Flame Retardants, PFAS and Firefighters

Graham Peaslee

University of Notre Dame

LAST CALL FOUNDATION
In Memory of Fallen Firefighter Michael Kennedy

February 8, 2020

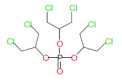
Plus ça change, plus la même chose…

The James and Jeanette Neckers Lectureship in Chemistry

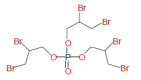
Winants Auditorium, Graves Hall
and the DeWitt Theatre
March 10-11, 2011
Hope College

Dr. Arlene Blum

Executive Director of the Green Science Policy Institute and Visiting Scholar in the Department of Chemistry University of California, Berkeley



Tris(1,3-dichloro-2-propyl) phosphate
Flame retardant in common use today



Tris(2,3-dibromopropyl) phosphate
Flame retardant banned in 1977 for use in children's clothing

Public Lecture
Seminar 7:00 pm
DeWitt Theatre

Climbing Your Own Everests: Peaks, Public Health, and Policy

Climbing the world's highest mountains is an excellent model for achieving other extremely demanding objectives. Dr. Blum will share photos and stories from her scientific and policy work protecting our health and environment from toxins in consumer products, as well as from her expeditions among the world's highest and most dangerous mountains. Dr. Blum's current challenge is bringing scientists, industry, government, and non-profits together to create a healthier, safer environment. Her work bringing science into regulatory decisions has stopped the unnecessary use of hundreds of millions of pounds of toxic chemicals.

Neckers Lecture
Refreshments 3:30, Seminar 4:00
Winants Auditorium, Graves Hall

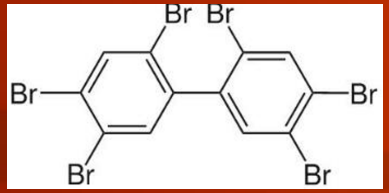
Organohalogens in Consumer Products: Do the Fire Safety Benefits Justify the Health and Environmental Risks?

Organohalogens are commonly used as flame retardants in consumer products, particularly furniture and baby products, although it is not clear that these compounds really lead to increased fire safety. In addition, some organohalogens are known to cause neurological, reproductive, and thyroid health problems, as well as cancer. As the products move to landfills and other waste streams, they also negatively impact the environment. In this talk, Dr. Blum will discuss how academic scientists can be engaged with policy making to stop the unnecessary use of potentially toxic flame retardants in consumer products.

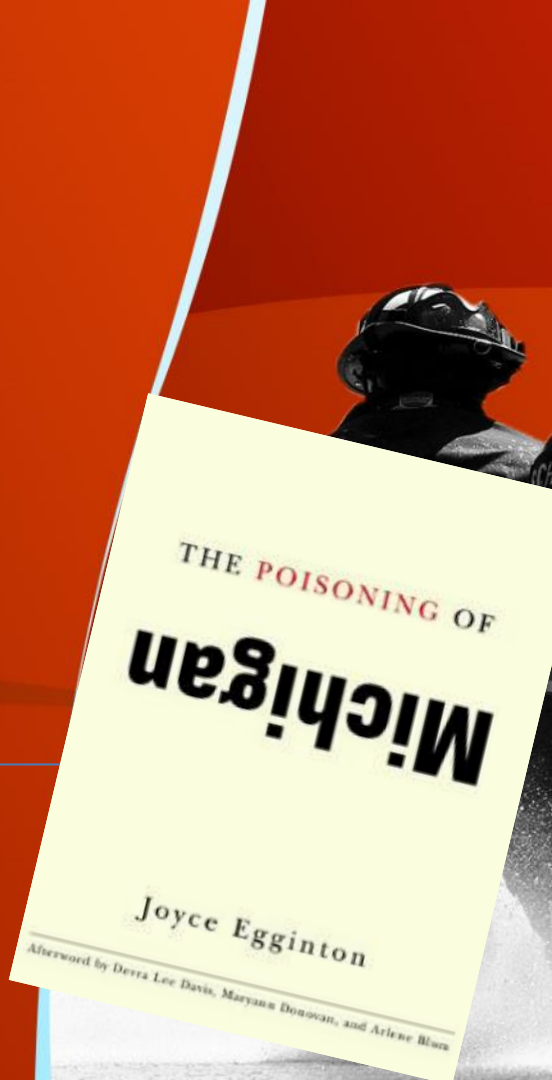
Dr. Arlene Blum received her bachelor's degree from Reed College and her Ph.D. in biophysical chemistry from the University of California, Berkeley, where she worked under the mentorship of Dr. Ignacio Tinoco. As a post-doc with Dr. Bruce Ames at Berkeley, Dr. Blum demonstrated the cancer-causing properties of two flame retardants widely used in children's sleepware, which led directly to their regulation (for example, the brominated molecule, above). Dr. Blum took a break from science to build a reputation as a mountain climber and author. She led the first American—and all-women's—ascent of Annapurna I (8,091m), considered one of the world's most dangerous and difficult mountains. She also led the first women's team up Mt. McKinley (6,194m) and was the first American woman to attempt Mt. Everest (8,848m). After three decades of climbing and writing books, Dr. Blum returned to science and policy work in 2006 after learning that the same chemicals she worked to remove from children's sleepware in the 1970's are currently used in furniture and baby products. Through the Green Science Policy Institute she seeks to bring scientific research to the forefront to inform policy decisions with regard to human health and environmental impact. For her work Dr. Blum has received a number of awards including being named as one of the 100 *"Women Taking the Lead to Save Our Planet"*, the Purpose Prize, given to those over 60 who are solving society's greatest problems, and a Gold Medal from the Society of Women Geographers, an honor previously given to only eight other women, including Amelia Earhart, Margaret Mead, and Mary Leakey.

In addition to the Chemistry Department's Neckers Fund, Dr. Blum's visit is co-sponsored by the Campus Sustainability Task Force, the Hope College HHMI grant, Geology and Environmental Sciences, and Women's Studies.

- 9 years ago…
- Flame retardants…

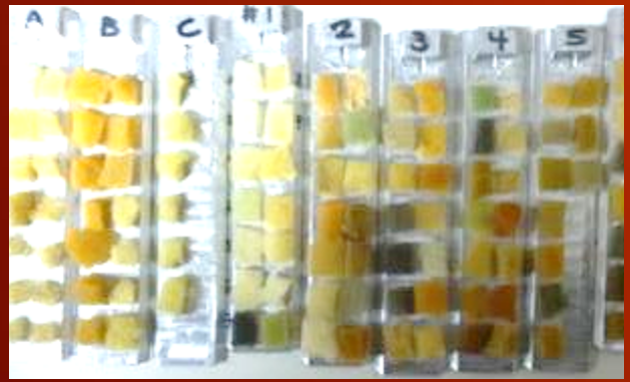


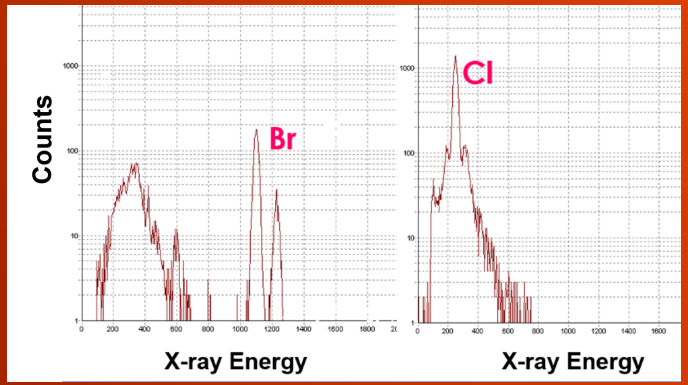
- Do something…



PIXE For Flame Retardant Detection

flame retardants: by detecting Br, Cl





Science & Policy

WINNER OF THE 2012 PULITZER PRIZE FOR COMMENTARY

Chicago Tribune

QUESTIONS? CALL 1-800-TRIBUNE — SUNDAY, MAY 6, 2012 — BREAKING NEWS AT CHICAGOTRIBUNE.COM

TRIBUNE WATCHDOG

Playing with fire

A deceptive campaign by industry brought toxic flame retardants into our homes and into our bodies. And the chemicals don't even work as promised.

CONSUMER PRODUCT SAFETY COMMISSION PHOTO

By Patricia Callahan and Sam Roe
Tribune reporters

Dr. David Heimbuch knows how to tell a story.

Before California lawmakers last year, the noted burn surgeon drew gasps from the crowd as he described a 7-week-old baby girl who was burned in a fire started by a candle while she lay on a pillow that lacked flame retardant chemicals.

"Now this is a tiny little person, no bigger than my Italian greyhound at home," said Heimbuch, gesturing to approximate the baby's size. "Half of her body was severely burned. She ultimately died after about three weeks of pain and misery in the hospital."

Heimbuch's passionate testimony about the baby's death made the long-term health concerns about flame retardants voiced by doctors, environmentalists and even firefighters sound abstract and petty.

But there was a problem with his testimony: It wasn't true. Records show there was no dangerous pillow or candle fire. The baby he described didn't exist.

Neither did the 9-week-old patient who Heimbuch told California legislators died in a candle fire in 2009. Nor did the 6-week-old patient who he told Alaska lawmakers was fatally burned in her crib in 2010.

Heimbuch is not just a prominent burn doctor. He is a star witness for the manufacturers of flame retardants.

His testimony, the Tribune found, is part of a decades-long campaign of deception that has loaded the furniture and electronics in American homes with pounds of toxic chemicals linked to cancer, neurological deficits, developmental problems and impaired fertility.

The tactics started with Big Tobacco, which wanted to shift focus away from cigarettes as the cause of fire deaths, and continued as chemical companies worked to preserve a lucrative market for their products, according to a Tribune review of thousands of government, scientific and internal industry documents.

Those powerful industries distorted science in ways that overstated the benefits of the

stoked the public's fear of fire and helped organize and steer an association of top fire officials that spent more than a decade campaigning for their cause.

Today, scientists know that some flame retardants escape from household products and settle in dust. That's why toddlers, who play on the floor and put things in their mouths, generally have far higher levels of these chemicals in their bodies than their parents.

Blood levels of certain widely used flame retardants doubled in adults every two to five years between 1970 and 2004. More recent studies show levels haven't declined in the U.S. even though some of the chemicals have been pulled from the market. A typical American baby is born with the highest recorded concentrations of flame retardants among infants in the world.

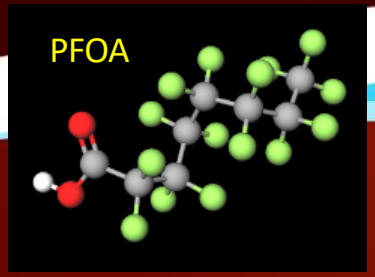
People might be willing to accept the health risks if the flame retardants packed into sofas and easy chairs worked as promised. But they don't.

The chemical industry often

FOR IMMEDIATE RELEASE:
Monday, June 18, 2012

Governor Brown Directs State Agencies to Revise Flammability Standards

What makes PFAS so good?

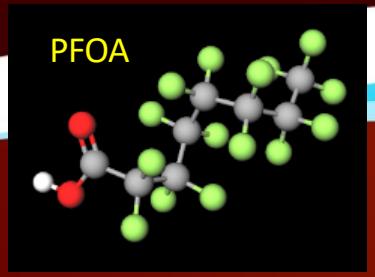


These compounds are used everywhere:

Average Bond Energies (kJ/mol)

Bond	Energy
Single Bonds	
H—H	432
H—F	565
H—Cl	427
H—Br	363
H—I	295
C—H	413
C—C	347
C—Si	301
C—N	305
C—O	358
C—P	264
C—S	259
C—F	453
C—Cl	339
C—Br	276
C—I	216

So what is the problem?



The carbon-fluorine bond is very hard to break- these compounds have environmental lifetimes ≈100's of years or more!

Many have no known biotic or abiotic degradation pathways….

ENVIRONMENTAL PERSISTENCE

The "forever chemicals" …

Average Bond Energies (kJ/mol)

Bond	Energy
Single Bonds	
H—H	432
H—F	565
H—Cl	427
H—Br	363
H—I	295
C—H	413
C—C	347
C—Si	301
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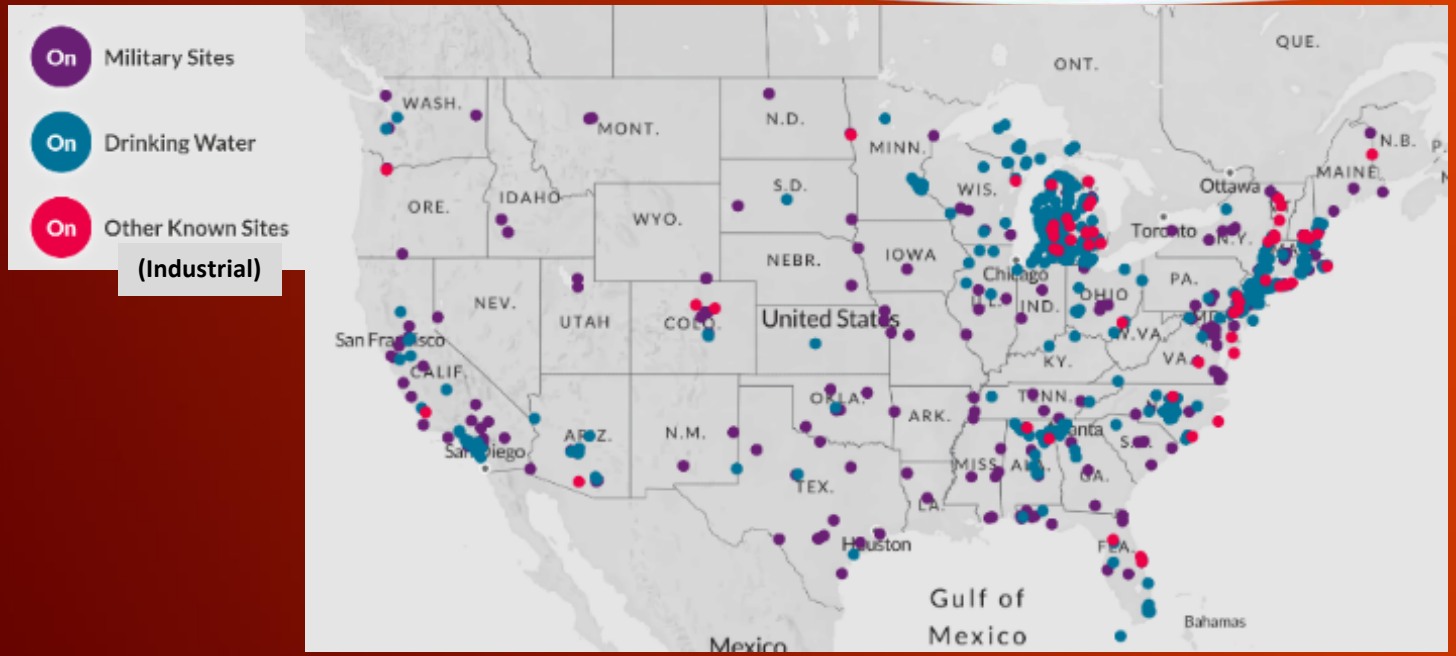
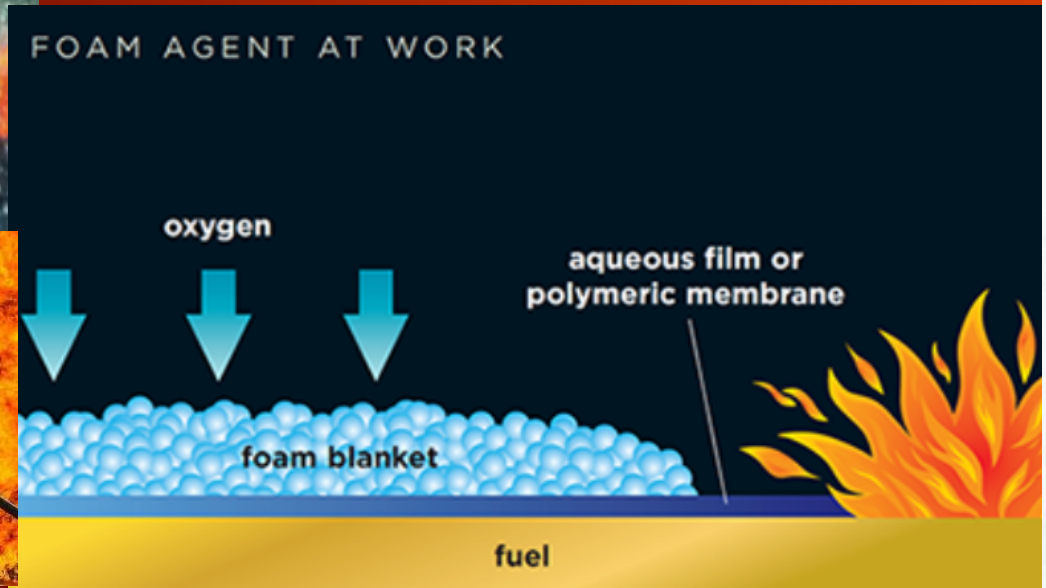
These are only the US sites to date…



https://www.ewg.org/interactive-maps/2019_pfas_contamination/map/

PFAS and Firefighters

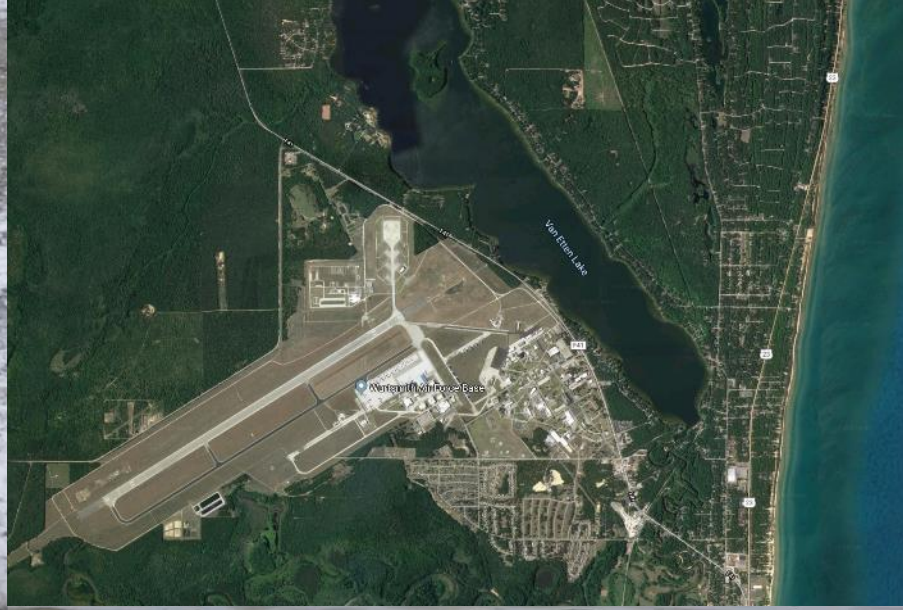
AFFF – Class B Foams



DoD extensive use…

A U.S. Air Force airman blows firefighting foam that was unintentionally released in an aircraft hangar at Travis Air Force Base, Calif., in 2013. Toxic chemicals in the foam have contaminated private wells in Box Elder and municipal wells in Sioux Falls.

"An undated photo of PFAS foam sampling on Van Etten Lake in Oscoda Township near Wurtsmith Air Force Base. Testing by the Air Force has found high levels of the toxic chemical PFOS in the foam near a plume coming from the former nuclear bomber base." (Courtesy | Michigan DEQ)



DoD extensive use…

AFFF – Class B Foams

PFAS Exposure sources:

- Active fire event
- Decon post event
- Aerosolized foam & combustion products
- Drinking water contamination***

Are there other PFAS exposure sources?

PIGE Analysis of Fluorine

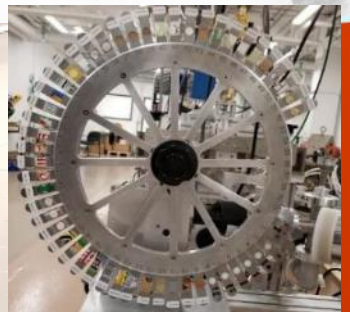
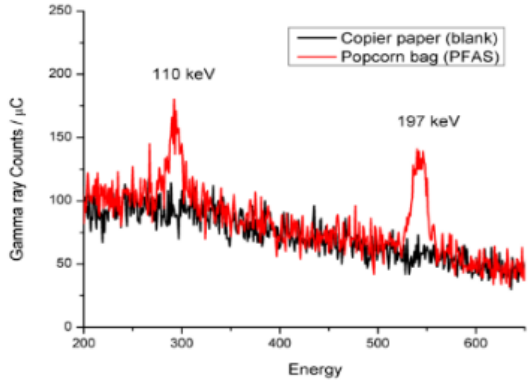
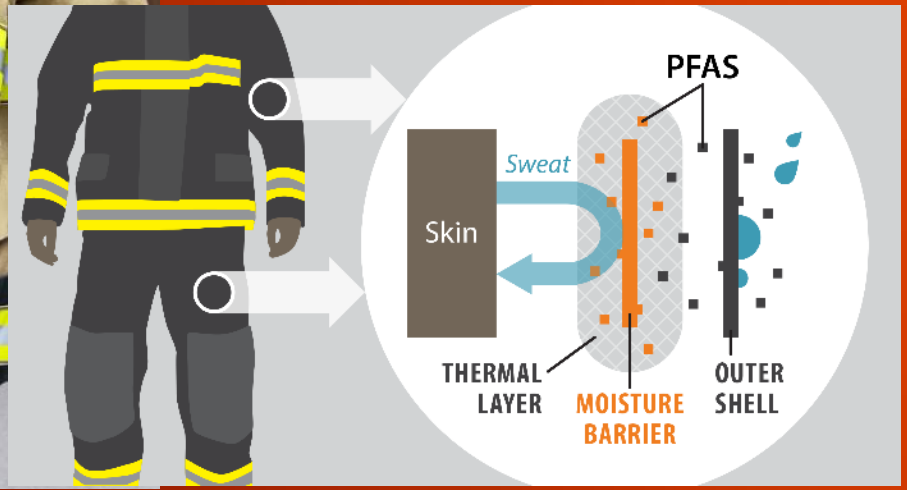


Fig. 3: PFAS-coated paper sample compared with uncoated paper. Irradiation time of 180 second with 9 nA of 3.4 MeV protons.



Turnout Gear Study @ ND

1. Are PFAS in all gear?
2. Do PFAS come off ?
3. Do PFAS get into FF?



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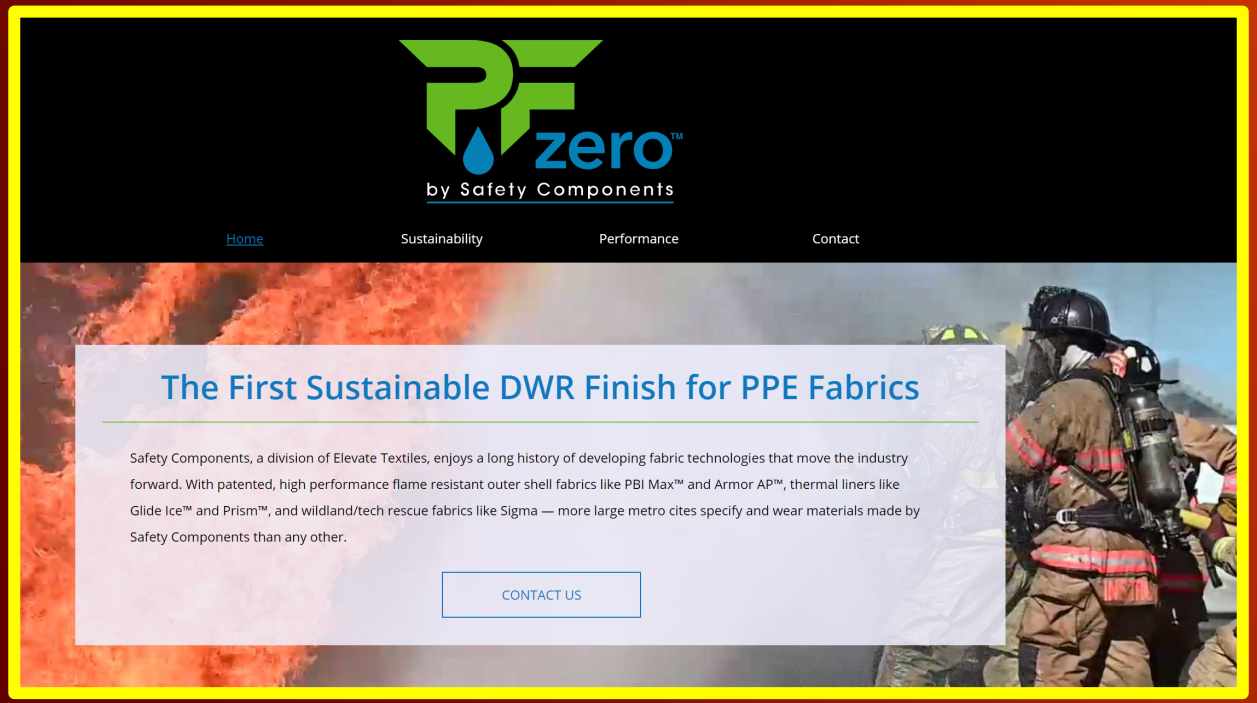


January, 2020

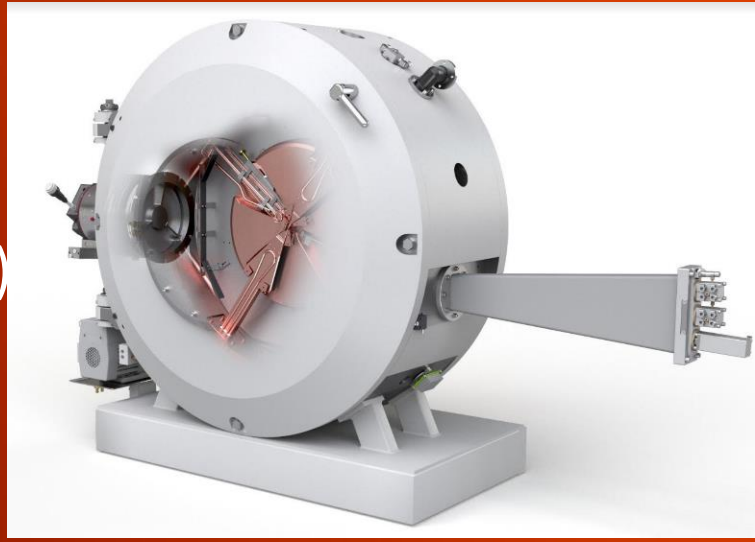
Next: Commercialization of PIGE

Partner with medical cyclotron manufacturer:

- Use GENTrace cyclotron (100,000 samples/yr)
  - Run 3 L of water through GAC felt filter (minutes in field)
  - Dry filters (hours)
  - Send filters for PIGE analysis (1-2 minutes per sample)
  - Identify all sum of all PFAS present

Screening method: **No F, no PFAS….**

GE Healthcare



Acknowledgements

John Wilkinson, Sean McGuinness, Meghanne Tighe, Ashabari Majumdar, Nick Caterisano, Matt Roddy, Alec Gonzales, Seryoeng Lee, Chase Miller

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Vista Analytical Laboratory