Using PIGE to Screen for an Environmental Toxin

Graham Peaslee
University of Notre Dame

Crete 2017
June 13, 2017

Outline

- Context: Environmental IBA Applications
- Motivation: PerfluoroAlkyl Substances
- Method: PIGE
- Results:

  Consumer products
  Contaminated groundwater samples
- Future Implications…

Ion Beam Analysis (IBA)

- The Techniques
  - PIXE, PIGE,
  - RBS, ERDA,
  - NRA,
  - PESA,
  - IBIL,
  - SIMS,…
- The Applications
  - Cultural History
  - Biomedical
  - Industrial
  - Environmental

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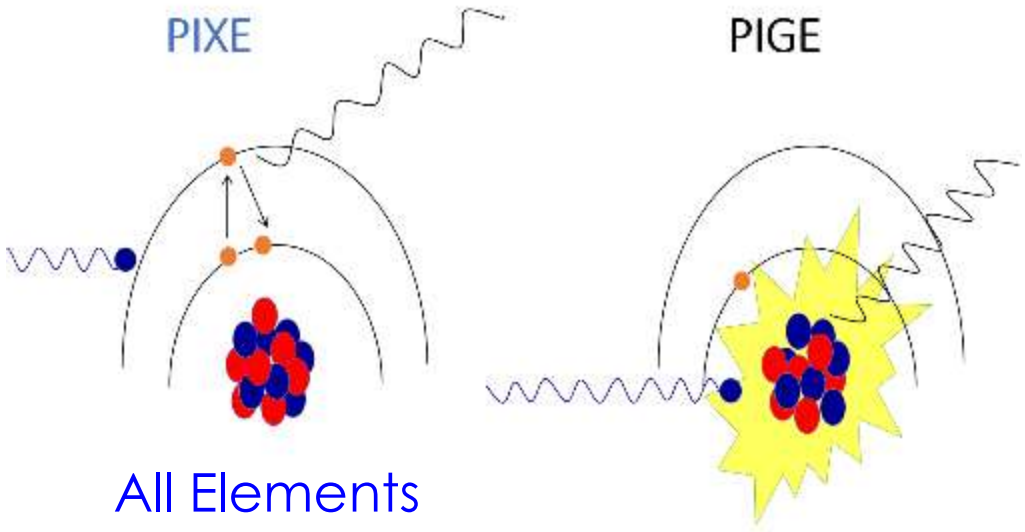

Ion Beam Analysis (IBA)

- The Techniques
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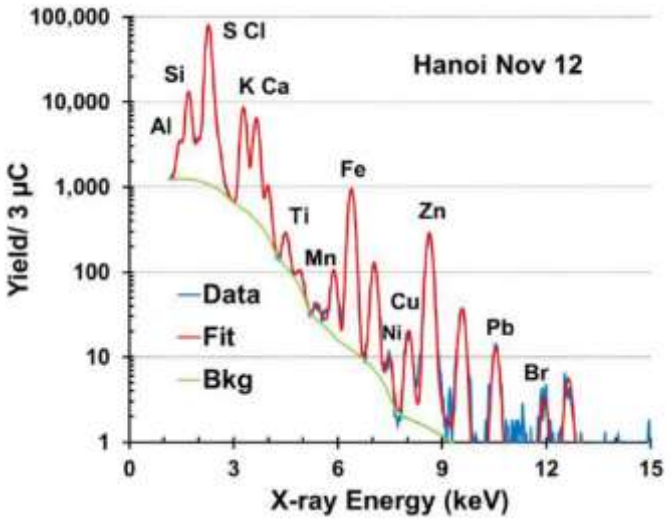


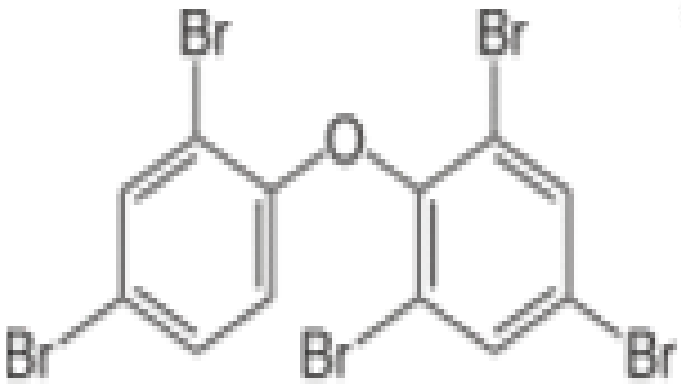
Aerosol Sampling Program: fine particle pollution research

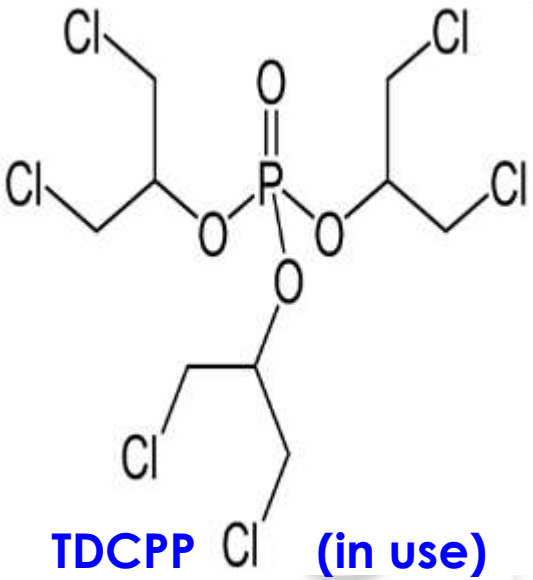
Key contacts: David Cohen, Eduard Stelcer, Armand Atanacio

Prof David Cohen revealing the sources of Sydney's air pollution

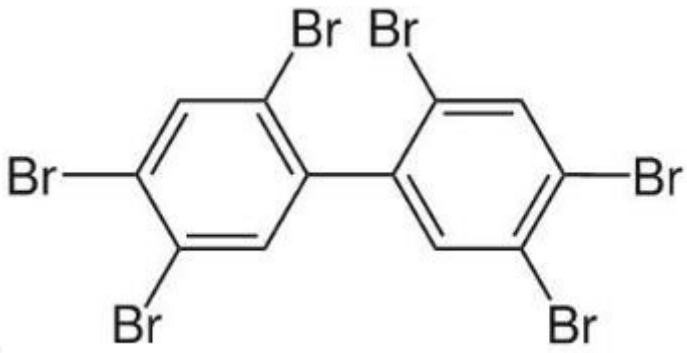
Commonly Used Flame Retardants

- Penta-BDE (Polybrominated Diphenyl Ethers)
  - Production discontinued ~ 2006
- Polybrominated biphenyls (PBB's)
- Removed from market ~2003



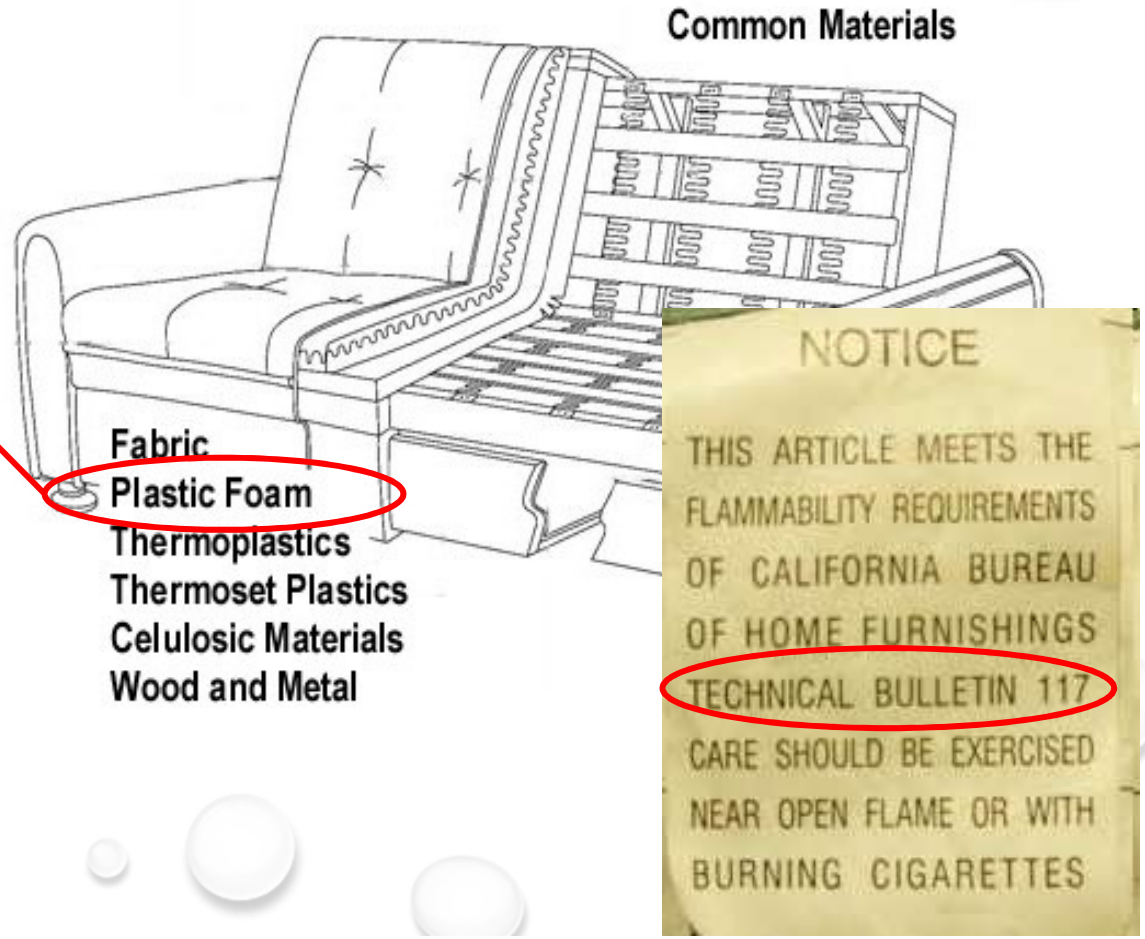


TDCPP (in use)

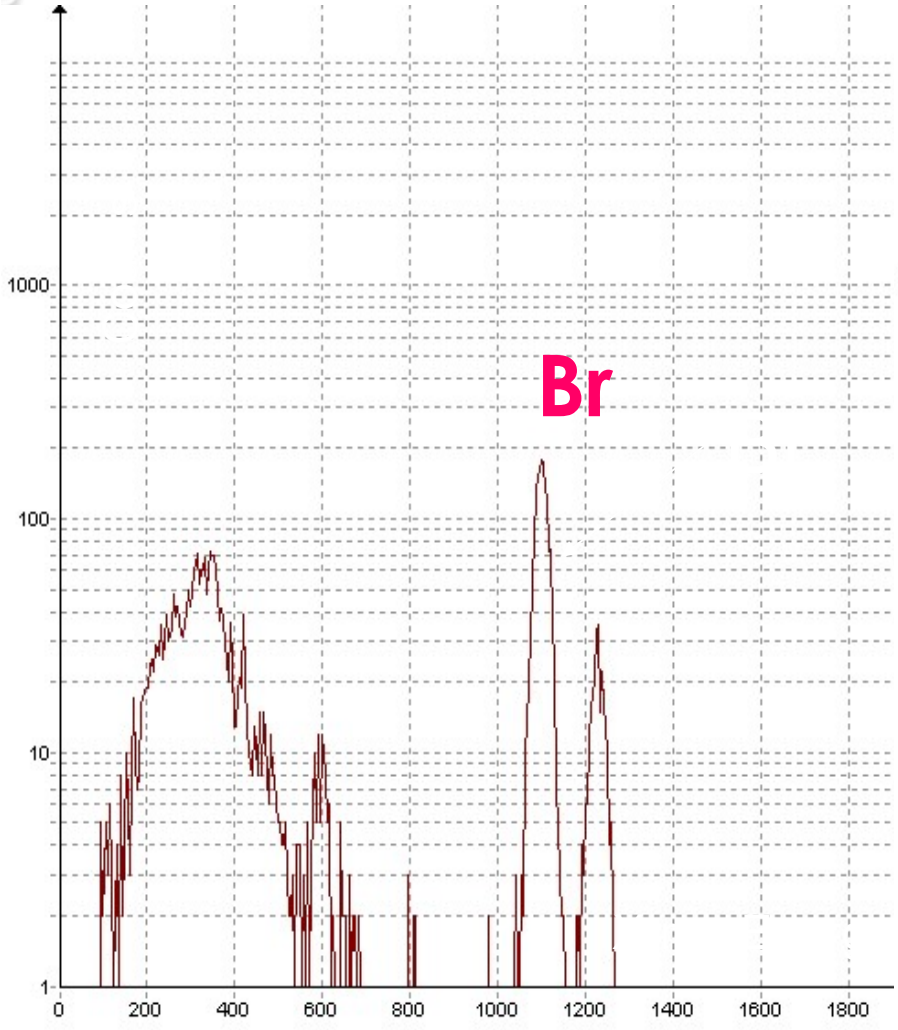


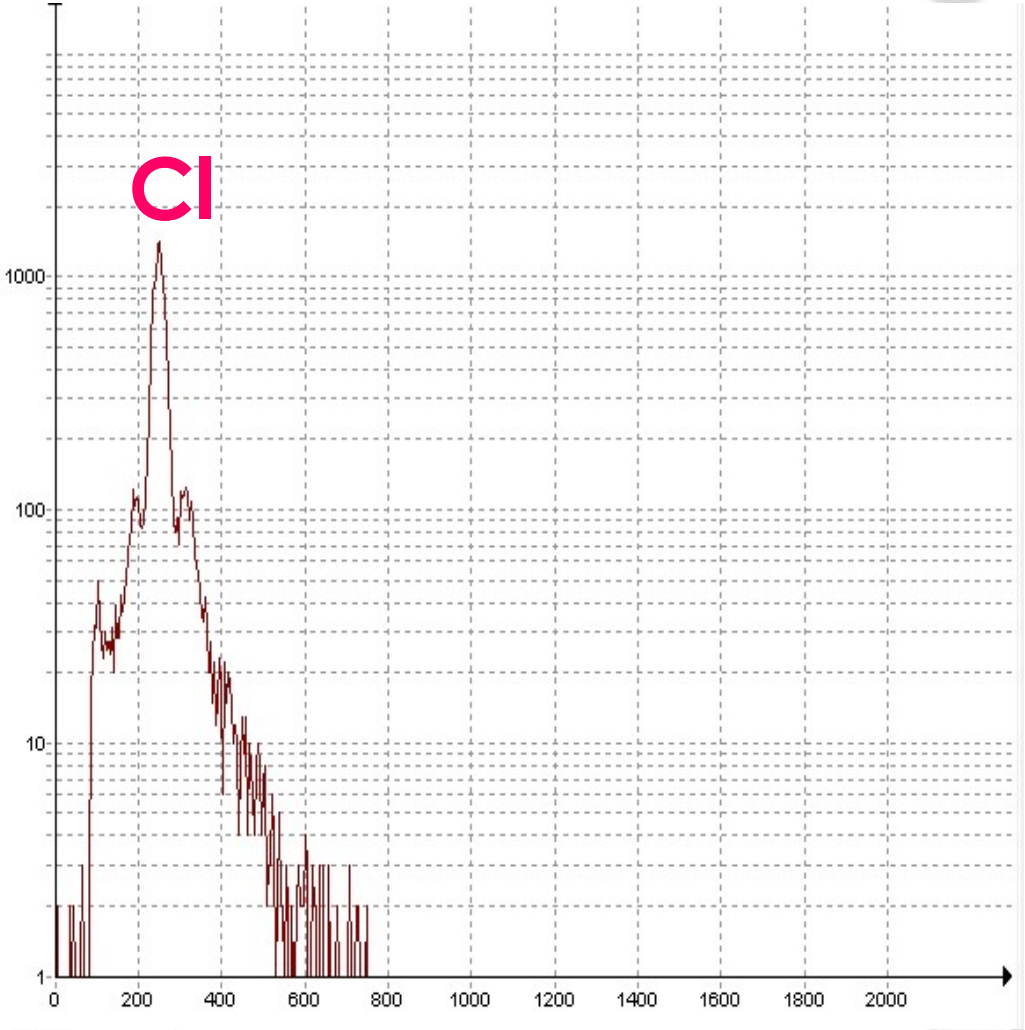
BFRs widely used in home furnishings…

Typically 3 - 6% by weight in polyurethane foam



Flame Retardant Spectra

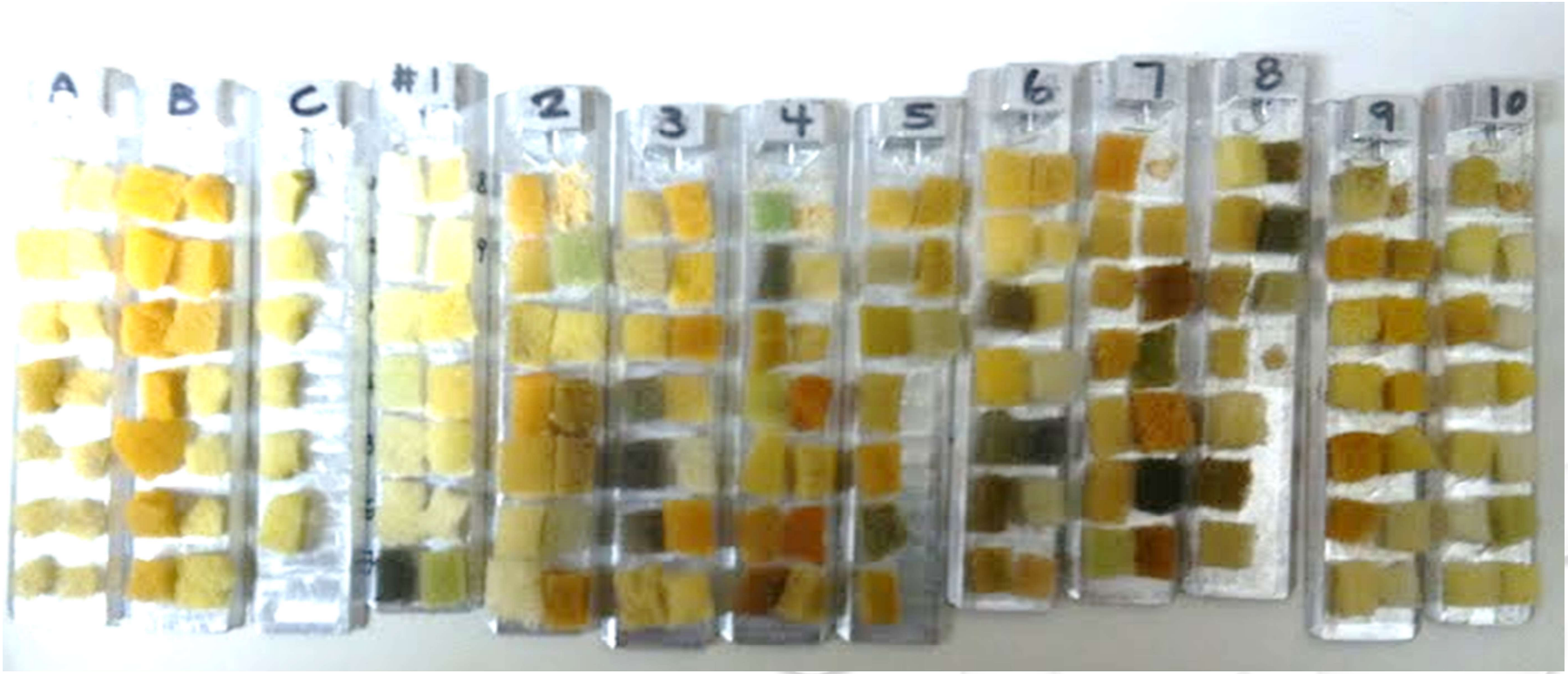




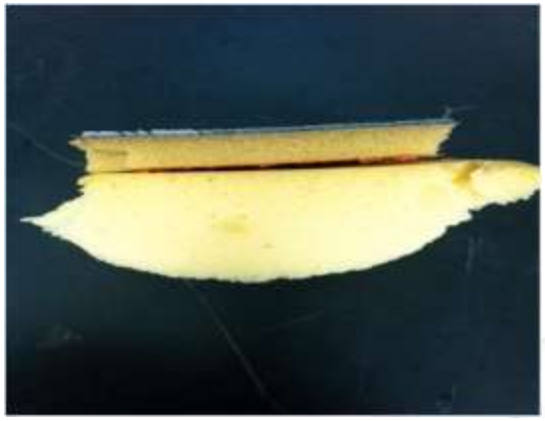
Typical levels around 1 - 5 wt %

PIXE Method Development

- Whole pieces of foam
- Placed onto adhesive mounts



PIXE Analysis of halogenated FRs in Automotive Seating



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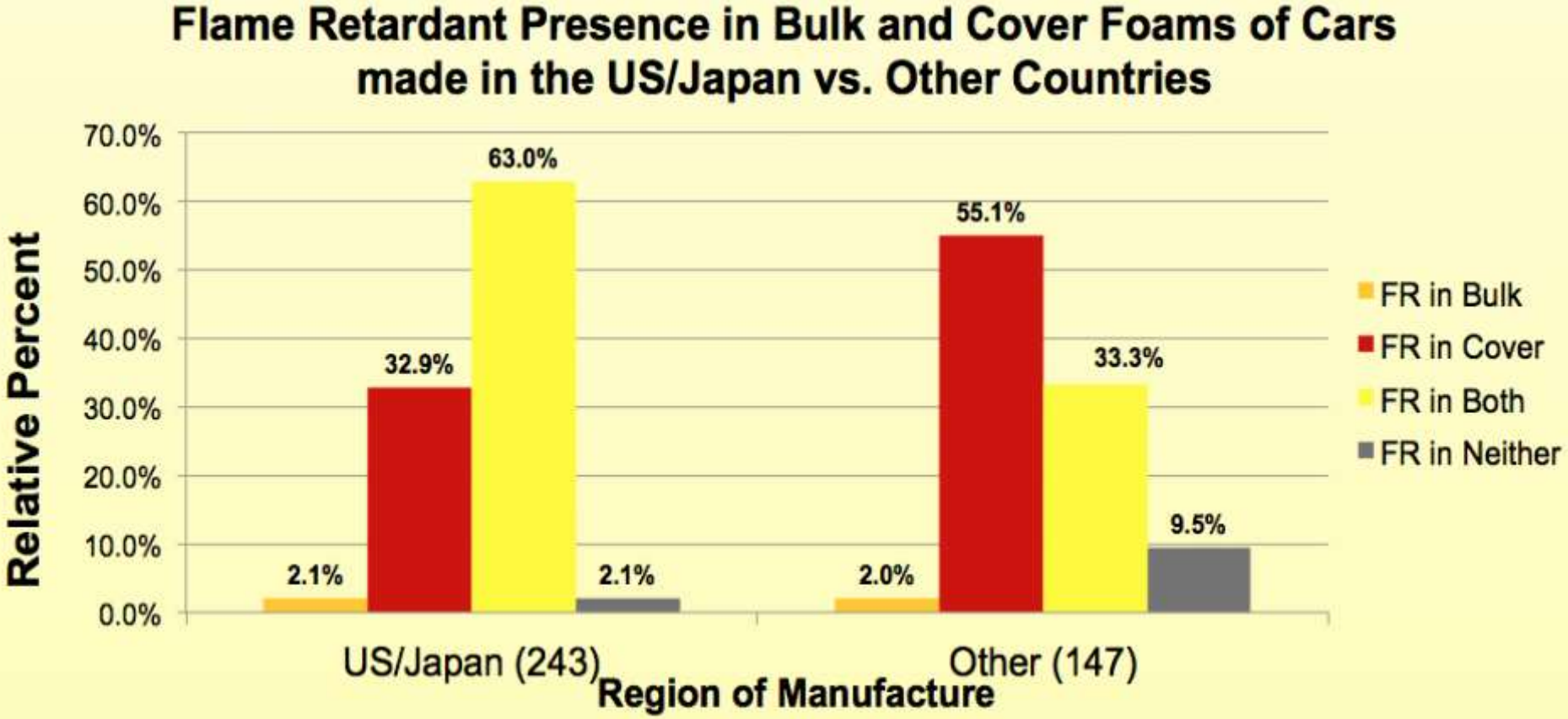


Figure 14: PIXE results for the presence and absence of chlorinated and brominated FRs in bulk and/or cover polyurethane foam seating layers of 390 automobiles based on region of automobile manufacturing plant.

A Happy Ending?

- **Press coverage: May 2012**

WINNER OF THE 2012 PULITZER PRIZE FOR COMMENTARY

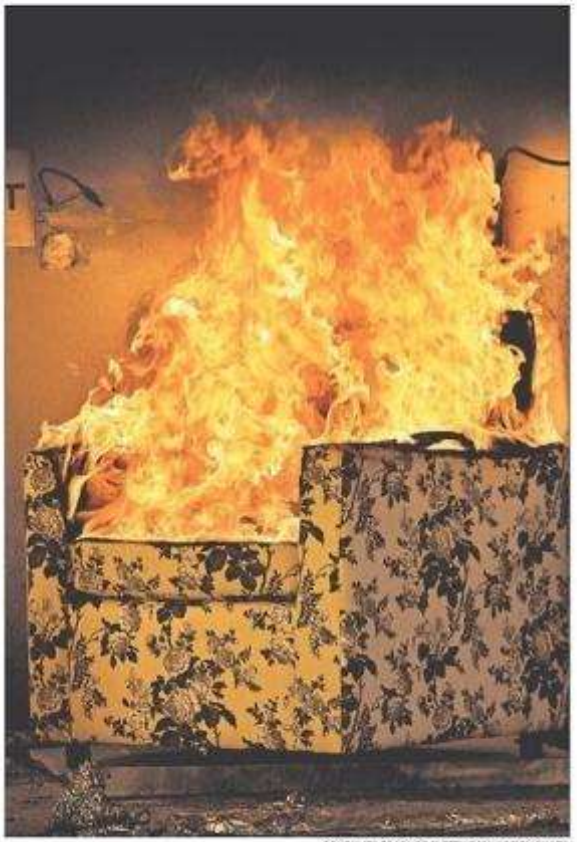
Chicago Tribune

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 Heimbach 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 Heimbach, 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."

Heimbach'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 Heimbach 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.

Heimbach 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.

These 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 those 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

GP1

FOR IMMEDIATE RELEASE:
Monday, June 18, 2012

Governor Brown Directs State Agencies to Revise Flammability Standards

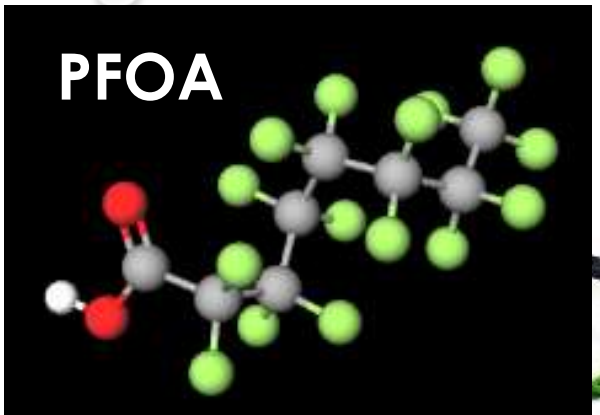
- Smolder standards for fabric
- Increased fire safety without flame retardants

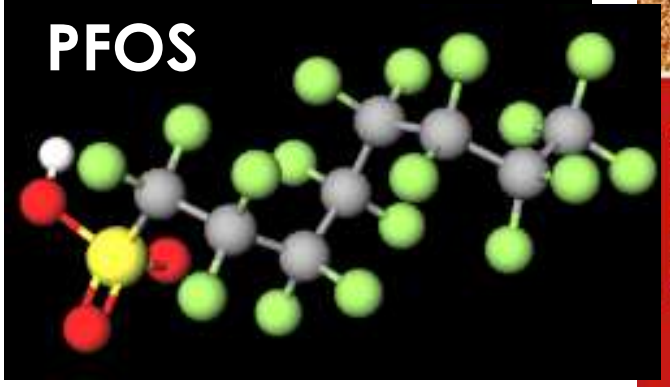
Science influencing policy…

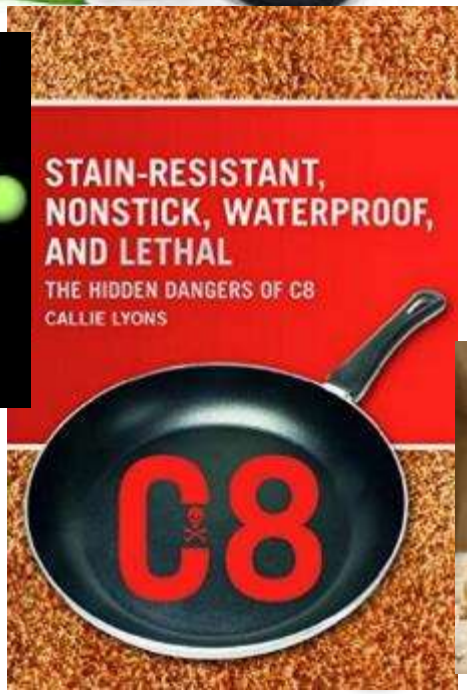
Slide 13

GP1 Graham Peaslee, 6/12/2017

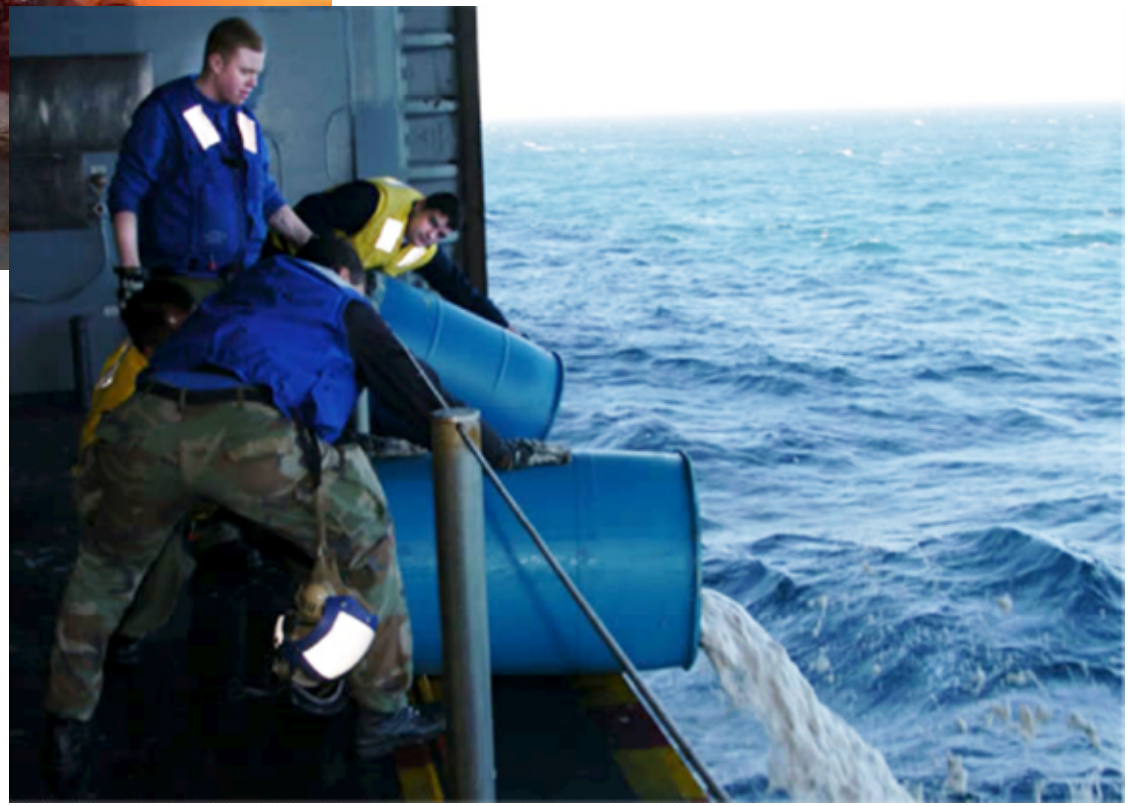
PFAS:
Per- & Polyfluorinated Alkyl Substances







AFFF: Aqueous Film-Forming Foam



ENVIRONMENTAL PERSISTENCE
BIOACCUMULATES
UBIQUITOUS

dustrial release

Flame retardant release

Surfactant release

Disease Correlations

DuPont loses another 'bellwether' C8 lawsuit

RELATED ITEMS

- DuPont faces fourth C8 trial
- DuPont's toxic C8 chemical still unchecked, group says
- DuPont settles one C8 case, loses bid for retrial in another

HEALTH HEADLINES

- Neuroscience experts in central Ohio say advances,

By Earl Rinehart

The Columbus Dispatch • Wednesday July 6, 2016 9:36 PM

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David Freeman hugged Michael Papantonio after a federal court jury awarded him $5.1 million on Wednesday in his lawsuit against DuPont.

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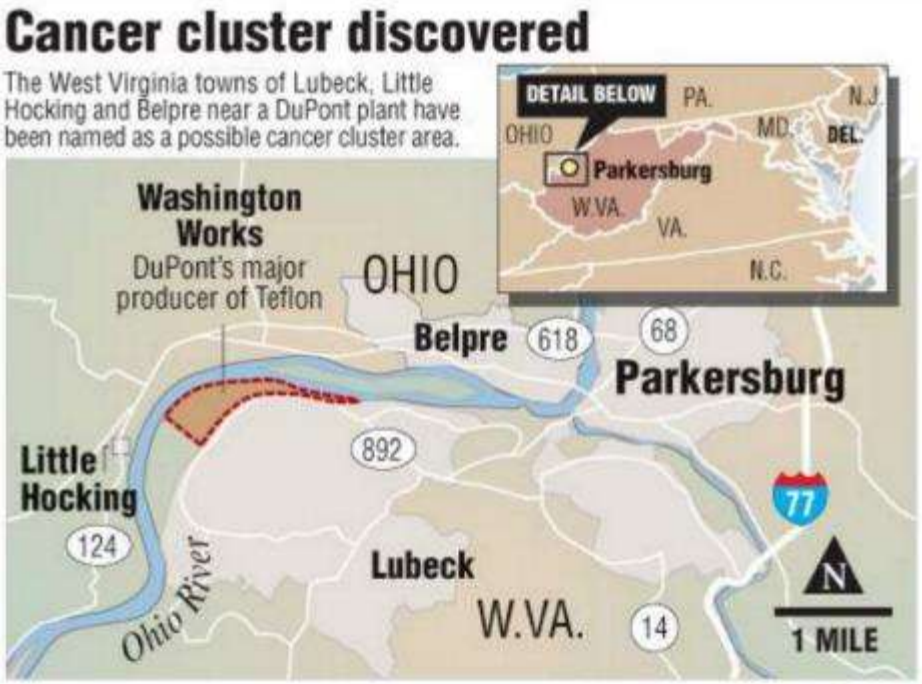
3500+ lawsuits = $671 M

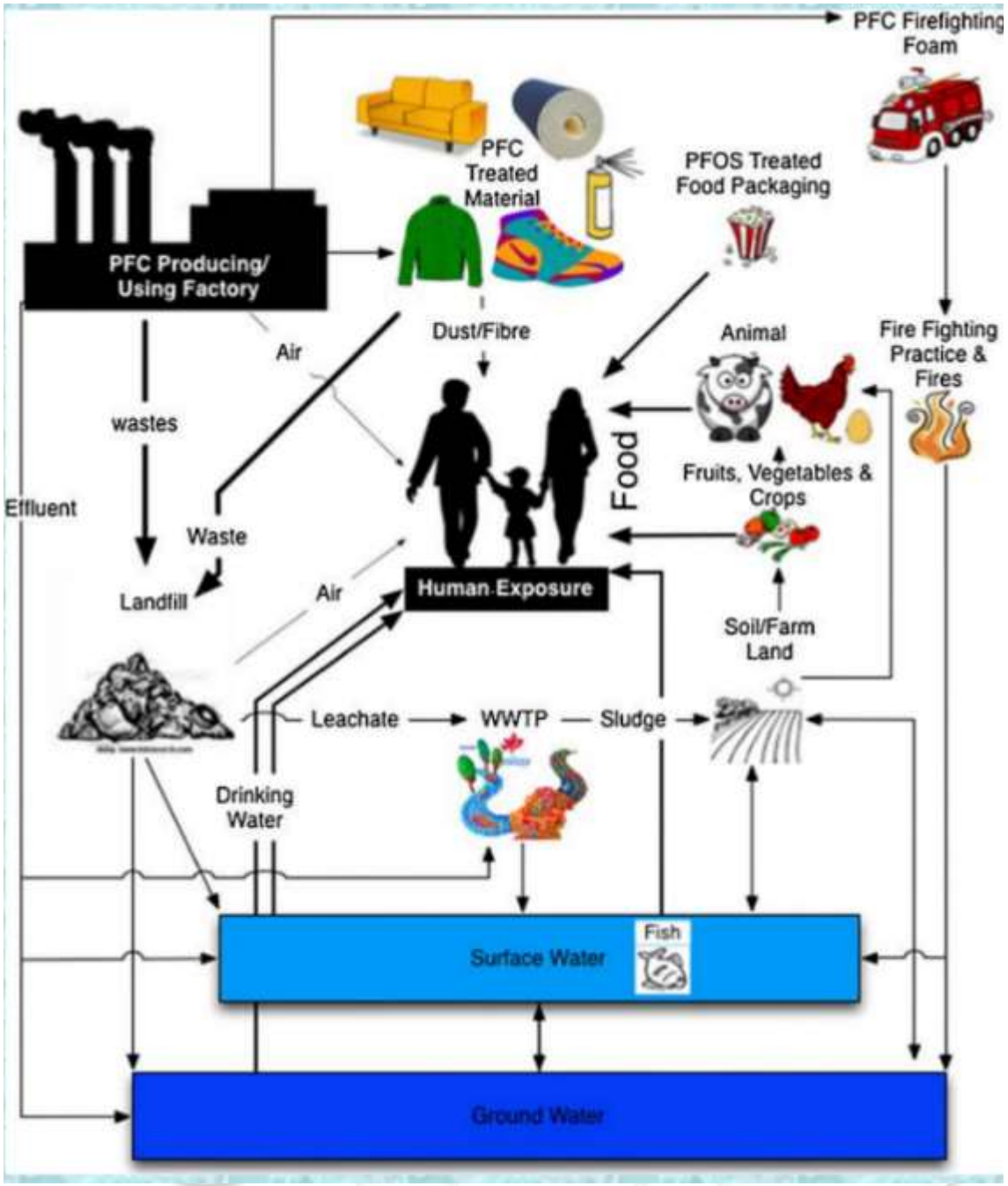
http://www.c8sciencepanel.org/



Testicular cancer
Kidney Cancer
Hypertension
High Cholesterol
Preclampsia
Ulcerative colitis

ENVIRONMENTAL PERSISTENCE

PFAS do not degrade; Pass through Waste-Water Treatment Plant…

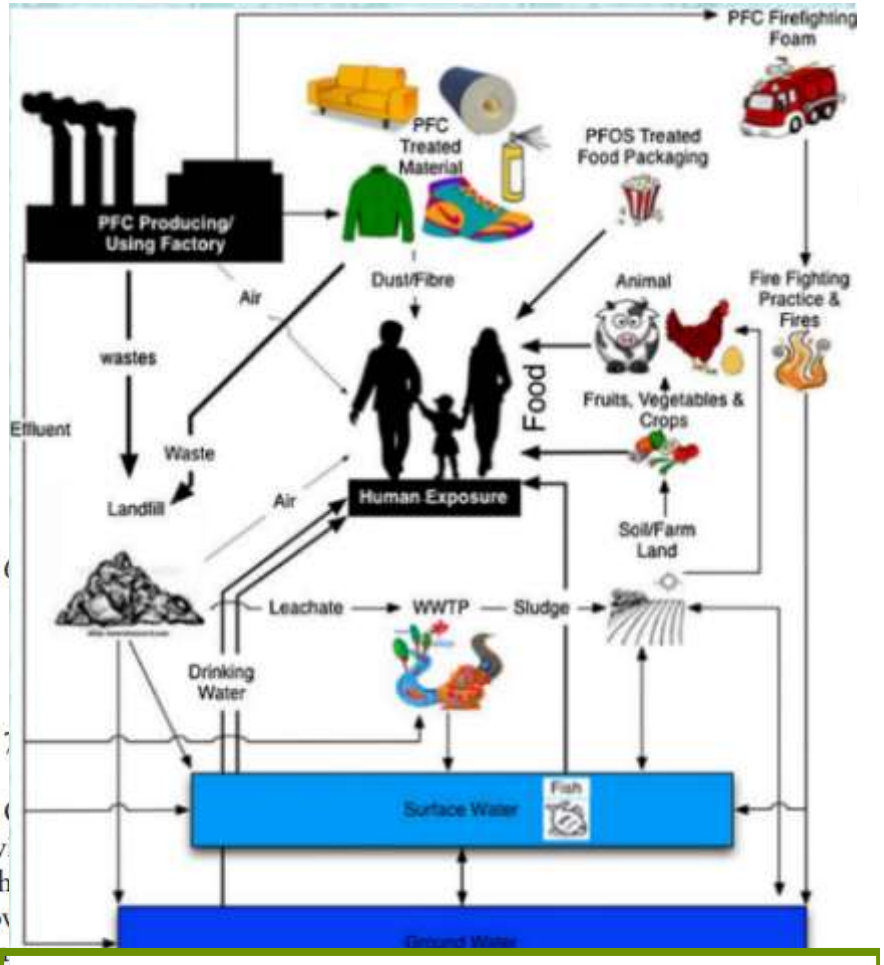


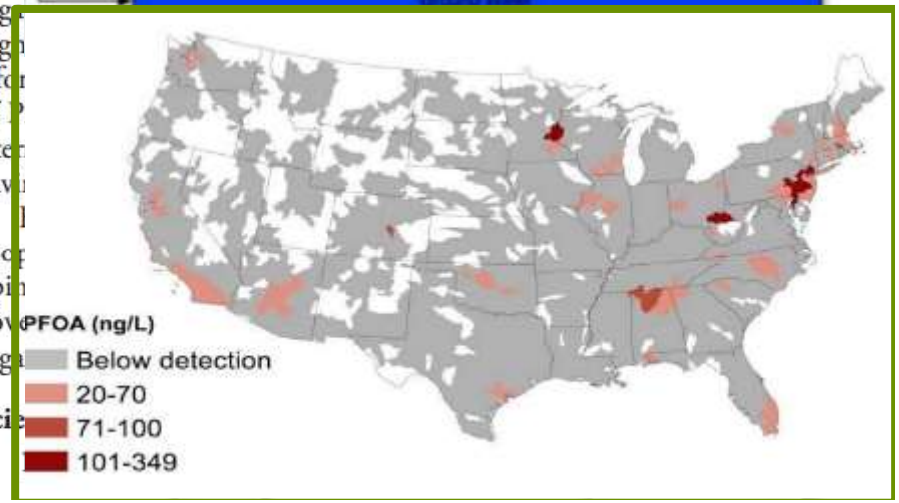
The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

http://dx.doi.org/10.1289/ehp.1509934

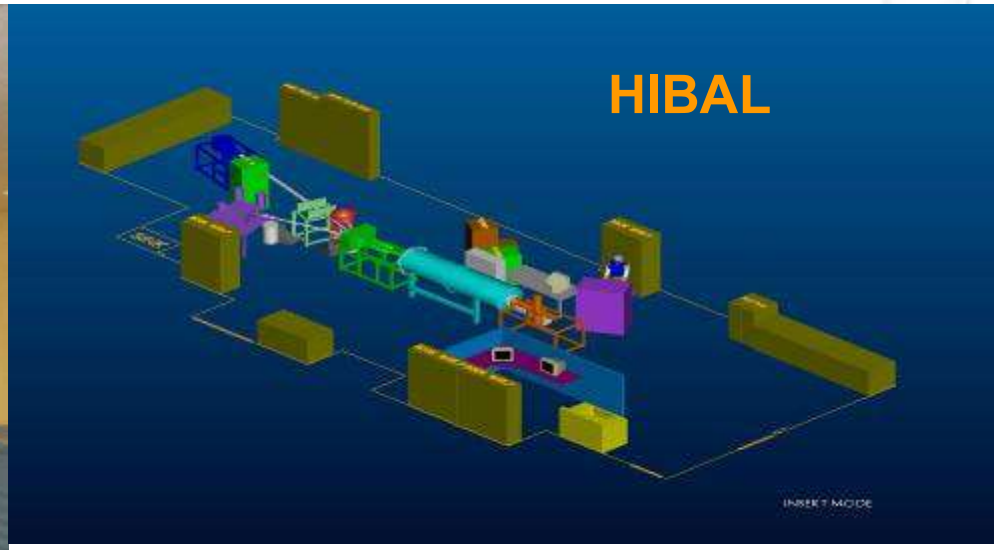
As scientists and other professionals from a variety of disciplines, we are concerned about the production and release into the environment of an increasing number of poly- and perfluoroalkyl substances (PFASs) for the following reasons:

1. PFASs are man-made and found everywhere. PFASs are highly persistent, as they contain perfluorinated chains that only degrade very slowly, if at all, under environmental conditions. It is documented that some polyfluorinated chemicals break down to form perfluorinated ones (D'Eon and Mabury 2007).
2. PFASs are found in the indoor and outdoor environments, wildlife, and human tissue and bodily fluids all over the globe. They are emitted via industrial processes and military and firefighting operations (Darwin 2011; Fire Fighting Foam Coalition 2014), and they migrate out of consumer products into air (Shoeib et al. 2011), household dust (Björklund et al. 2009), food (Begley et al. 2008; Tittlemier et al. 2007; Trier et al. 2011), soil (Sepulvado et al. 2011; Strynar et al. 2012), ground and surface water, and make their way into drinking water (Eschauzier et al. 2012; Rahman et al. 2014).
3. In animal studies, some long-chain PFASs have been found to cause liver toxicity, disruption of lipid metabolism and the immune and endocrine systems, adverse neurobehavioral effects, neonatal toxicity and death, and tumors in multiple organ systems (Lau et al. 2007; Post et al. 2012). In the growing body of epidemiological evidence, some of these effects are supported by significant or suggestive associations between specific long-chain PFASs and adverse outcomes, including associations with testicular and kidney cancers (Barry et al. 2013; Benbrahim-Tallaa et al. 2014), liver malfunction (Gallo et al. 2012), hypothyroidism (Lopez-Espinosa et al. 2012), high cholesterol (Fitz-Simon et al.



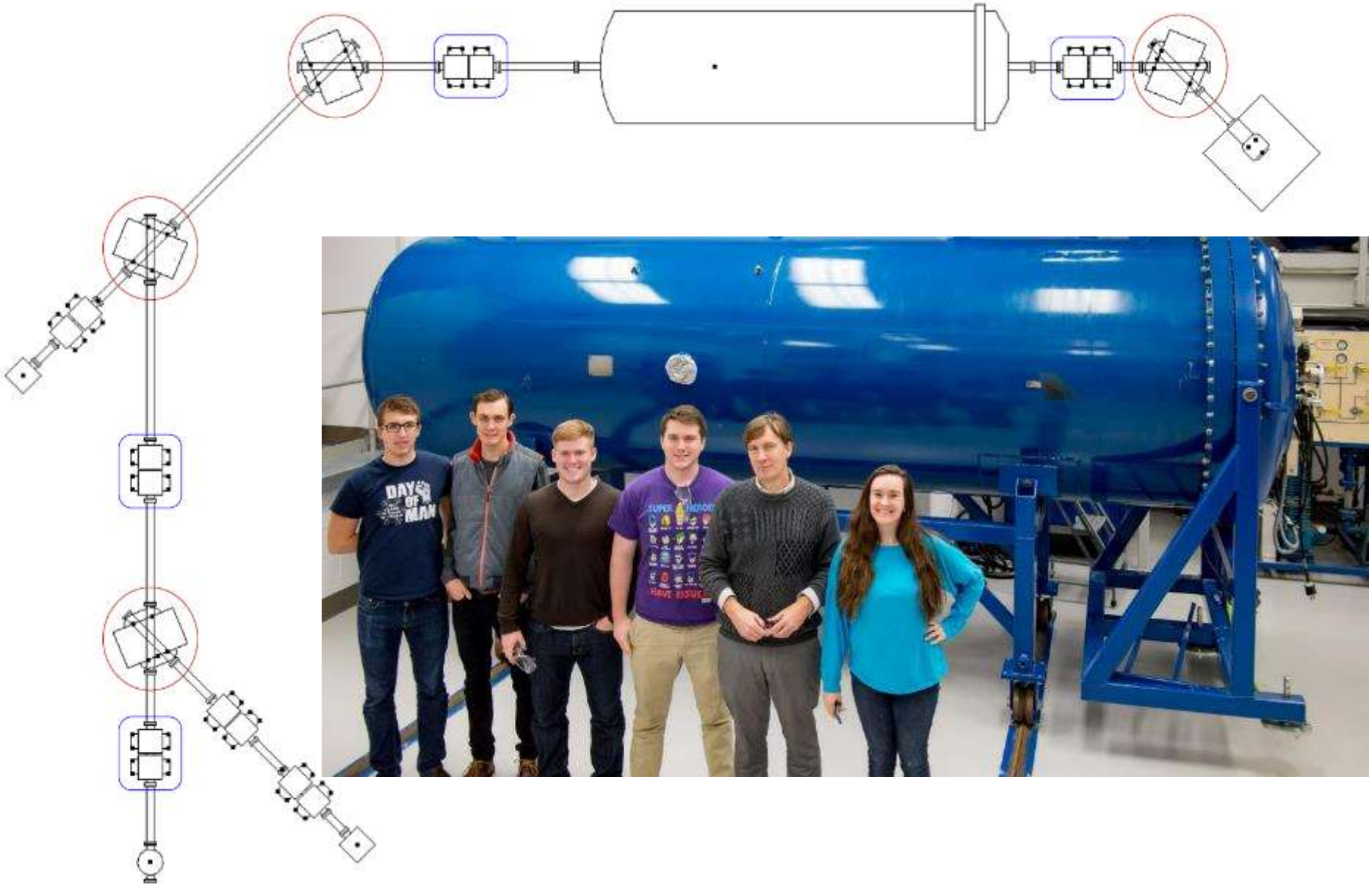


Hope College Ion Beam Analysis Lab



Van de Graaff Accelerator 1.7 MV

Notre Dame 3 MV Pelletron



PIGE Analysis of Fluorine

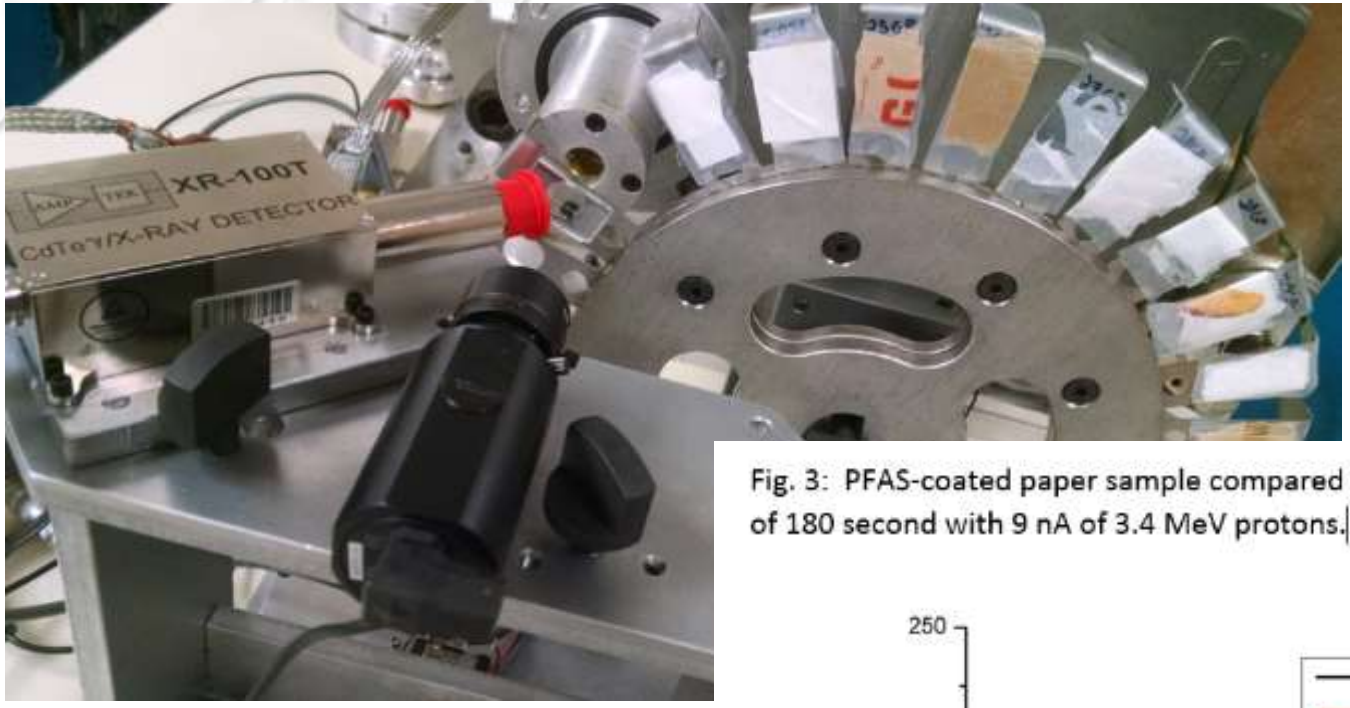
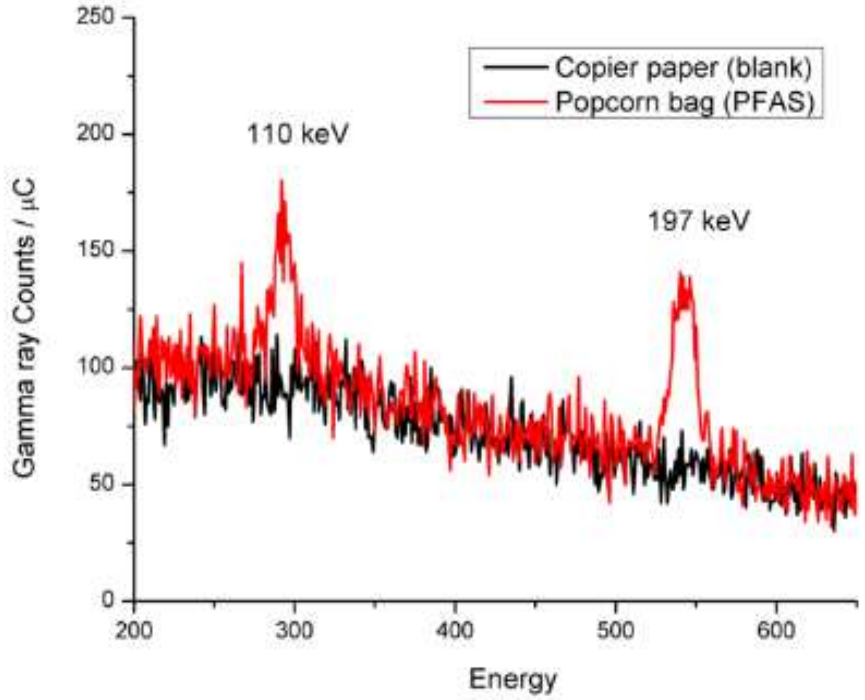


Fig. 3: PFAS-coated paper sample compared with uncoated paper. Irradiation time of 180 second with 9 nA of 3.4 MeV protons.



ENVIRONMENTAL Science & Technology LETTERS

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Letter

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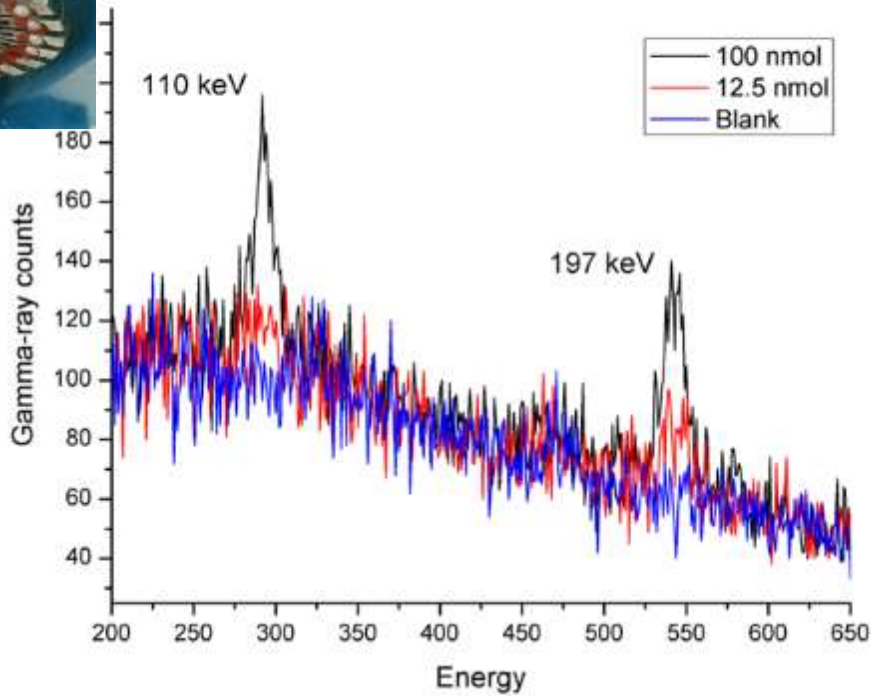
Fluorinated Compounds in U.S. Fast Food Packaging

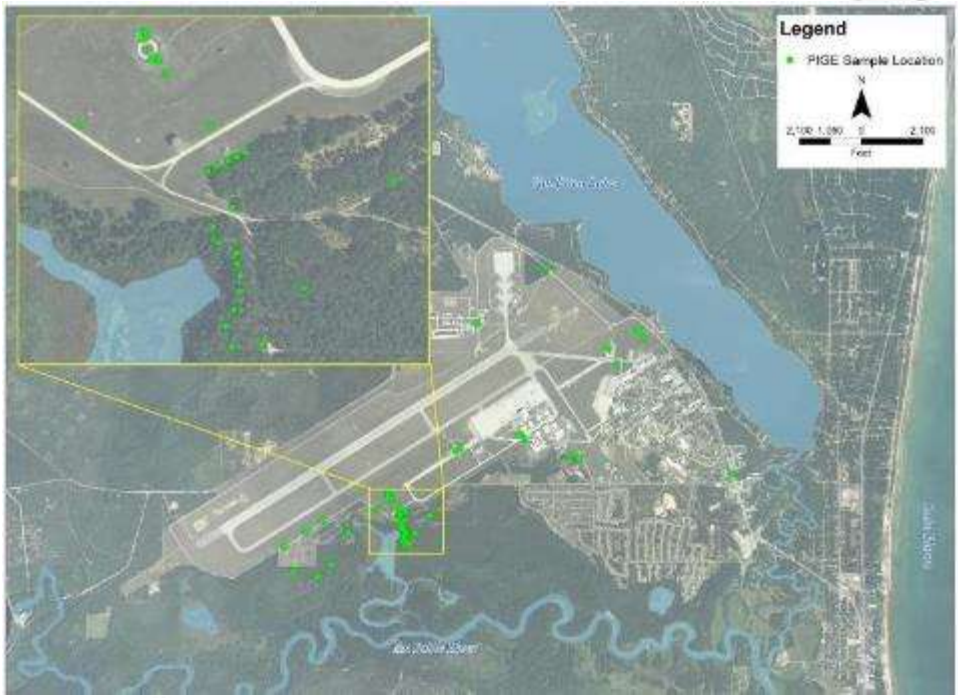
Laurel A. Schaider,*[,†] Simona A. Balan,[‡] Arlene Blum,[§,∥] David Q. Andrews,[⊥] Mark J. Strynar,[#] Margaret E. Dickinson,[▽] David M. Lunderberg,[▽] Johnsie R. Lang,[○] and Graham F. Peaslee[@]

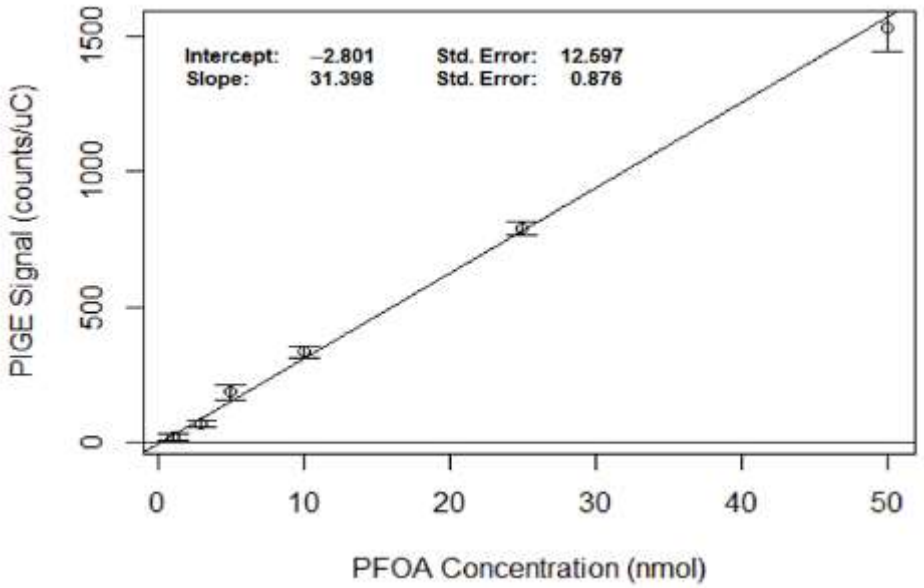
Extension to Groundwater Studies

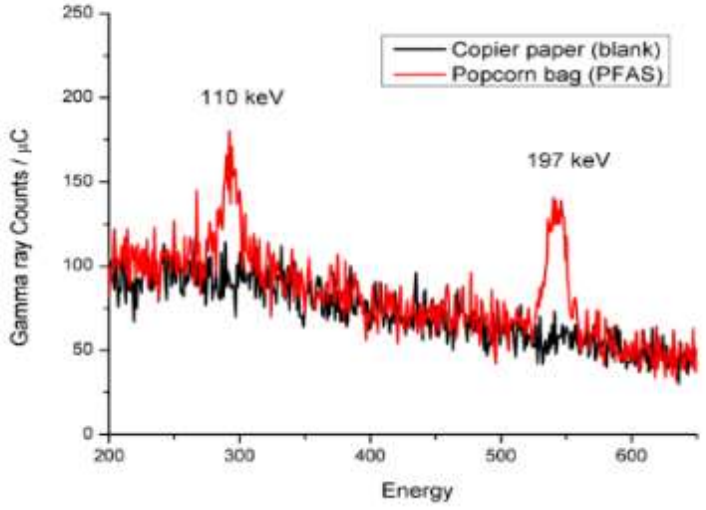
PIGE spectra of PFOA extracted onto the surface of WAX
s. The two gamma rays detected at 110 keV and 197 keV arise
tations of ^{19}F nuclei.



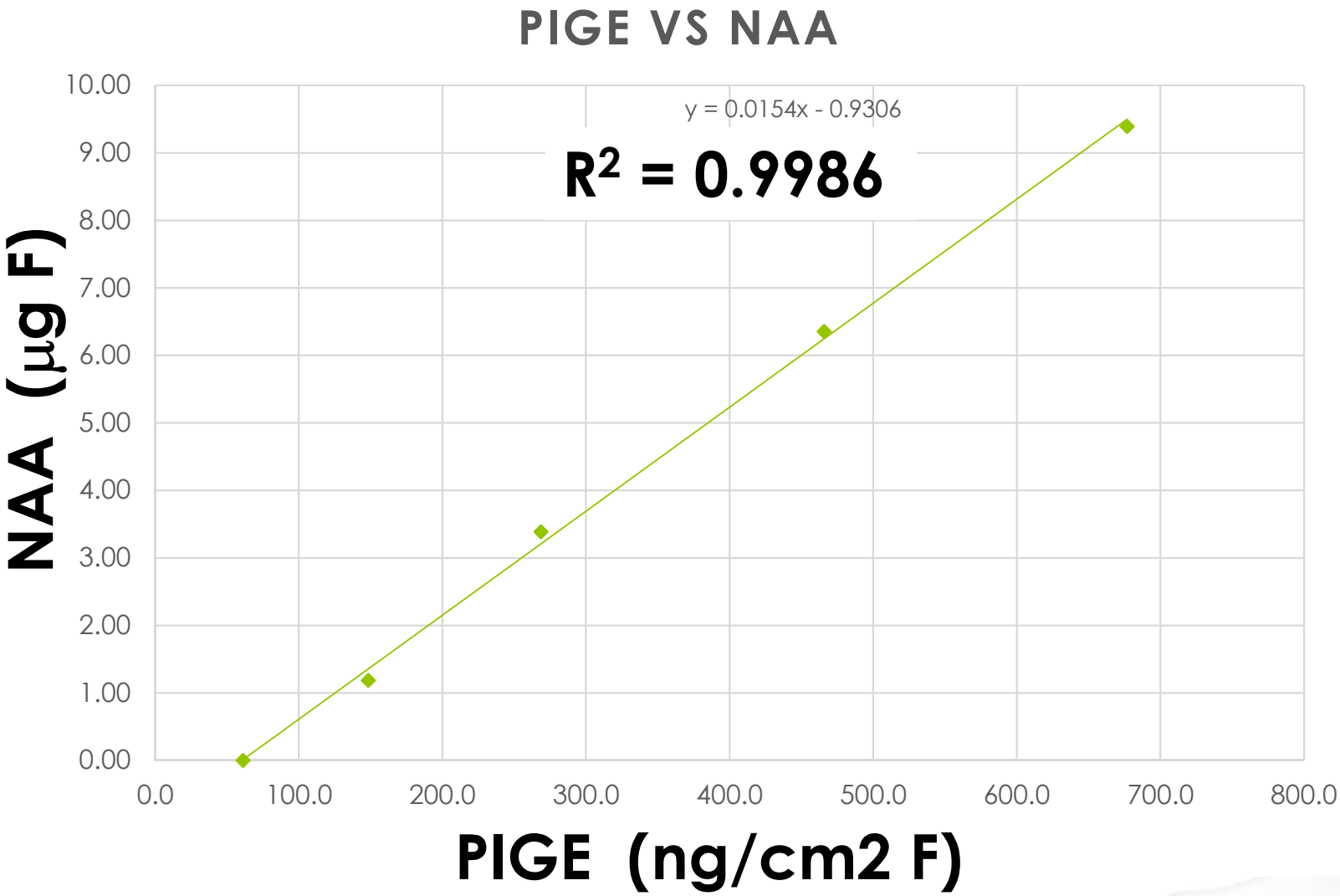
PIGE Analysis of Total Fluorine







Comparison with NAA Total F



Take home points…

Lots of student-accessible science…

Very interdisciplinary…

Interesting enough to:

- Publish
- Attract students
- Attract funding

Limited only by imagination…

Because of the rapid, non-destructive elemental analysis, opportunities for new science exists in large-scale environmental sampling projects…

Spinning off a company:

UMP ANALYTICAL

National Science Foundation
WHERE DISCOVERIES BEGIN

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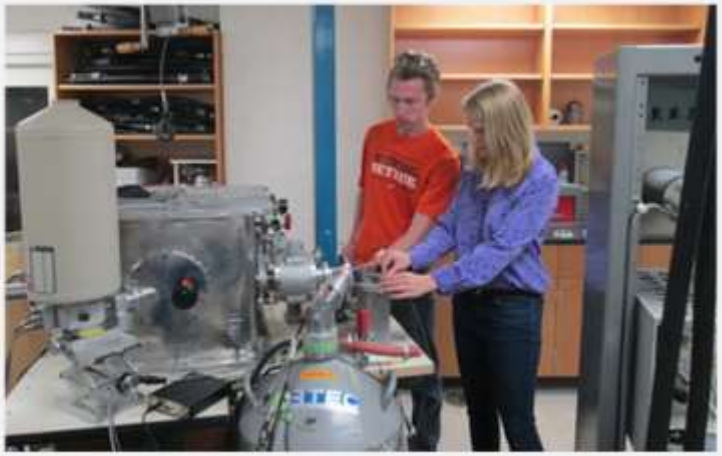
Discovery

Nuclear physics technique helps companies detect dangerous compound

Scientist develops new approach to rapidly identify toxic compounds in everyday materials such as clothing



Students are using nuclear physics to detect dangerous chemicals in everyday products.

Peaslee's method helps manufacturers detect a type of dangerous chemical in their raw materials.
Credit and Larger Version

www.nsf.gov

The Future…

Consumer products – already in hand
– natural advantage

Aqueous samples – Ground water
– Drinking water

(method developed) ➔ need portability

Anybody that can produce MeV scale beams of protons or neutrons on a bench would have interest from environmental concerns….

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NSF RUI: PHY-0969058
NSF RUI: PHY-1306074
NSF CAREER CHE-0952768

Basic vs. Applied Science

Environmental Science & Technology Letters

Letter

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Radiosynthesis and Biological Distribution of ^{18}F-Labeled Perfluorinated Alkyl Substances

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Supporting Information

ABSTRACT: A novel method for radiolabeling perfluorinated alkyl substances (PFAS) with fluorine 18 has been developed, and after purification, the stability and biological distribution in healthy mice were evaluated. Three PFAS, [^{18}F]PFOA (C8), [^{18}F]PFHxA (C6), and [^{18}F]PFBA (C4), were readily labeled and isolated in average yields between 12 and 31%. The stability of each compound was monitored in 0.1% ammonium hydroxide (NH_4OH) in methanol, in saline, and in human, mouse, and rat sera. The amount of intact, radiolabeled PFAS was determined by radiometric instant thin layer chromatography and was calculated by the amount of free fluorine 18 observed over time. All compounds were highly stable in 0.1% NH_4OH in methanol and saline, with <10% defluorination observed after 4 h. Interestingly, each compound had differing affinities for the serum proteins. *In vivo* biodistribution studies in mice showed uptake in all organs examined, with the highest uptake being exhibited in the liver for both [^{18}F]PFOA and [^{18}F]PFHxA and the stomach for [^{18}F]PFBA. The results of this initial study suggest that this method could be valuable in helping to determine the biological uptake of any PFAS in mammals.