

PFAS Chemicals: Tragedy and Challenge

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CSWAB.org - October 16, 2018**

Overview

- ▶ What is PFAS?
- ▶ What are the environmental health concerns?
- ▶ What happens when PFAS is released to the environment?
- ▶ What's happening here in Wisconsin?
- ▶ What's next?

PFAS (Per- and Polyfluoroalkyl Substances)

- ▶ Per- and polyfluoroalkyl substances (PFAS) are a large group of man-made toxic chemicals used to make consumer products resistant to water, grease or stains.
- ▶ PFAS are very persistent in the environment and in the human body - meaning they don't break down and can accumulate over time.
- ▶ Research has shown probable links between PFAS exposure and cancer, thyroid disease, high cholesterol, ulcerative colitis, and pregnancy-induced hypertension.

Source: ITRC, 2017



Discovery and Manufacturing History of PFAS

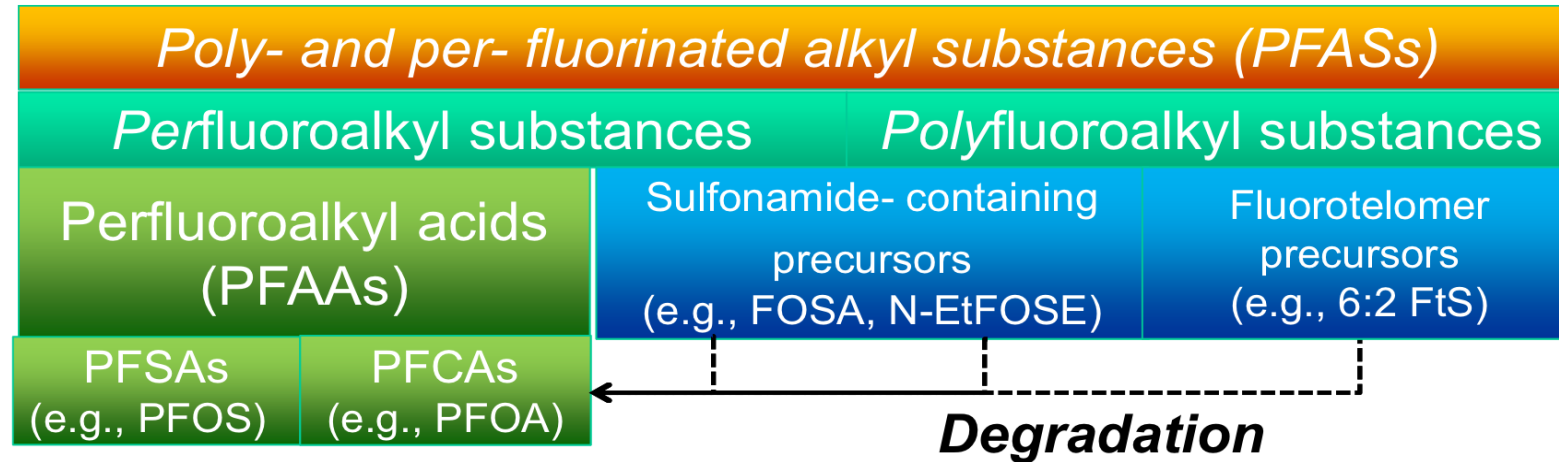
Table 2-1. Discovery and manufacturing history of select PFAS

PFAS ¹	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS ²)
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams	Predominant form of firefighting foam	
Dominant Process ³		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Source: ITRC



Alphabet Soup



Acronyms

- Perfluorinated carboxylic acids (PFCAs)
- Perfluorinated sulfonic acids (PFSAs)
- Perfluorooctanoic acid (PFOA)
- Perfluorooctanesulfonic acid (PFOS)
- Perfluorooctane sulfonamide (FOSA)
- 2-N-Ethyl-perfluoro-1-octanesulfamido ethanol (N-EtFOSE)
- Fluorotelomer sulfonate (FtS)

Source: Buck et al., 2011; Houtz, 2013

PFAS: Toxicity Over-Achievers

- ▶ Four of these chemicals are found in humans globally: PFOS, PFOA, PFNA, PFHxS
- ▶ Half lives of 3-9 years
- ▶ Found in human breast milk and cord blood: the fact that serum levels are highest in babies is a huge concern because they are a **developmental** toxin
- ▶ PFOS and PFOA are “likely carcinogenic” (USEPA, 2006)



Risk is Additive...

- ▶ “Currently, ATSDR considers effects from **all PFAS exposures to be additive**, including PFHpA and PFHxS.” (Arizona DOH, 2016)
- ▶ Massachusetts recommends “an additive toxicity approach be used for these compounds when they occur together. For example, when all or some of the five compounds PFOS, PFOA, PFHxS, PFNA and PFHpA occur together in drinking water, the detected concentrations for these PFAS **should be summed** and compared to 0.07 ug/L (70 ppt). (Massachusetts DEP, June 2018)

The best way to protect public health...

- ▶ “Approaching PFAS as a **class** for assessing exposure and biological impact is the best way to protect public health.”

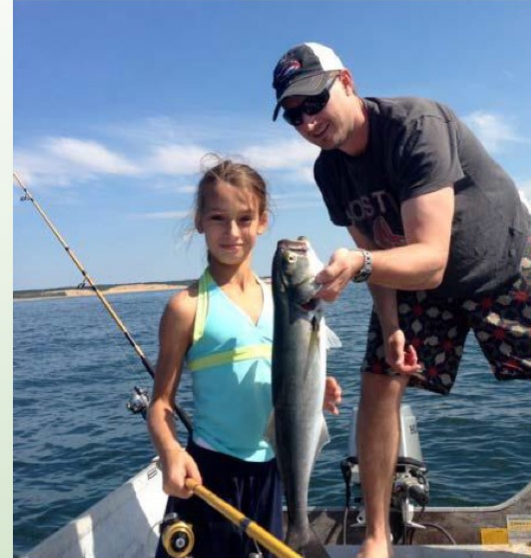
Dr. Linda Birnbaum, Director NIEHS

September 26, 2018

REFERENCE: Dr. Birnbaum (Director of the National Institute of Environmental Health Sciences and National Toxicology Program of the National Institutes of Health) in testimony before the Senate Committee on Homeland Security and Governmental Affairs, Subcommittee on Federal Spending Oversight and Emergency Management, Sept. 26, 2018.

Human Exposure Pathway

- Major^{1,2}
 - Diet (bioaccumulation)
 - Fish and seafood
 - Homegrown produce
 - Drinking water
 - Incidental soil/dust ingestion
- Usually insignificant or minor
 - Dermal absorption
 - Inhalation



1 Oliaei et al., 2013. Environ. Sci. Pollut. Res. Manag. 20:1977-1992
2 Domingo, 2012. Environment International 40:187-195

PFAS: VERY SOLUBLE!!

7 AECOM

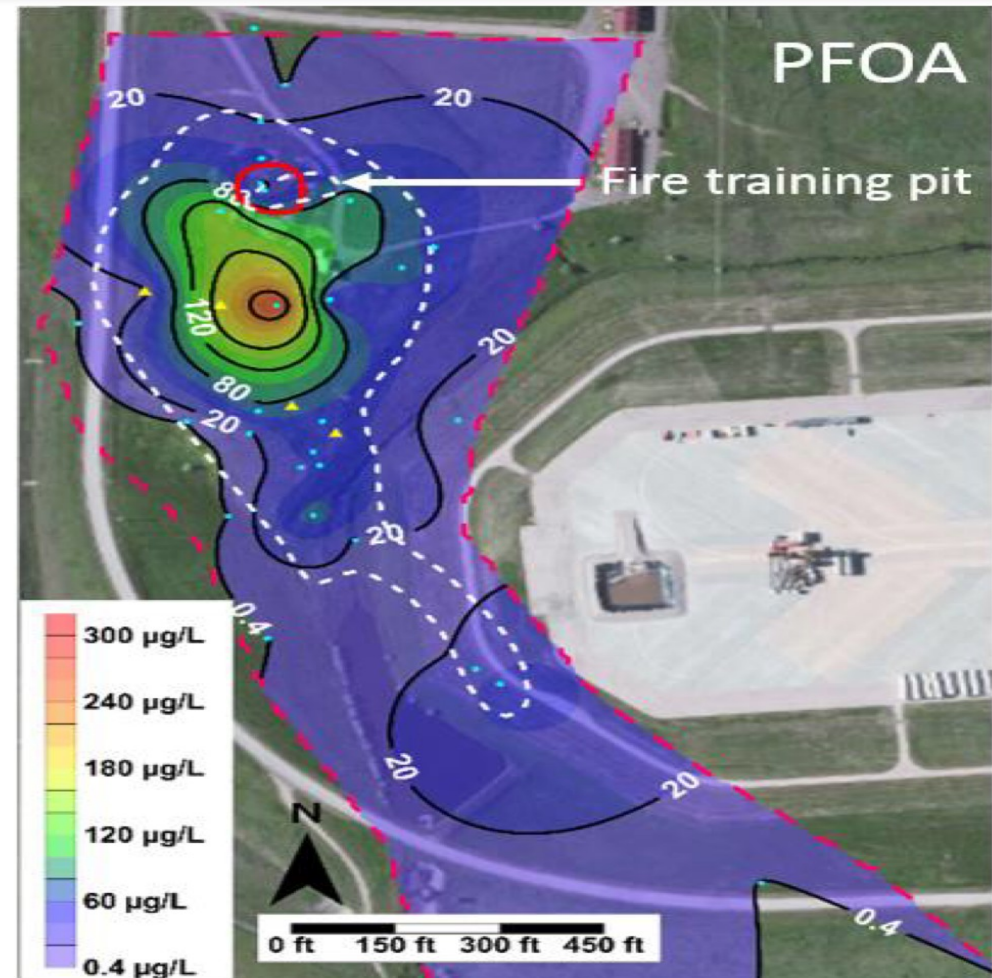
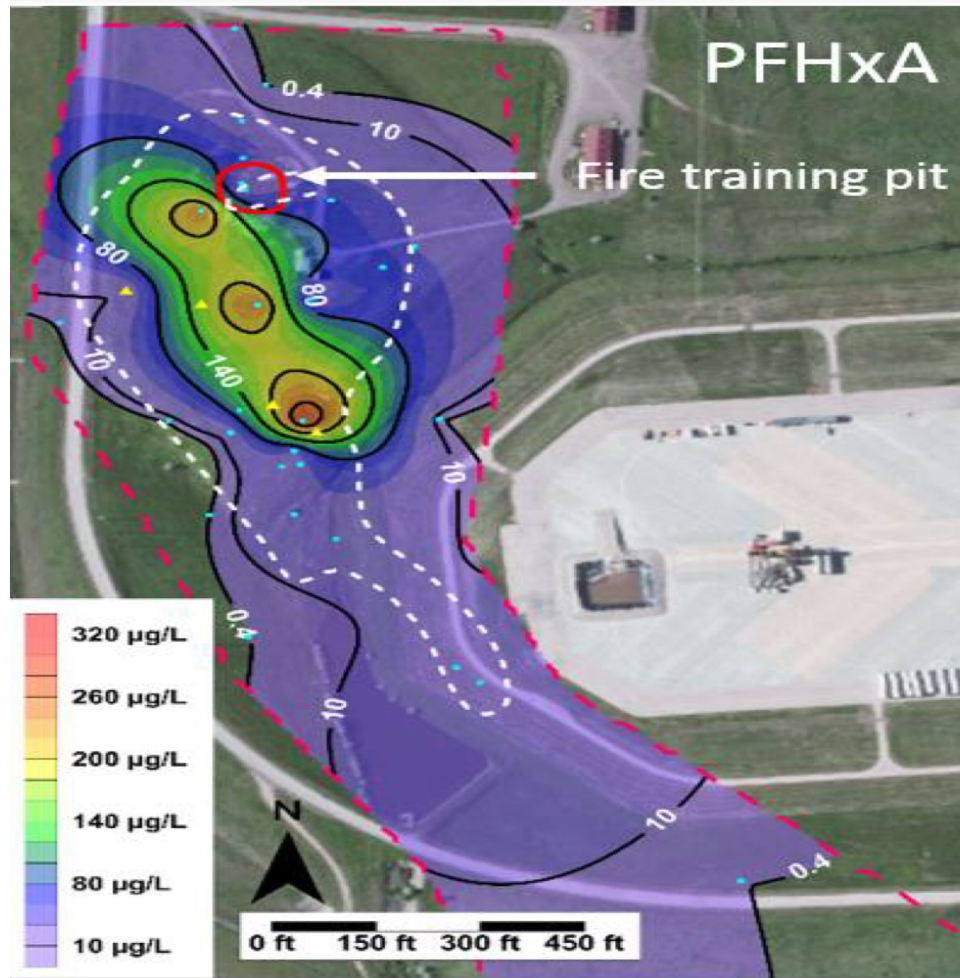
Characteristic - PFAS Properties

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	414.07	538	131.5	78.11
Solubility	0.0027 mg/L @24°C	3400–9500 mg/L @25°C	519 mg/L @20°C	1100 mg/L @ 20°C	1780 mg/L @20°C
Vapor Pressure (25°C)	4.05x10 ⁻⁵ mmHg	0.5-10 mmHg	2.48x10 ⁻⁶ mmHg	77.5 mmHg	97 mmHg
Henry's Constant	4.6x10 ⁻³ atm-m ³ /mol	0.0908 atm-m ³ /mol	3.05 x10 ⁻⁶ atm-m ³ /mol	0.0103 atm-m ³ /mol	0.0056 atm-m ³ /mol
Organic Carbon Part. Coeff. (Log K _{oc})	4.8-6.8	2.06	2.57	2.42	2.15

- High solubility, low volatility in water
- High detection frequency in soil and sediment

Subsurface Plume Map: Wurtsmith AFB

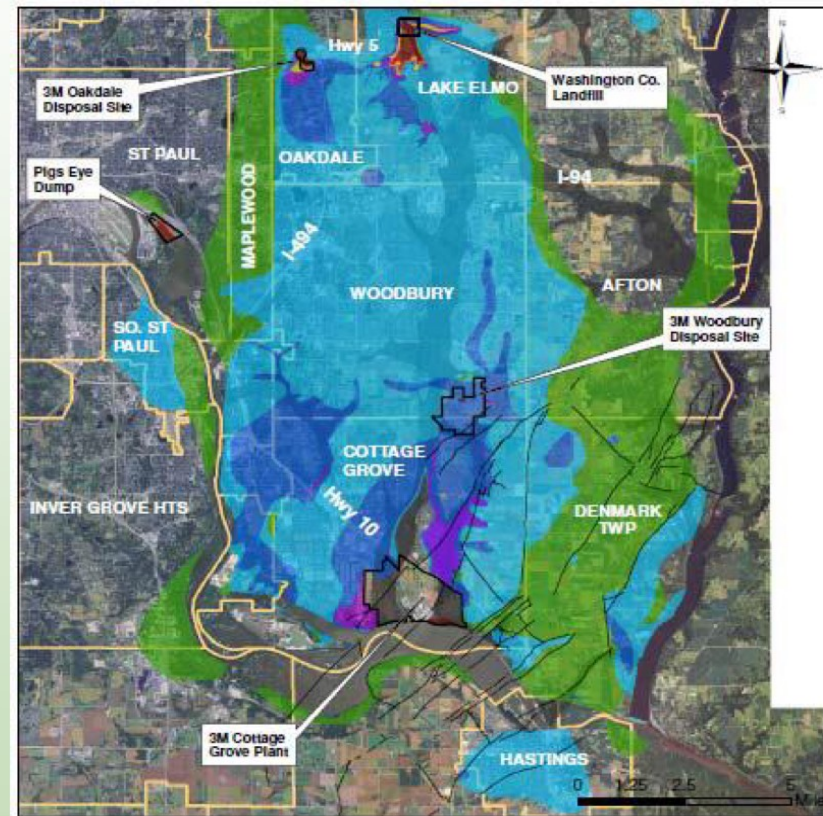
EPA LHA for PFOA = 0.07 $\mu\text{g}/\text{l}$



Subsurface Plume in MN is 100 square miles.

Environmental Fate

- **PFAS Plumes can be Huge!**
- **Minnesota PFAS plumes in groundwater**
 - 10+ miles long
 - cover over 100 mi²



3M Woodbury Site, MN

(MDH, 2012)

Regulatory Status:

- ▶ **WISCONSIN**: Currently no environmental standards however, WDNR has authority to address PFAS under the Spills Law.
- ▶ **FEDERAL**: PFAS are currently **NOT** regulated under the following:
 - ▶ Emergency Planning and Community Right-to-know Act (EPCRA)
 - ▶ Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, aka Superfund)
 - ▶ Resource Conservation and Recovery Act (RCRA)
 - ▶ Clean Water Act
 - ▶ Clean Air Act and
 - ▶ Safe Drinking Water Act

Aqueous Film Forming Foam (AFFF) is a significant source nationally



Wisconsin Families Exposed to PFAS

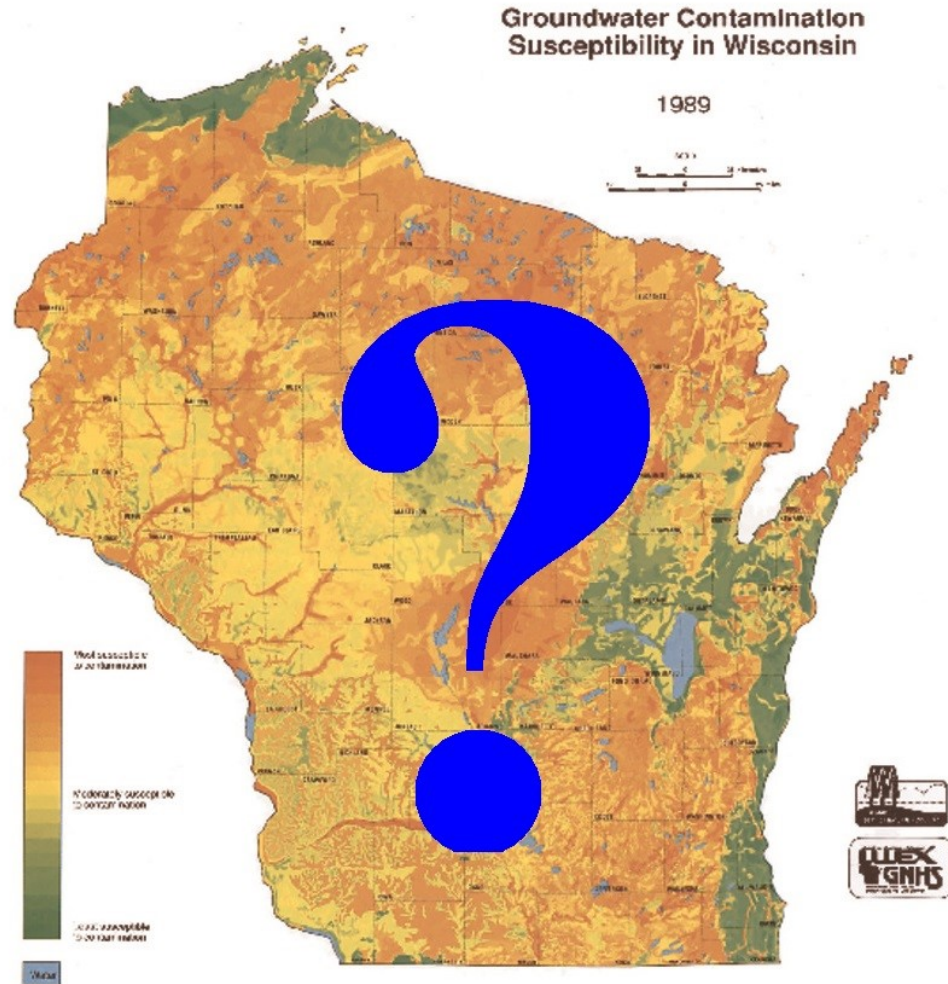
- ▶ Industrial sites like the Tyco/Johnson Controls facilities in Marinette, Wisconsin are sources of PFAS groundwater contamination that has spread from these sites, threatening nearby fisheries and affecting residential wells.
- ▶ So far, at least 36 families have been exposed to PFAS in their drinking water. The highest concentration detected in a private well was 1900 ng/L, far above the EPA's Lifetime Advisory Level of 70 ng/L (parts per trillion).

What about Groundwater?

EPA Health Advisory Level for Drinking Water = 70 ng/L		
Site Name	Location	PFOS + PFOA Max Conc.
Ansul Fire Technology Center	Marinette, WI	202,000 ng/L
Badger Army Ammunition Plant	Baraboo, WI	<i>not tested</i>
Fort McCoy Fire Training Burn Pit #1	Sparta, WI	31,900 ng/L
Fort McCoy Fire Training Burn Pit #2	Sparta, WI	72,400 ng/L
Fort McCoy Fire Training Burn Pit #3	Sparta, WI	121,000 ng/L
General Mitchell – 440 th	Milwaukee, WI	10,800 ng/L
Volk Field Air National Guard	Camp Douglas, WI	23,000 ng/L
WI Air National Guard Truax Field	Madison, WI	39,841 ng/L

Where are the Potential Sources?

Airports, Chrome Platers, Chemical Manufacturing...

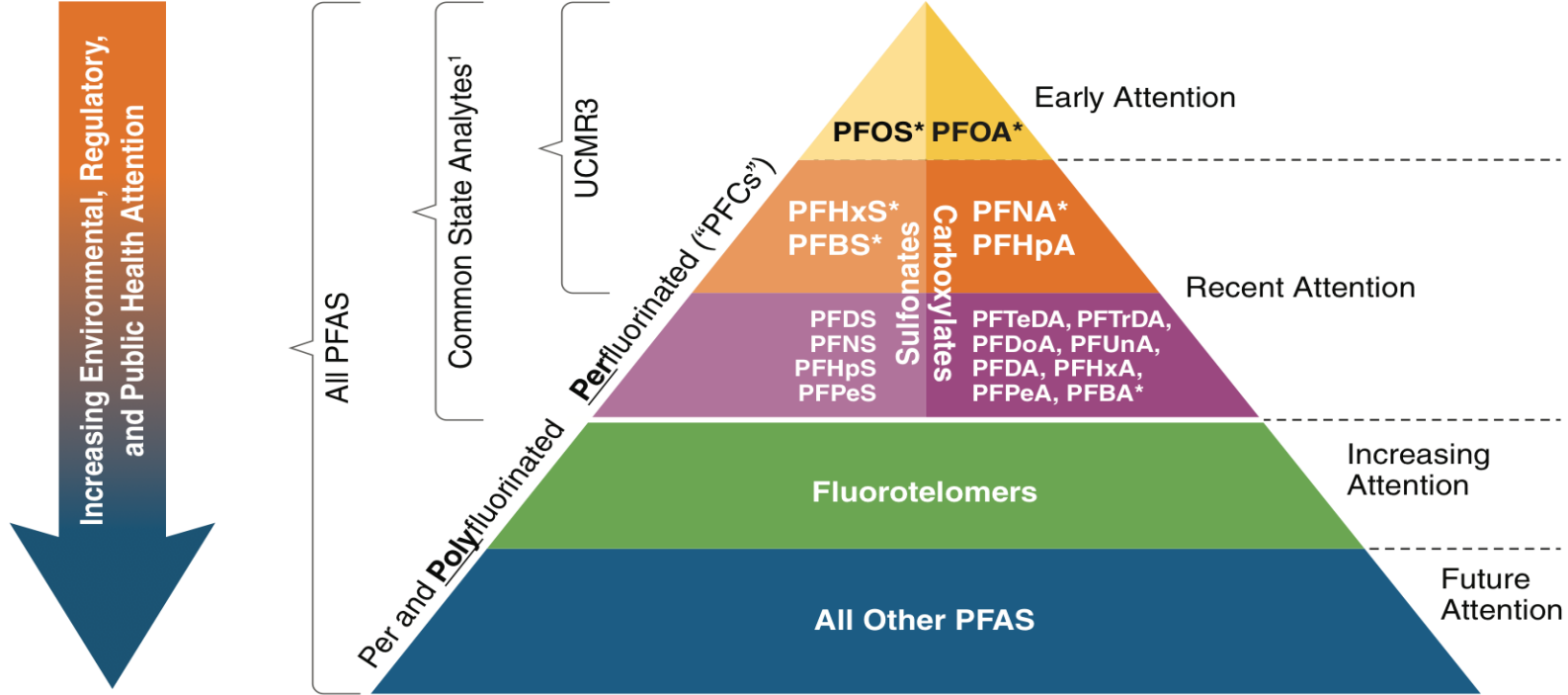


Public drinking water systems in Wisconsin?

- ▶ Of the more than **11,000** public drinking water systems tested in Wisconsin, only **90** have been tested for PFAS.
- ▶ The one-time testing in 2013-2015 detected unsafe levels in 2 municipal wells: La Crosse and Rhinelander. (Tested: Only 6 analytes.)

(Source: EPA Unregulated Contaminant Monitoring Rule 3 database)

Analyte-Specific Testing Misses Full Spectrum



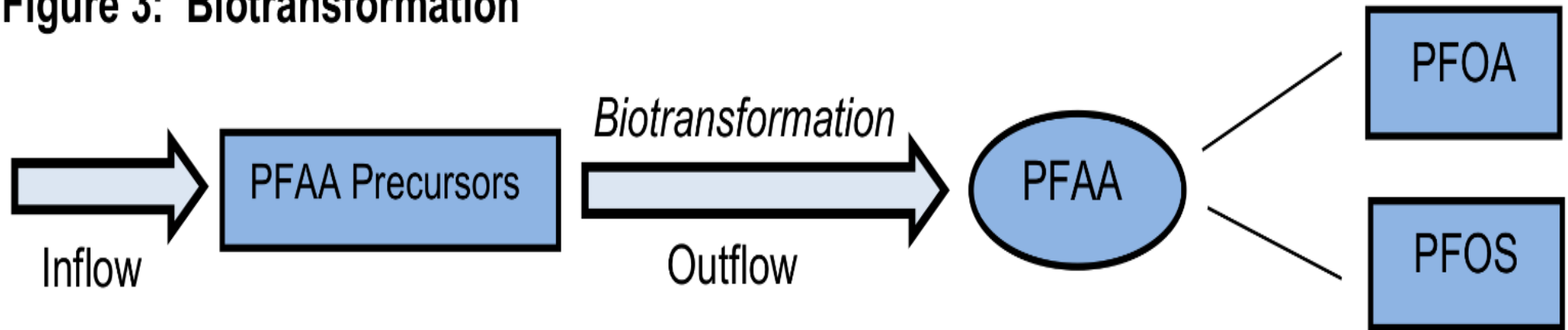
*Common regulatory criteria or health advisories
 ¹Sum of informal poll (NJ, NH, MN)

Thematic and not proportional.
 Bottom of triangle indicates additional number of compounds;
 not a greater quantity by mass, concentration, or frequency
 of detection.

Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment
 (Source: J. Hale, Kleinfelder, used with permission)

PFOS/PFOA and their parents: the precursors matter because they turn into PFOS/PFOA

Figure 3: Biotransformation



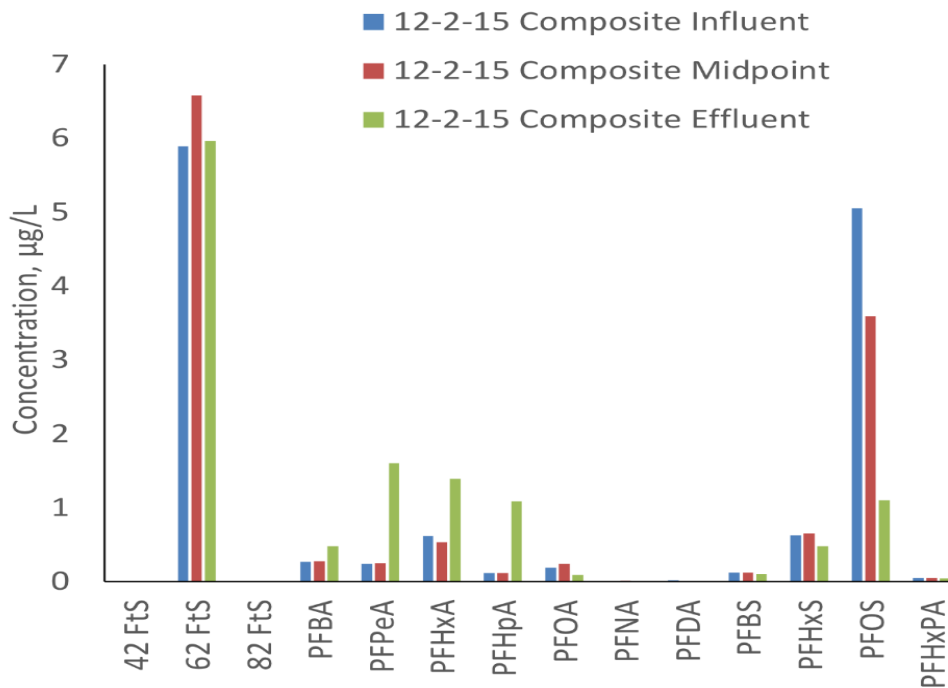
Low levels of discrete compounds are detected

High levels of discrete compounds are detected, which can include PFOA and PFOS

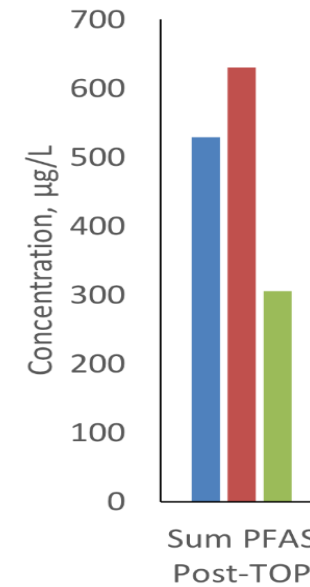
Total Oxidizable Precursor (TOP) Assay...

37

Directly Measured Analytes vs. Post-TOP Assay Total PFAS Mass



~95-98% of PFAS mass is not directly measured by target analyte list



Treatment Methods: For Better and Worse

- ▶ Granulated Activated Carbon (GAC) is not efficient in removing shorter chain PFAS. Implications for drinking water, surface water.
- ▶ PFAS-contaminated GAC units are regenerated by incineration. Municipal waste incinerators are not designed to burn hot enough to destroy PFAS.
- ▶ Poorly controlled incineration leads to air emissions of PFAS.
- ▶ Alternatively, if you bury PFAS chemicals, they will eventually reach groundwater.



GOALS for Ending and Preventing Exposures

- ▶ Interim **Health Advisory Levels** will be issued by state health officials now for the summed-total concentration of all PFAS including precursors.
- ▶ **Analysis of fish tissue** will be conducted now at known PFAS-contaminated sites including Truax ANG, Fort McCoy and the Tyco/Ansul facility in Marinette.
- ▶ Private well water users (4-mile radius), public water system operators and tribes (10-mile radius) will be immediately **notified** of discovered PFAS groundwater contamination.
- ▶ **ALL public water** supply systems will be analyzed for PFAS. (Michigan has initiated this same effort.)
- ▶ A comprehensive statewide **inventory** of known and potential PFAS sources will be initiated.
- ▶ Protective **state standards** for all environmental media will be established for all PFAS including precursors.
- ▶ **Better analytics** will be utilized to detect all PFAS including precursors.
- ▶ Effective **treatment** methods that do not re-disperse PFAS to the environment will be developed and deployed.
- ▶ A **cost recovery plan** will be developed and implemented.
- ▶ By date certain, the manufacture and use of PFAS will be **banned**.



The Good News!!

- ▶ The PFAS Community Campaign is a coalition of organizations based in Wisconsin working together to prevent exposures to PFAS through drinking water and other pathways.

PFAS Community Partners

Annie Appleseed Project

Casa Maria Catholic Worker - Milwaukee

Citizens for Safe Water Around Badger

Clean Water Action Council of Northeast Wisconsin

Community members affected by contamination from Tyco/Johnson Controls

Crawford Stewardship Project

Family Farm Defenders

Fire Fighter Cancer Foundation

Green Wisdom School of Natural and Botanical Medicine - Women's Environmental Institute

Headwater, LLC

Madison Audubon Society

Midwest Environmental Advocates

Midwest Environmental Justice Organization

Mt. Sally Sanctuary, Inc.

Nukewatch

People Empowered (PEPL) Protect the Land of Rosendale

Physicians for Social Responsibility Wisconsin

Sustain Rural Wisconsin Network

Toxics Action Center

Wisconsin Environmental Health Network

Wisconsin League of Conservation Voters

Wisconsin Network for Peace, Justice, & Sustainability

Wisconsin Resources Protection Council

We're making a difference!

- ▶ We successfully petitioned the State for groundwater standards for two forms of PFAS.
- ▶ A second petition to WDNR for the summed-total concentration of all PFAS in groundwater is currently being considered.
- ▶ We submitted formal public comment (co-signed by 17 organizations) to WDNR supporting the establishment of water quality standards for PFAS.
- ▶ More than 130 residents, including Badger Restoration Advisory Board members, endorsed a resolution calling for a thorough investigation of PFAS at the former Badger Army Ammunition Plant.
- ▶ We have raised awareness of PFAS through effective media including local TV News and newspapers like the Milwaukee Journal Sentinel.

- ▶ We've alerted municipalities, including the City of West Bend and City of Madison of known/potential PFAS contamination at the West Bend Army National Guard facility and Truax Air National Guard base. Low levels of PFAS have been detected in both public water systems.
- ▶ We continue to organize and participate in meetings with local, state, tribal and federal government, regulators and the military.
- ▶ We have established an online library, dedicated webpage, petition, listserv, facebook page, and more.
- ▶ We are working on protective national PFAS policy in collaboration with affected communities around the country.
- ▶ We are invited speakers at a national PFAS Summit next fall.

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Together, we can make a difference.

