, 56, 3471−3479

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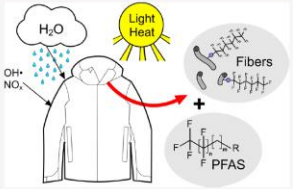
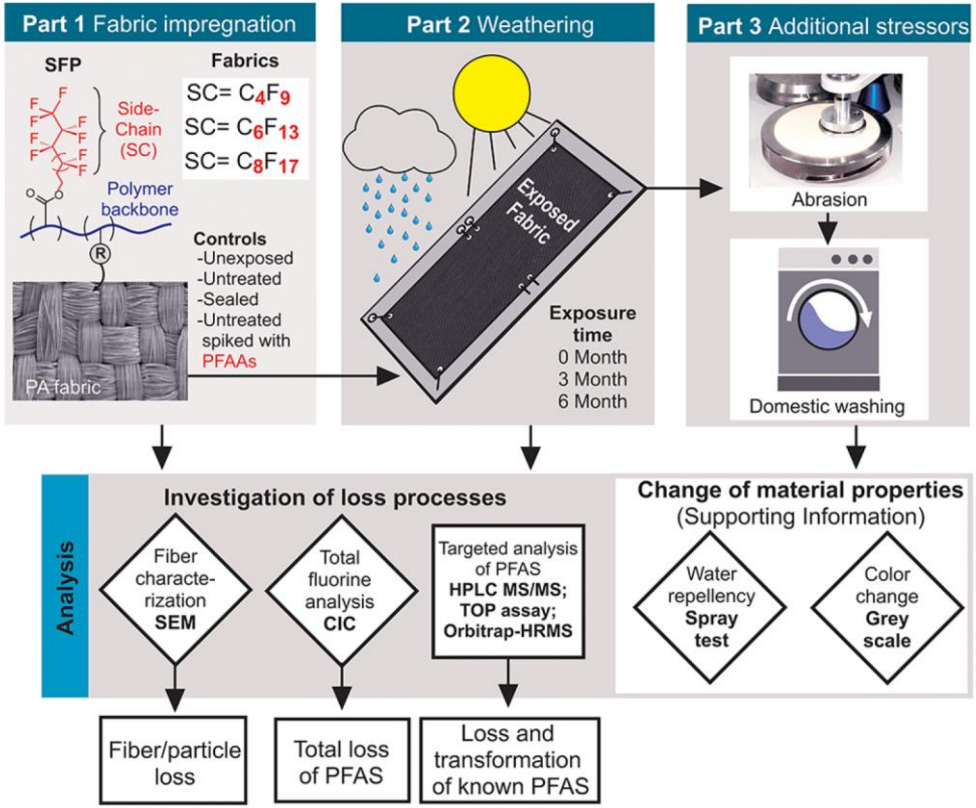
ABSTRACT: The emission of per- and polyfluoroalkyl substances (PFAS) from functional textiles was investigated via an outdoor weathering experiment in Sydney, Australia. Polyamide (PA) textile fabrics treated with different water-repellent, side-chain fluorinated polymers (SFPs) were exposed on a rooftop to multiple natural stressors, including direct sunlight, precipitation, wind, and heat for 6-months. After weathering, additional stress was applied to the fabrics through abrasion and washing. Textile characterization using a multiplatform analytical approach revealed loss of both PFAS-containing textile fragments (e.g., microfibers) as well as formation and loss of low molecular weight PFAS, both of which occurred throughout weathering. These changes were accompanied by a loss of color and water repellency of the textile. The potential formation of perfluoroalkyl acids (PFAAs) from mobile residuals was quantified by oxidative conversion of extracts from unweathered textiles. Each SFP-textile finish emitted a distinct PFAA pattern following weathering, and in some cases the concentrations exceeded regulatory limits for textiles. In addition to transformation of residual low molecular weight PFAA-precursors, release of polymeric PFAS from degradation and loss of textile fibers/particles contributed to overall PFAS emissions during weathering.



KEYWORDS: *PFAS, diffuse emissions, textile weathering, microplastic fibers, total fluorine analysis, functional textile*



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