Welcome to *The Current*, the North Central Region Water Network's Speed Networking Webinar Series

Emerging Contaminants: The Latest Research on PFAS 2PM CT

1. Submit your questions for presenters via the chat box. The chat box is accessible via the purple collaborate panel in the lower right corner of the webinar screen.
2. There will be a dedicated Q & A session following the last presentation.
3. A phone-in option can be accessed by opening the Session menu in the upper left area of the webinar screen and selecting "Use your phone for audio".

This session will be recorded and available at northcentralwater.org and learn.extension.org.

Today's Presenters:

- **Courtney Carignan**, Assistant Professor, Food Science and Human Nutrition, Pharmacology and Toxicology, Michigan State University
- **Mahsa Modiri-Gharehveran**, Post-Doctoral Research Assistant, Purdue University
- **Cheryl Murphy**, Associate Professor, Ecotoxicology of Fish, Michigan State University

Follow @northcentralh2o and #TheCurrent on Twitter for live tweets!

Courtney Carignan

Dr. Carignan is an exposure scientist and environmental epidemiologist whose research helps protect reproductive and child health by investigating exposure to contaminants in food, water, consumer and personal care products. She conducts biomonitoring and health studies for a wide range of populations, including communities exposed to contaminated drinking water. Her research has contributed to public health interventions aimed at reducing exposures to flame retardants, perfluoroalkyl substances (PFAS), and arsenic.

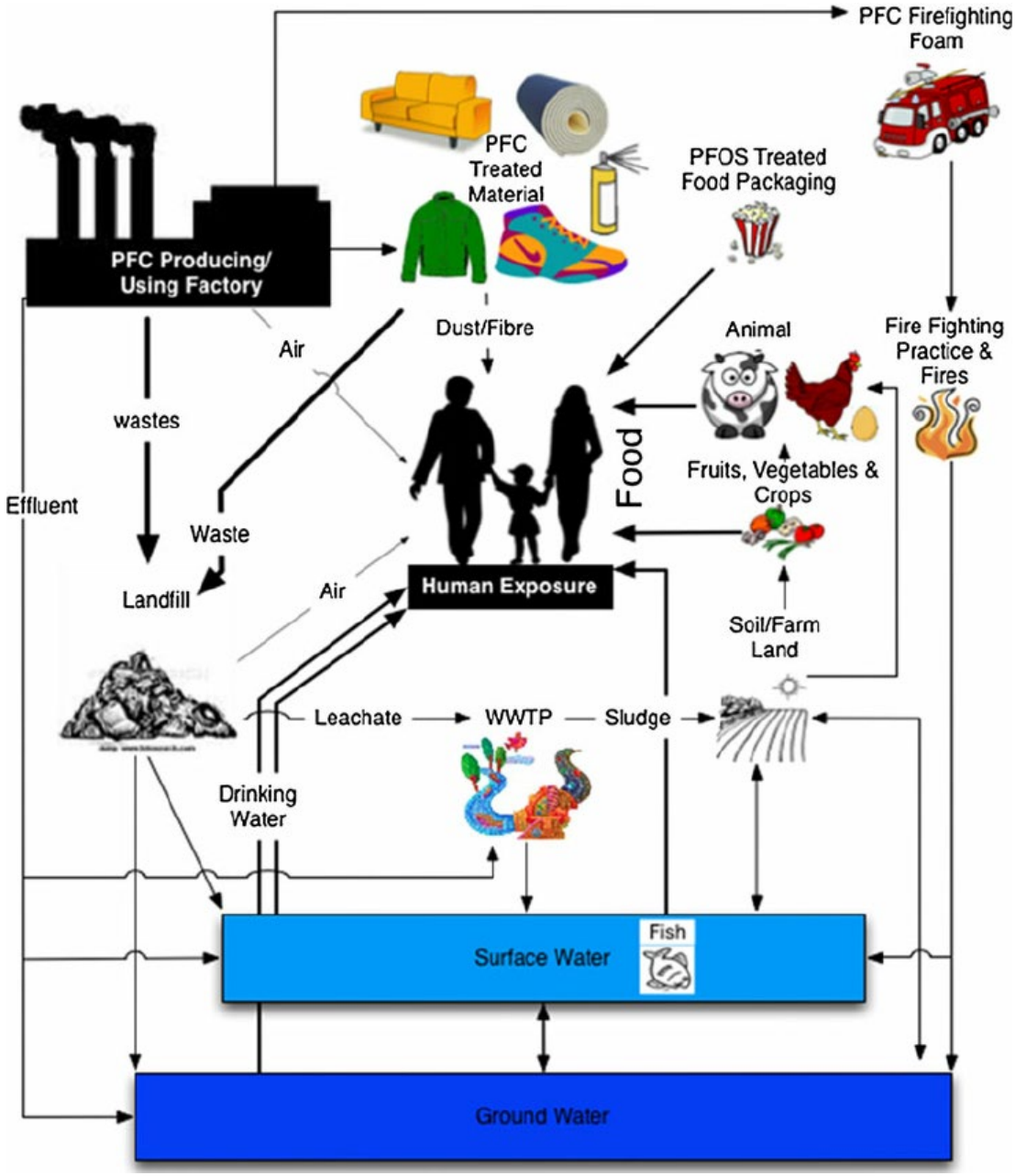
PFAS Exposure and Impacts on Health

Courtney Carignan, PhD
Michigan State University

The Current Webinar Series
North Central Region Water Network
November 13, 2019

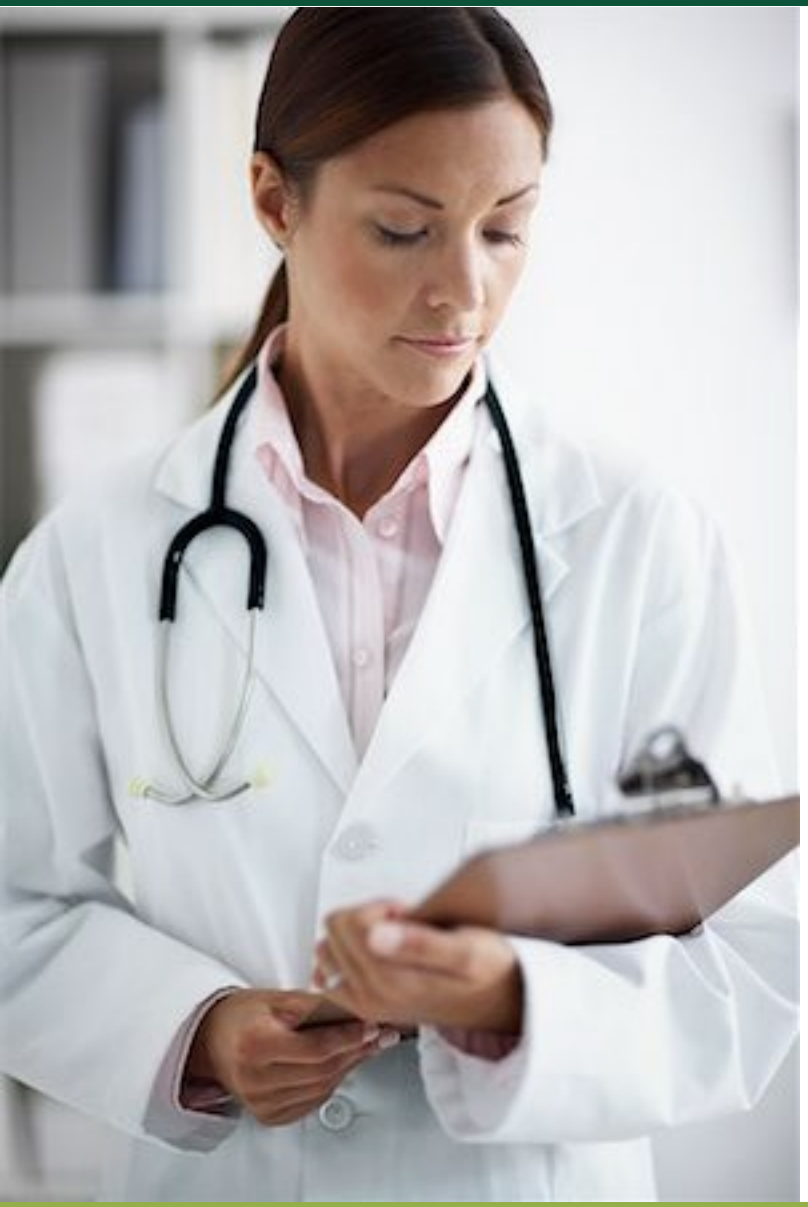
Poly- and Perfluoroalkyl Substances (PFAS)

Stain and Water Repellency



Oliaei et al. 2012


C8
PFOS
PFOA
https://www.youtube.com/watch?v=jmZUJJ8keBE



Health Concerns:

- elevated cholesterol
- changes in immune and hormone function
- decreased fertility
- kidney, testicular and prostate cancer

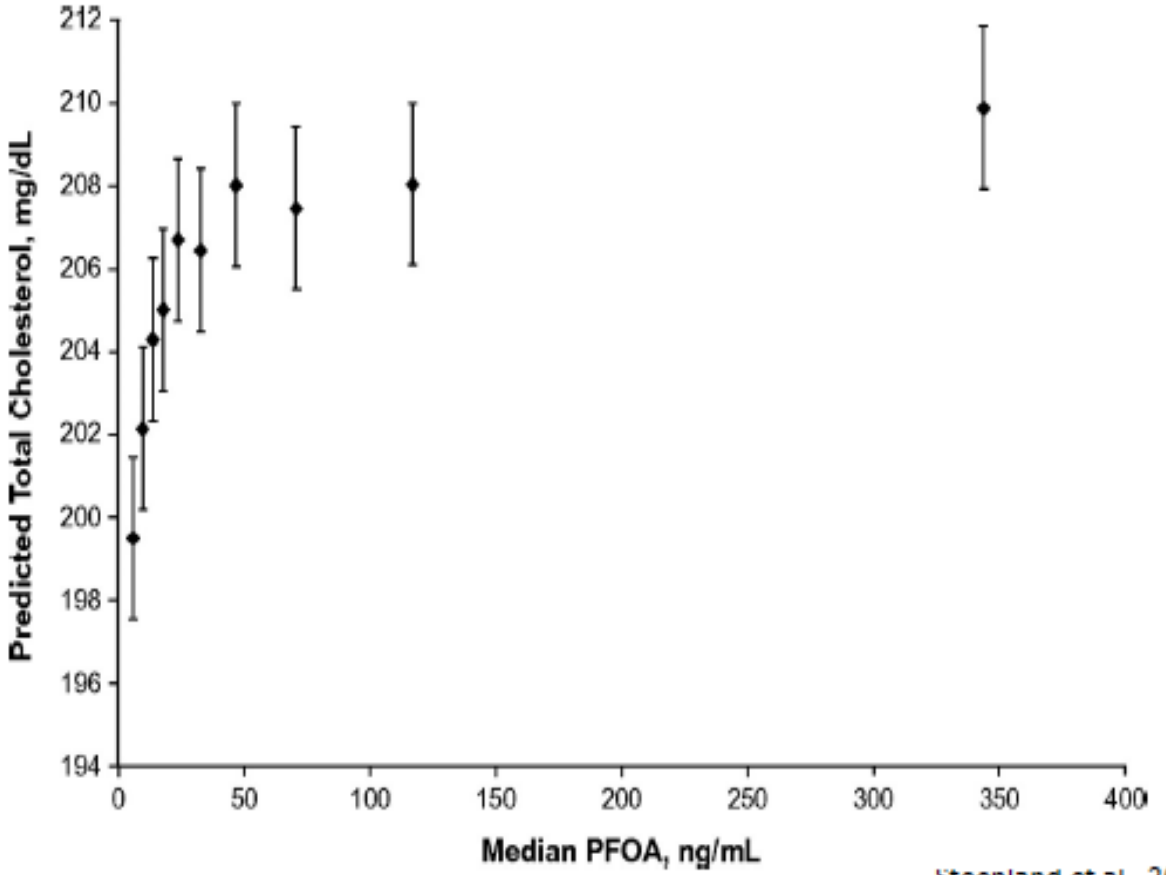
C8 Contamination in the Mid-Ohio River Valley

C8 Science Panel – Probable Links

C8sciencepanel.org

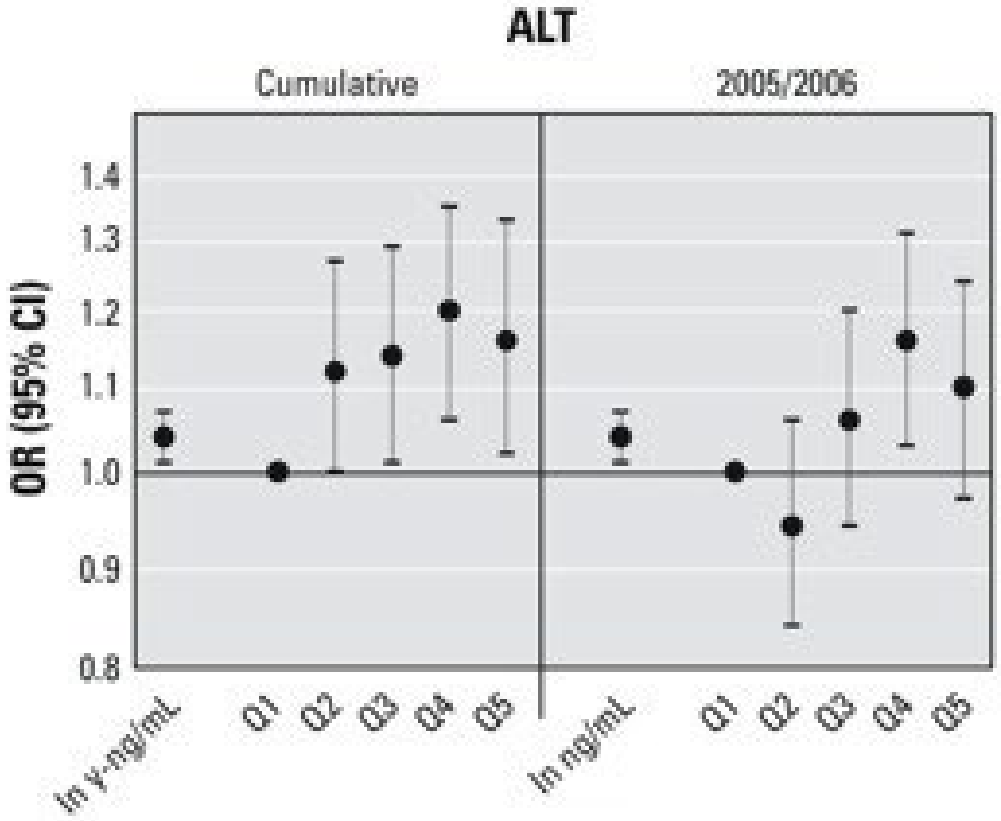
- High cholesterol
- Pregnancy induced hypertension
- Thyroid disease
- Ulcerative colitis
- Testicular cancer
- Kidney cancer

High Cholesterol



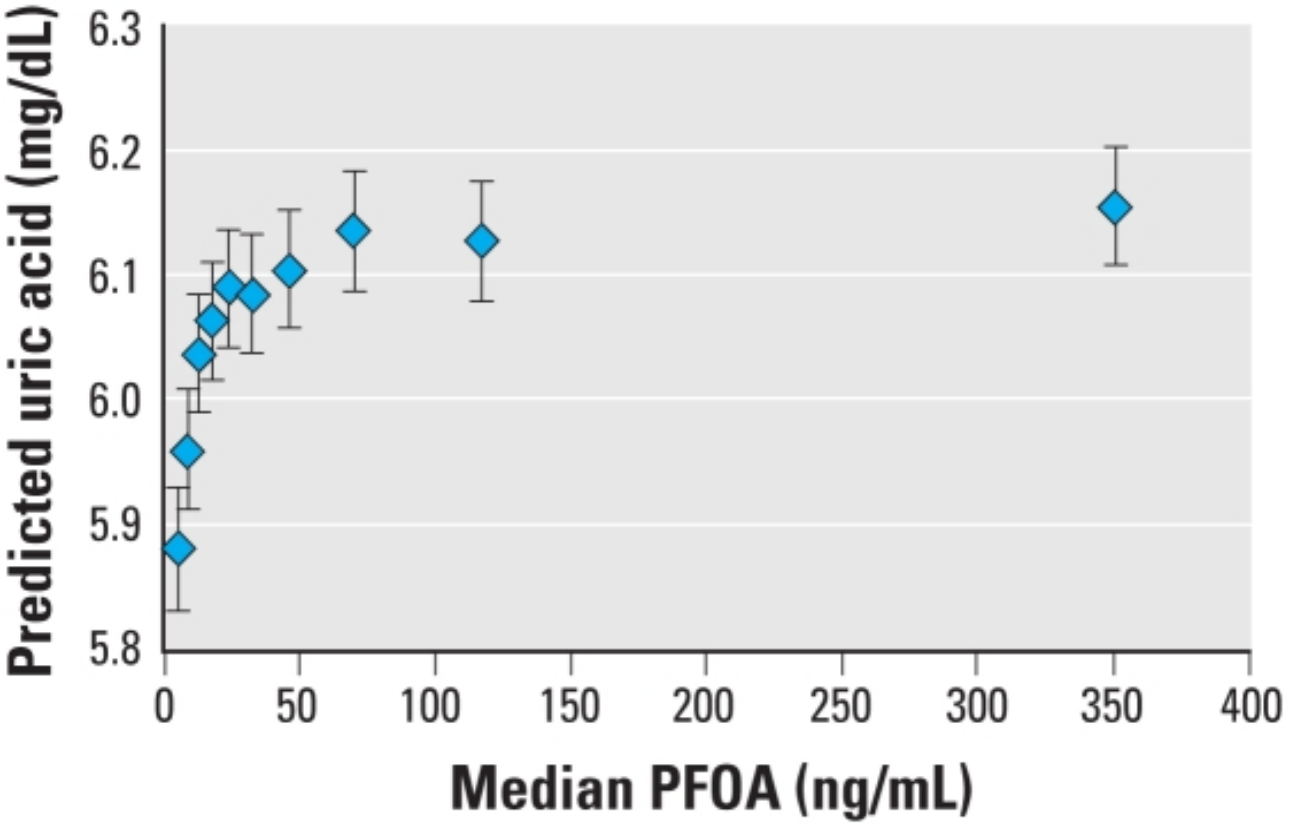
Steenland et al., 2009

Liver Function



Darrow et al. 2016

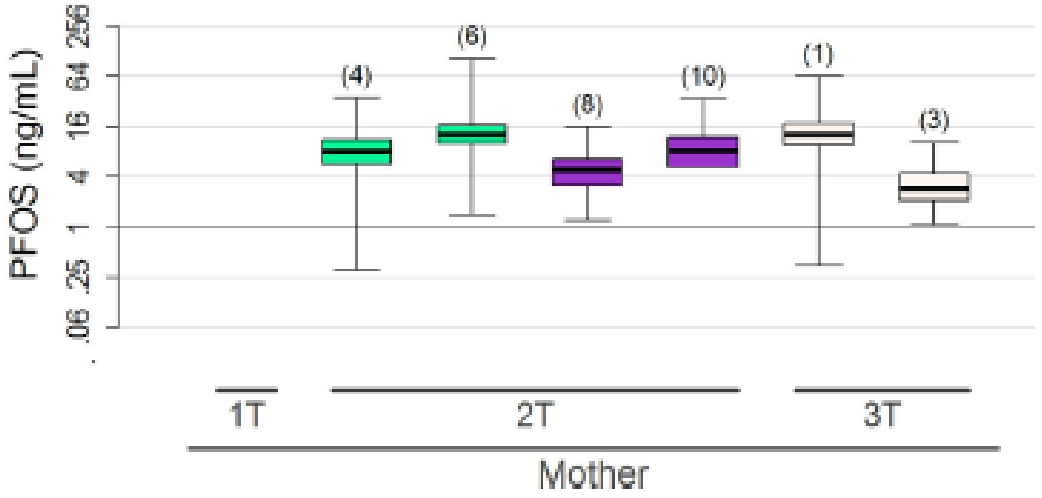
Kidney Function



Steenland et al. 2010

Thyroid Hormone Disruption

Increased thyroid stimulating hormone (TSH)



Ballesteros et al. *Environ Int* (2016)

Evidence of Carcinogenicity

- Rodent studies published in 1980s and 1990s reported evidence of carcinogenicity (Cook, et al. 1992 reported Leydig cell tumors)
- 3M Worker mortality studies reported excess **prostate cancer** (1993, 2009) and **bladder cancer** (2003).
- DuPont internal cancer registry showed excess incidence of **kidney cancer,** and WV workers study (2008) reported a slight excess of kidney cancer mortality [SMR=152 (95% CI: 78-265).

Odds of Cancer by Exposure Category

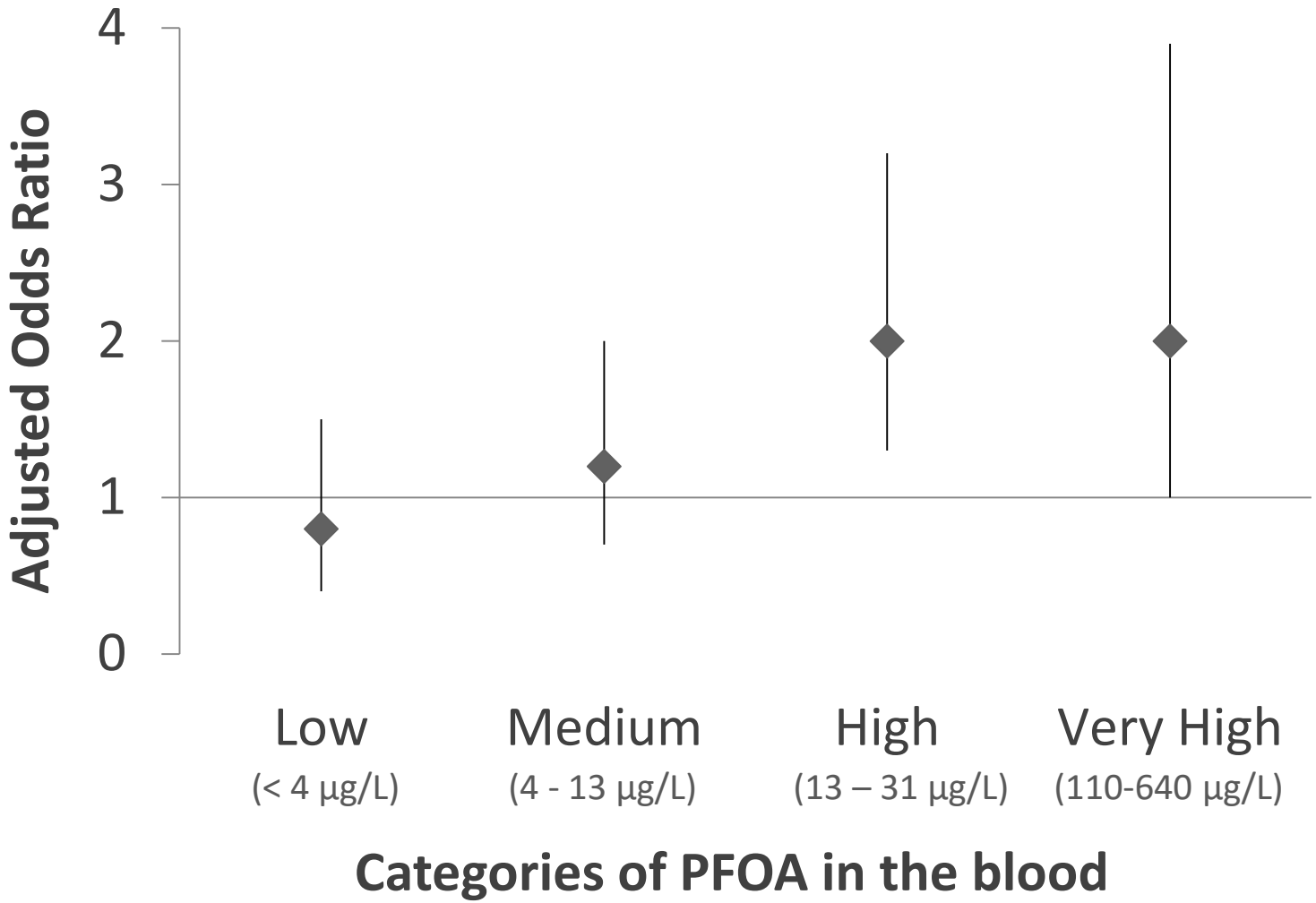
(95% Confidence Interval)

Cancer Type	Low	Medium	High	Very High
Brain	1.5 (0.8, 2.7)	**1.8 (1.1, 3.2)**	0.6 (0.2, 1.6)	—
Female breast	0.9 (0.7, 1.2)	1.1 (0.8, 1.5)	0.7 (0.5, 1.0)	1.4 (0.9, 2.3)
Kidney	0.8 (0.4, 1.5)	1.2 (0.7, 2.0)	**2.0 (1.3, 3.2)**	**2.0 (1.0, 3.9)**
Non-Hodgkin lymphoma	1.0 (0.6, 1.6)	**1.5 (1.0, 2.2)**	1.1 (0.7, 1.9)	**1.8 (1.0, 3.4)**
Ovary	0.5 (0.2, 1.4)	1.4 (0.7, 2.7)	1.4 (0.7, 2.9)	2.1 (0.8, 5.5)
Prostate	1.1 (0.8, 1.5)	0.8 (0.6, 1.0)	0.8 (0.5, 1.1)	1.5 (0.9, 2.5)
Testis	0.2 (0.0, 1.6)	0.6 (0.2, 2.2)	**1.3 (0.0, 2.7)**	**2.8 (0.8, 9.2)**

Adapted from Vieira et al. 2013

Wide confidence intervals are because study was underpowered

Odds of Kidney Cancer by Exposure Category



Adapted from Vieira et al. 2013

IARC Possible Carcinogen (2B)

Based on limited evidence in human and animal studies.

Testicular cancer
- 2 human studies
- 2 rat studies

Kidney cancer
- 4 human studies

Liver cancer
- 2 rat studies
- 2 studies of rainbow trout

Pancreatic cancer
- 1 rat study, male only

IARC Monographs, 2016

C8 Medical Monitoring Program

SCREENING BY AGE	
< 15 years	– High cholesterol – Thyroid disease (at parents' discretion) – Testicular cancer (exam not part of Program, but done as regular care)
15-18 years	– High cholesterol – Thyroid disease (at parents' discretion) – Ulcerative colitis – Testicular cancer
18-19 years	– High cholesterol – Thyroid disease – Ulcerative colitis – Testicular cancer
20 or older years	– High cholesterol – Thyroid disease – Ulcerative colitis – Testicular cancer – Kidney cancer
Pregnant Females	– Blood pressure & urine protein should be measured at each prenatal visit – these tests are part of standard prenatal care and may not be reimbursed by the Program. **Pregnant women may receive blood pressure monitoring devices provided by the Program.**

http://www.c-8medicalmonitoringprogram.com/docs/med_panel_education_doc.pdf

Impacts on Immune Function

Systematic review of 33 human, 93 animal and 27 *in vitro*/mechanistic studies concluded that PFOA and PFOS are presumed to be immune hazards to humans.

National Toxicology Program Monograph on Immunotoxicity Associated with Exposure to Perfluorooctanoic Acid (PFOA) or Perfluorooctane Sulfonate (PFOS) (September 2016)

Fertility and Reproduction

Proper functioning of thyroid and sex hormones are important for fertility, health pregnancy, and fetal development.

Decreased Fertility

- Odds of infertility increased by 31% for each standard deviation increase of PFOA and by 21% for PFHxS (Valez et al. 2015).
- Lower sperm concentration and sperm count (Vested et al. 2013) 35% reduction in morphology of normal sperm (Toft et al. 2012) with increased exposure to PFOA and PFOS.
- Increased post-implantation loss (i.e., miscarriage)

Decreased Fetal Growth

Systematic review of 18 human and 21 animal toxicology studies concluded that developmental exposure to PFOA adversely affects human health based on sufficient evidence of decreased fetal growth both in human and nonhuman mammalian species (Lam et al. 2014).

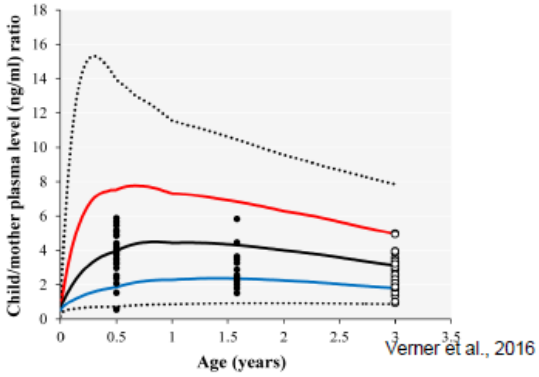
Delayed Mammary Gland Development

- Occurs at **much lower doses** than most other developmental effects.
  - Most sensitive endpoint with data for dose-response modeling.
- Conclusions of detailed evaluation: **adverse** and **relevant to humans**.
- Reported in **nine separate studies** from perinatal (fetal or neonatal) exposure to mice.
  - Reported in dams and female offspring, in two strains of mice, and from gestational and/or lactational exposure.
  - Not found in one study with problematic issues.
  - **Structural changes that persist until adulthood**.
- Effects differ with lifestage (perinatal v. peripubertal exposure).
- Insufficient toxicology data to make conclusions about effects on lactational function.
  - Possibly relevant – several humans studies associated PFOA with decreased duration of breastfeeding.

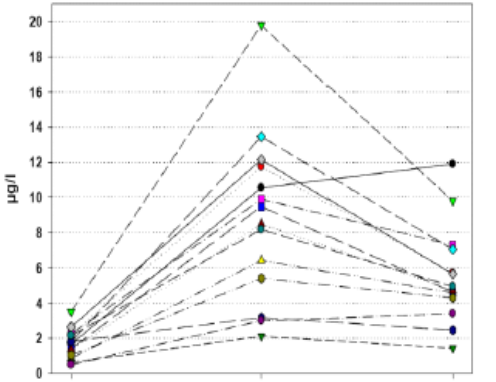
NJ DWQI, 2016

Increased Exposure during Early Life

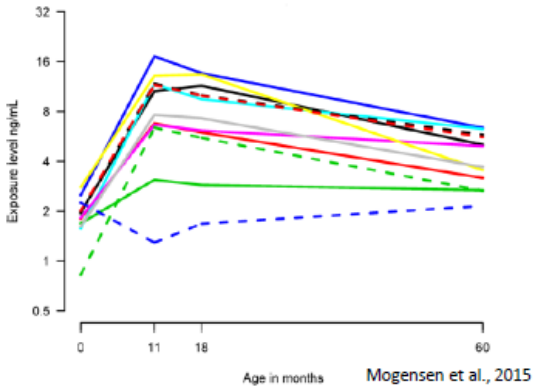
Increases in Infant PFOA Serum Levels after Birth



Verner et al., 2016



Fromme et al., 2010



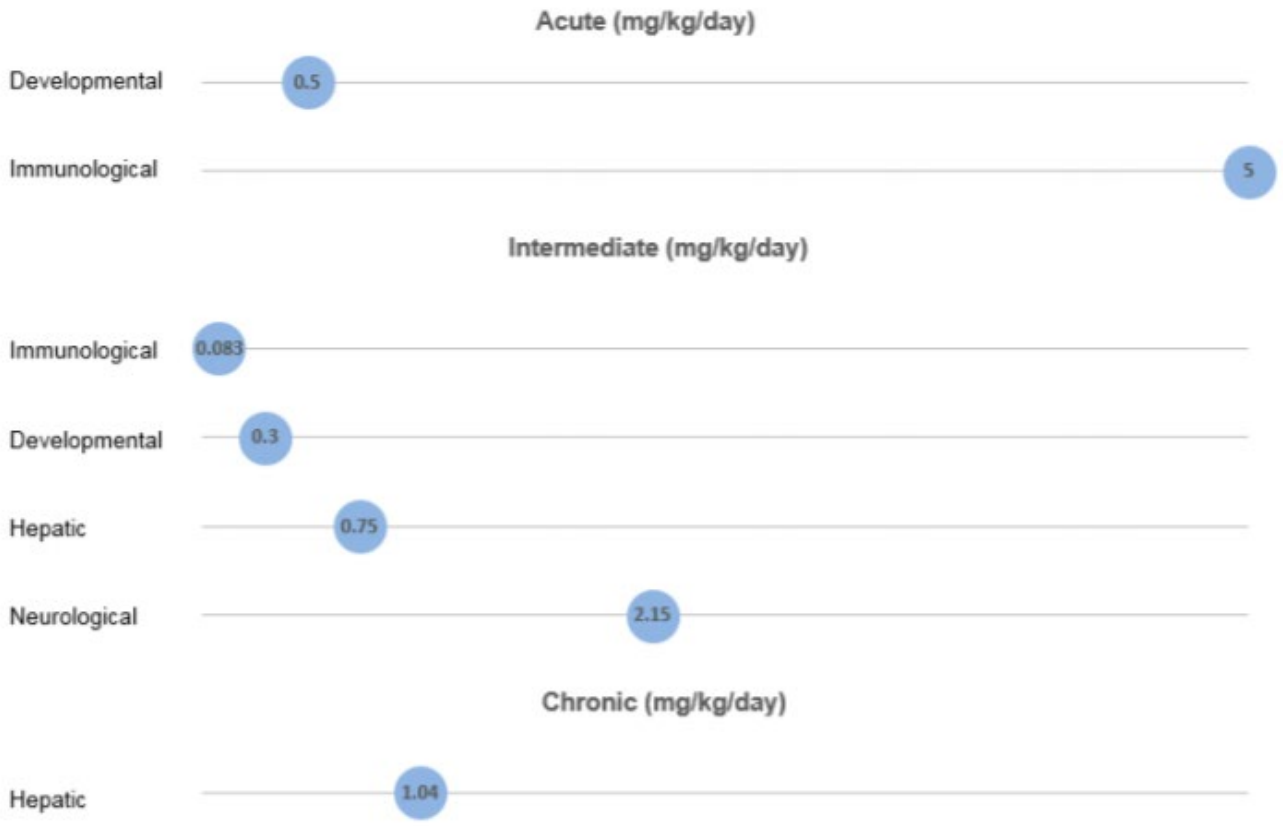
Mogensen et al., 2015

Toxicological Profile

Agency of Toxic Substances and Disease Control Registry

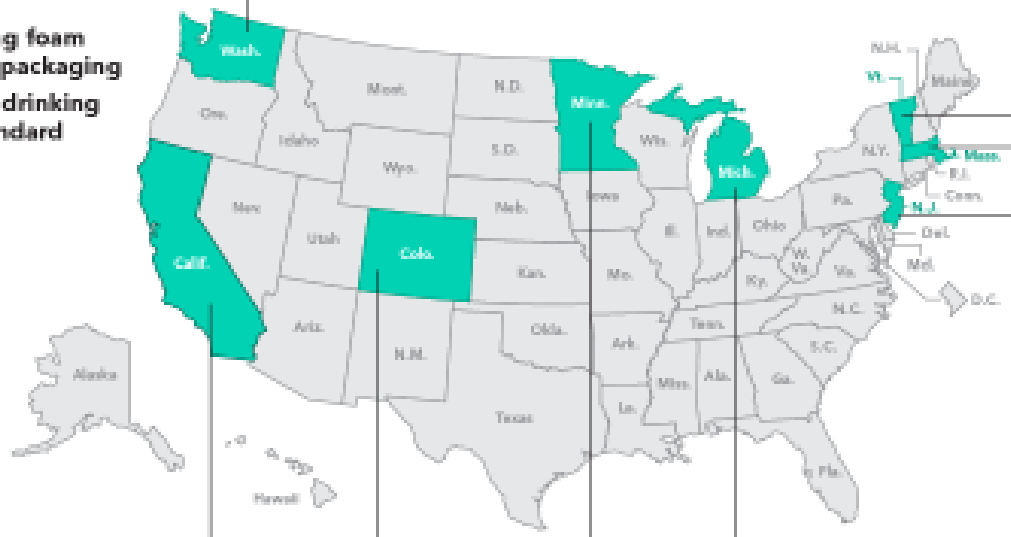
Figure 1-5. Summary of Sensitive Targets of PFOS – Oral

The immune system and developing organism are the most sensitive targets of PFOS.
Numbers in circles are the lowest LOAELs for all health effects in animals.



ATSDR 2018

States With Numerical PFAS Limits



Washington

- Banned in firefighting foam and food packaging
- Proposed drinking water standard

Vermont

- 20 PPT (PFAS)
- Drinking water health advisory for 5 PFAS

Massachusetts

- 70 PPT (PFAS)
- State guidance for concentrations of 5 PFAS in drinking water

New Jersey

- Set PFNA standard at 13 ppt
- Weighing proposed standards for:
  PFOA at 14 ppt
  PFOS at 13 ppt

California

- 14 PPT (PFOA)
- 13 PPT (PFOS)
- Drinking water notification guidance

Colorado

- PFOA/PFAS listed as hazardous waste
- 70 PPT (Combined PFOA/PFOS)
- Groundwater quality standard for El Paso County only

Minnesota

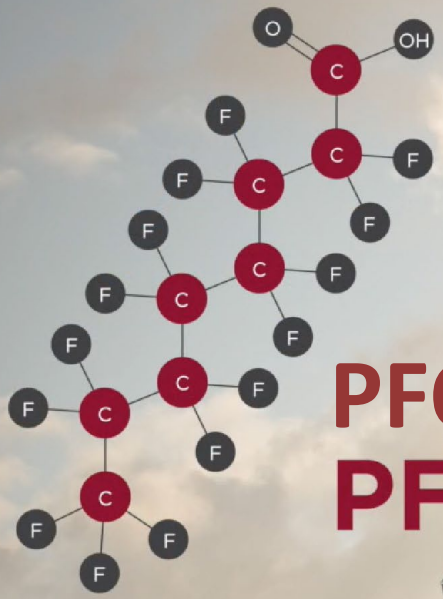
- 35 PPT (PFOA)
- 27 PPT (PFOS)
- Health-based guidance values

Michigan

- 70 PPT (Combined PFOA/PFOS)
- State standard for concentrations in drinking water

Bloomberg Environment


C8
PFOS
PFOA
https://www.youtube.com/watch?v=jmZUJJ8keBE



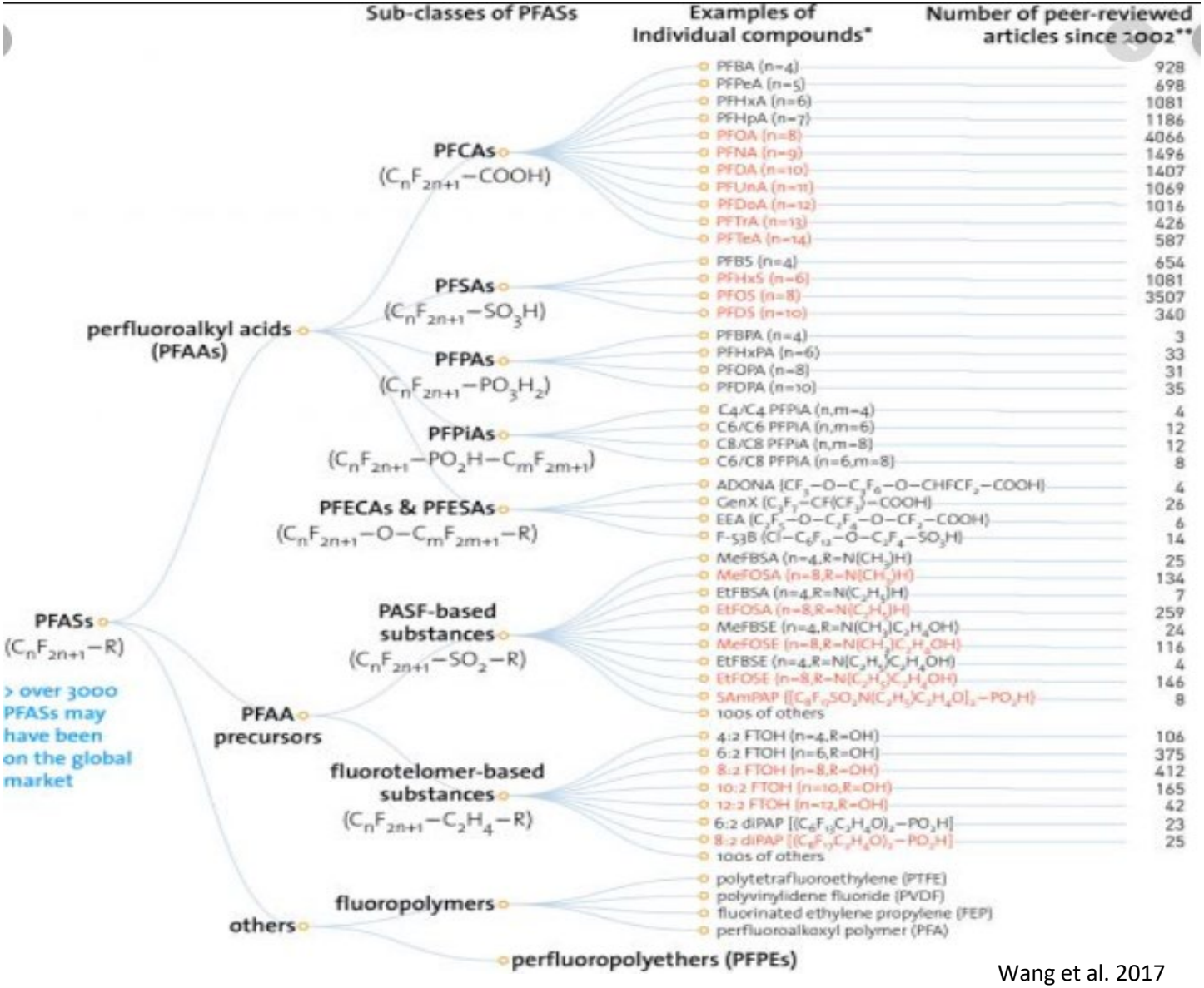
C8

PFOS

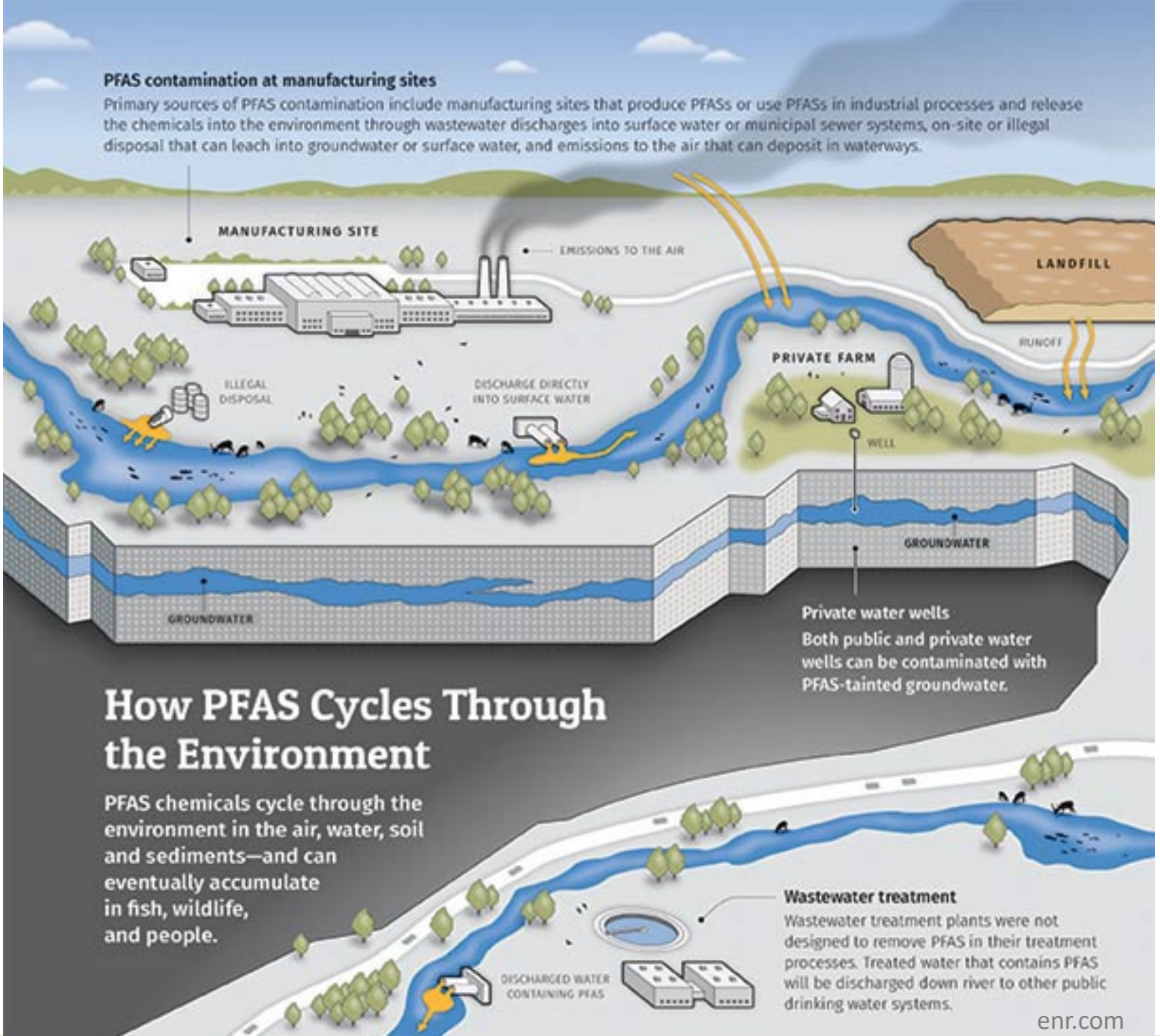
PFOA

C6 | C4 | C3

https://www.youtube.com/watch?v=jmZUJJ8keBE

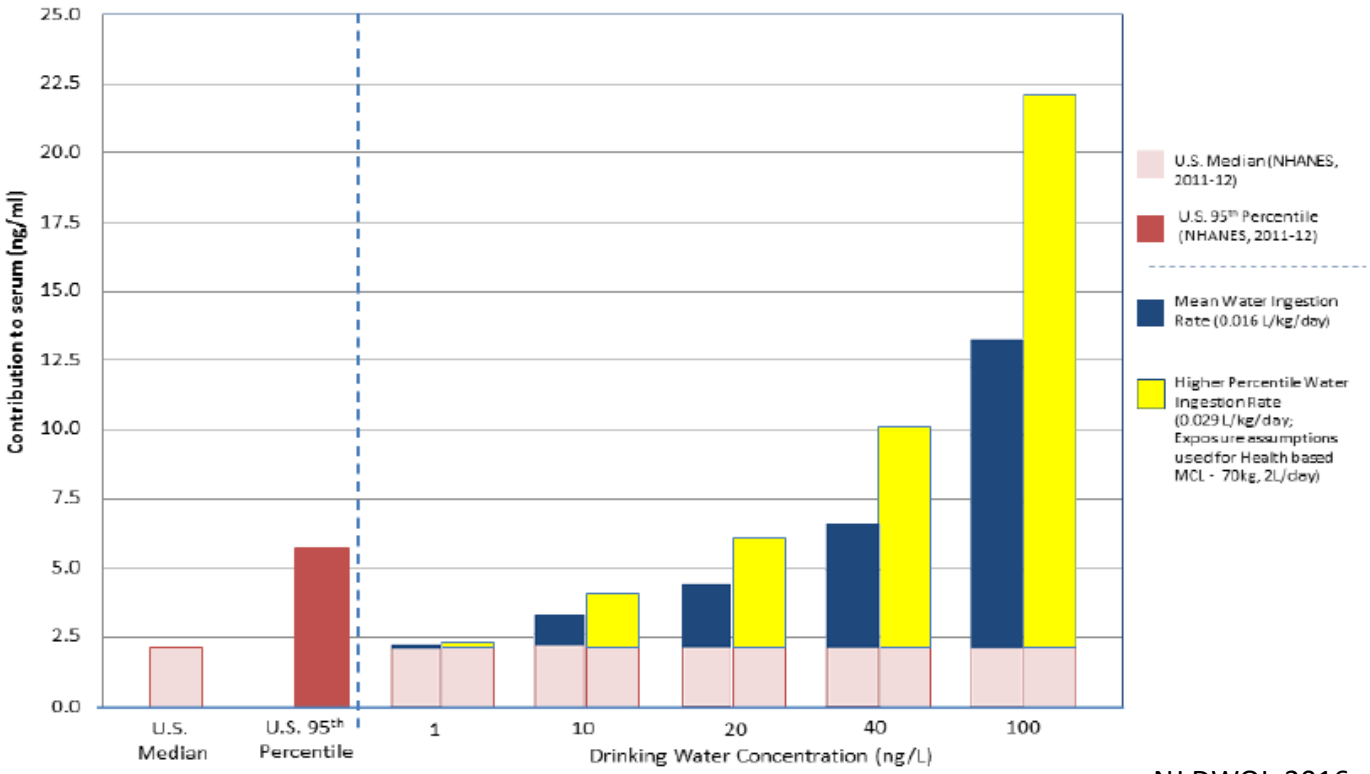


Wang et al. 2017


PFAS contamination at manufacturing sites
Primary sources of PFAS contamination include manufacturing sites that produce PFASs or use PFASs in industrial processes and release the chemicals into the environment through wastewater discharges into surface water or municipal sewer systems, on-site or illegal disposal that can leach into groundwater or surface water, and emissions to the air that can deposit in waterways.
MANUFACTURING SITE
EMISSIONS TO THE AIR
LANDFILL
RUNOFF
PRIVATE FARM
ILLEGAL DISPOSAL
DISCHARGE DIRECTLY INTO SURFACE WATER
WELL
GROUNDWATER
GROUNDWATER
Private water wells
Both public and private water wells can be contaminated with PFAS-tainted groundwater.
How PFAS Cycles Through the Environment
PFAS chemicals cycle through the environment in the air, water, soil and sediments—and can eventually accumulate in fish, wildlife, and people.
DISCHARGED WATER CONTAINING PFAS
Wastewater treatment
Wastewater treatment plants were not designed to remove PFAS in their treatment processes. Treated water that contains PFAS will be discharged down river to other public drinking water systems.

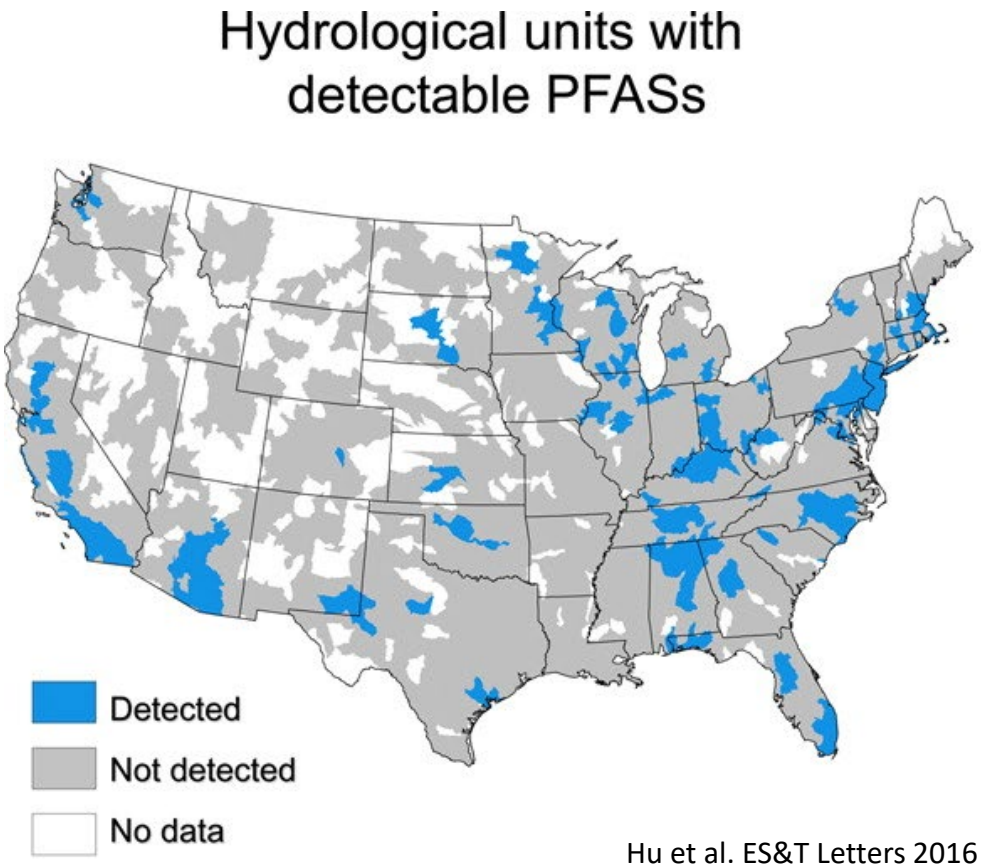
Drinking water exposure is important

Increases in Serum Concentrations Predicted from Ongoing Exposure to PFOA in Drinking Water

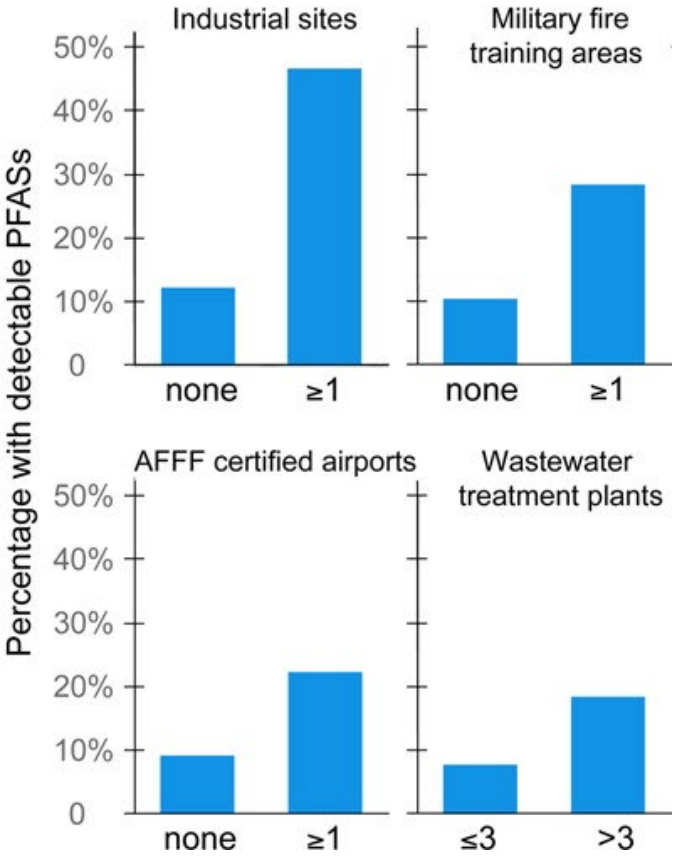


NJ DWQI, 2016

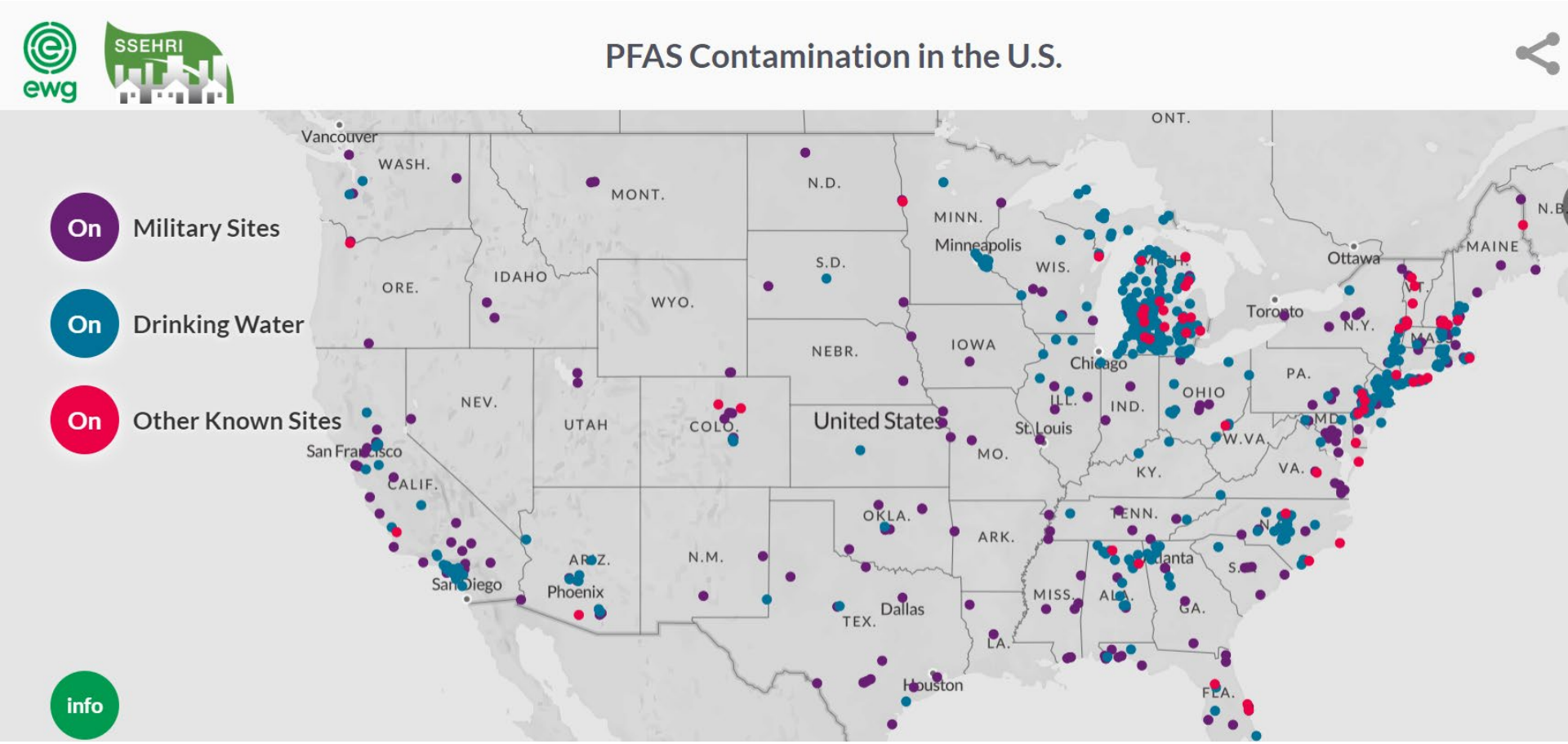
> 6 Million Americans with Impacted Water

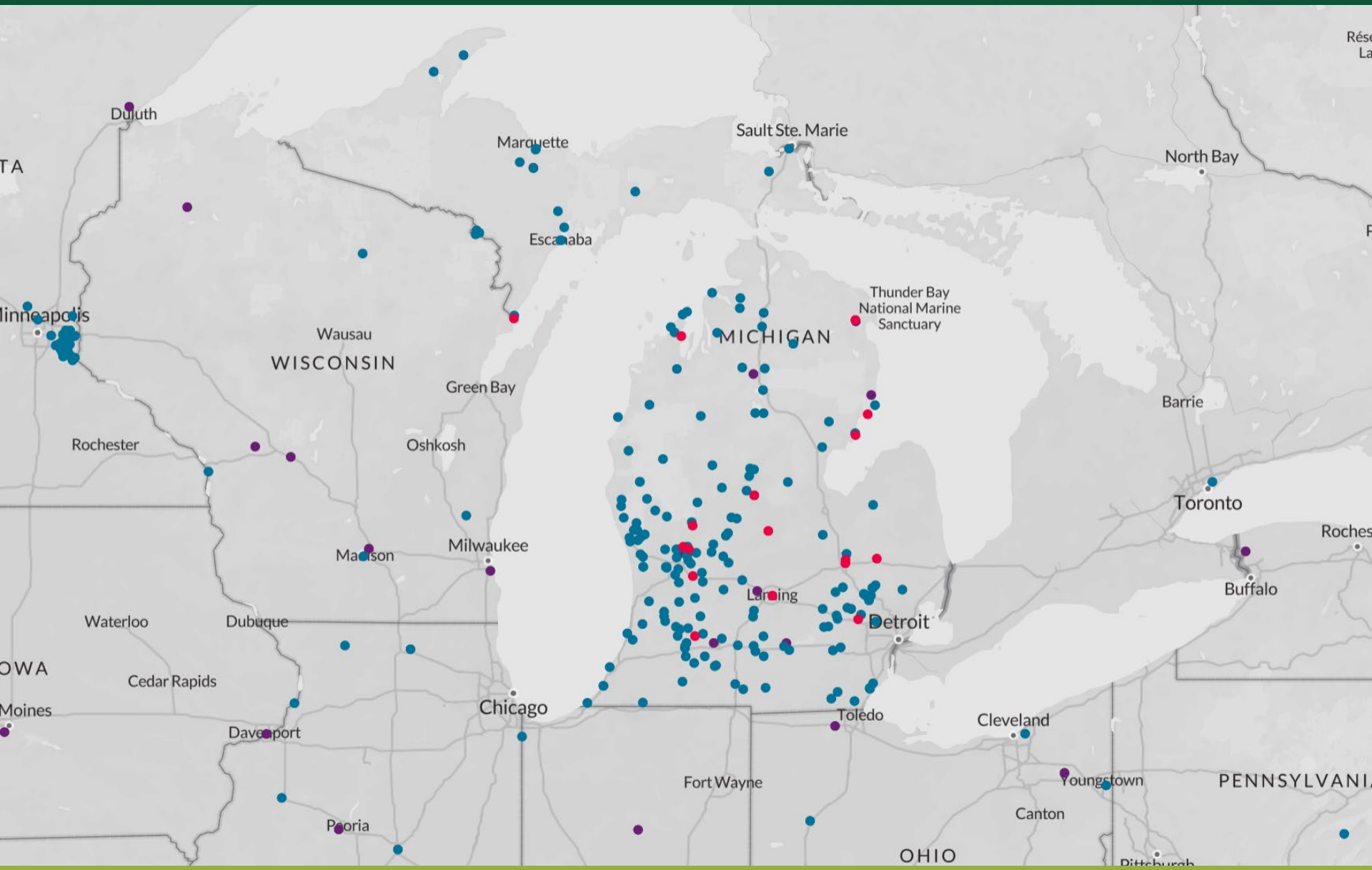


Hu et al. ES&T Letters 2016



110 Million Americans with Impacted Water



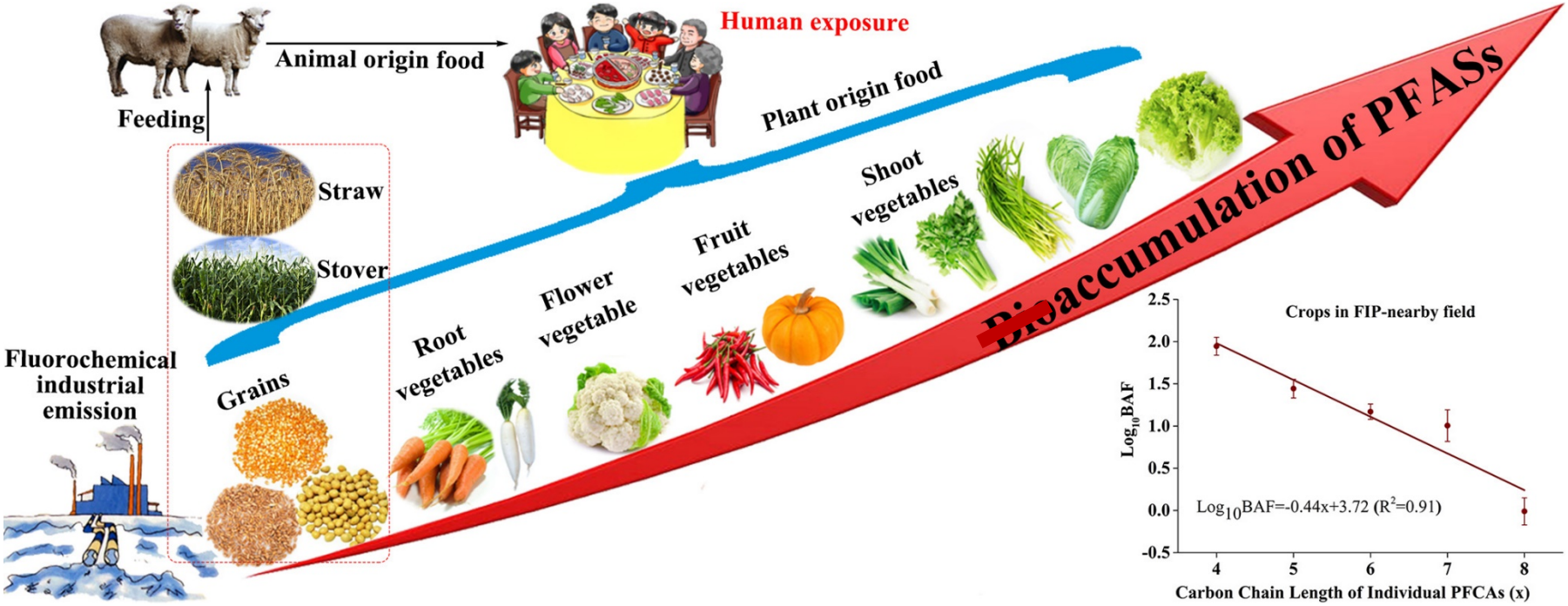

Duluth
Marquette
Sault Ste. Marie
North Bay
Escanaba
Thunder Bay
National Marine
Sanctuary
MICHIGAN
Wausau
WISCONSIN
Green Bay
Barrie
Rochester
Oshkosh
Toronto
Madison
Milwaukee
Buffalo
Waterloo
Dubuque
Detroit
Cedar Rapids
Chicago
Toledo
Cleveland
Davenport
Fort Wayne
Youngstown
PENNSYLVANI
Peoria
Canton
OHIO

Duluth
Marquette
Sault Ste. Marie
North Bay
Escanaba
Minneapolis
Wausau
WISCONSIN
MICHIGAN
Barrie
Rochester
Milwaukee
Madison
Lansing
Detroit
Waterloo
Dubuque
Cedar Rapids
Moines
Davenport
Toledo
Cleveland
Fort Wayne
Youngstown
PENNSYLVANI
Canton
Peoria
OHIO
Buffalo

Drinking Water Interventions

Foam and Deer Advisories

Do Not Eat Advisories



Liu et al 2019

PFAS UNITEDD

U.S. National Investigation of Transport and Exposure from Drinking Water and Diet

"Community concerns extend beyond drinking water to include locally grown, produced and captured foods such as garden produce and fish."

Courtney Carignan, PhD – Michigan State University

https://pfasunitedd.org

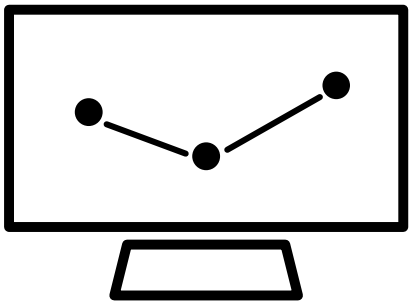
PFAS UNITEDD is a partnership of Colorado School of Mines, Colorado School of Public Health, Duke University, Michigan State University, and North Carolina State University funded under grant 83948201.

This map will be updated quarterly to reflect additional sites where ATSDR and state partners are involved. The location and size of Alaska, Hawaii, and Puerto Rico were altered to fit this map view. Data sources: ATSDR Environmental Health Portfolio Management database and internal updates from ATSDR Regional and Technical Project Officer staff.

Science Support Branch
data organization . analysis . visualization
Updated May 2018

PFAS-REACH

Effects on children's immune systems



PFAS Exchange: Online resource center

Experiences of affected communities

NIH NIEHS

PFAS-REACH is a partnership of Silent Spring Institute, Northeastern University, and Michigan State University, funded under grant R01ES028311.

TESTING *for* PEASE

National Conference on PFAS

https://pfasproject.com/2019/02/05/2019-pfas-conference/

Toxins in the Water: PFAS in Michigan

Environmental Science
& Policy Program
at Michigan State University

Fate of the Earth Symposium

Federal-State-Community-Academic Partnerships

Contact

Courtney Carignan

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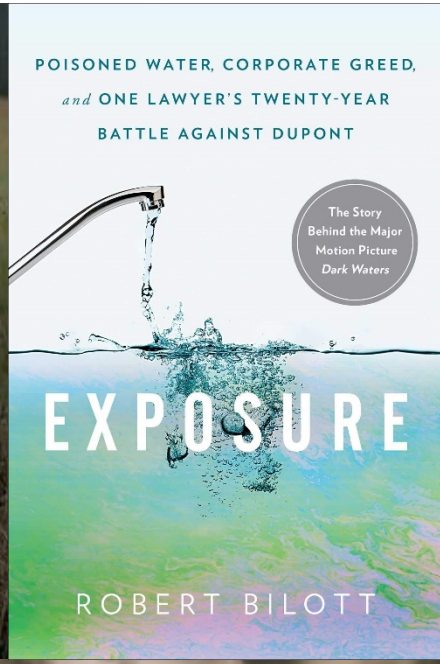
@cccarignan

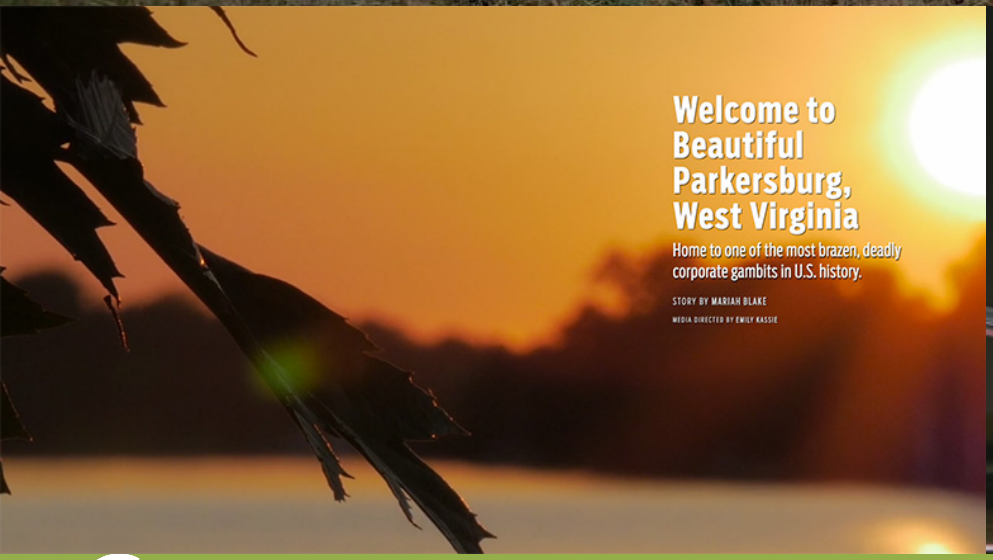
Michigan's Draft Drinking Water MCLs

- PFOA: 8 ppt
- PFOS: 16 ppt
- PFHxS: 51 ppt
- PFNA: 6 ppt
- PFBS: 420 ppt
- PFHxA: 400,000 ppt
- GenX: 370 ppt

DeWitt et al. 2019
https://www.michigan.gov/pfasresponse


The New York Times
The Lawyer Who Became DuPont's Worst Nightmare
Rob Bilott was a corporate defense attorney for eight years. Then he took on an environmental suit that would upend his entire career — and expose a brazen, decades-long history of chemical pollution.
By NATHANIEL RICH JAN. 6, 2016

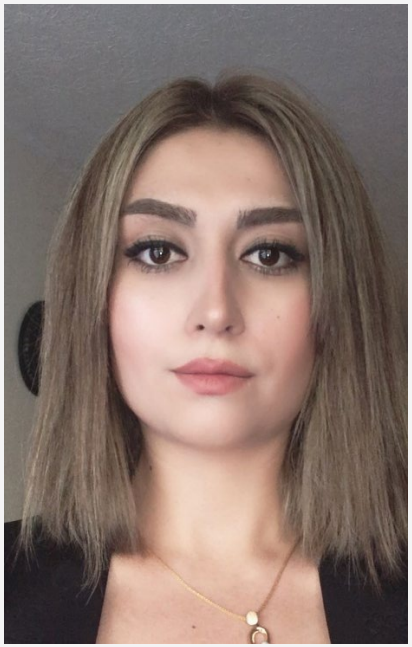

POISONED WATER, CORPORATE GREED, and ONE LAWYER'S TWENTY-YEAR BATTLE AGAINST DUPONT
The Story Behind the Major Motion Picture Dark Waters
EXPOSURE
ROBERT BILOTT


Welcome to Beautiful Parkersburg, West Virginia
Home to one of the most brazen, deadly corporate gambits in U.S. history.
STORY BY MARIAH BLAKE
MEDIA DIRECTED BY EMILY KASSIE


THE DEVIL WE KNOW

Dark Waters – Premiers November 22nd

Mahsa Modiri-Gharehveran



Mahsa is a post-doctoral research assistant in Environmental Chemistry at Purdue University and in the department of Agronomy, under the guidance of Dr. Linda Lee. She joined this research group after completing her Ph.D. in Environmental Engineering at Purdue University. She is also holding a B.Sc. degree in Civil Engineering and M.Sc. degree in Water Engineering. Currently, her research focuses on the fate, transport, and remediation of per- and polyfluoroalkyl substances (PFAS) in different media.

PFAS: Occurrence in Composts and Biosolids and Remediation Approaches

Mahsa Modiri Gharehveran

Linda S. Lee

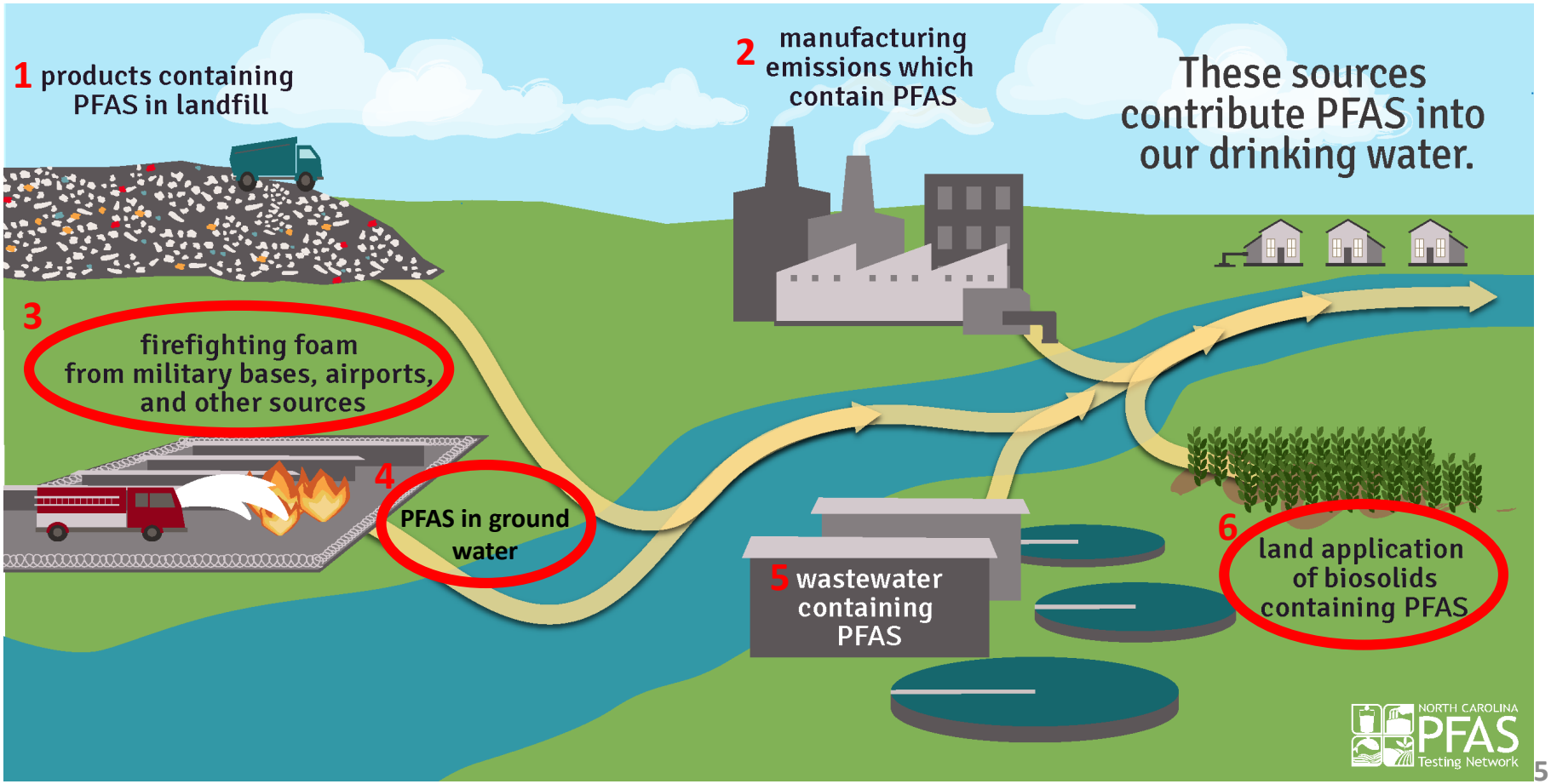
PURDUE UNIVERSITY

AGRONOMY grows here.

November 13, 2019

North Central Region Water Network Speed Networking Webinar Series

PFAS Sources Into the Environment



Adapted from NC PFAS Testing Network. https://ncpfastnetwork.com/printed-materials/ **(accessed Nov 11th, 2019)**

PFAS Subclass Perfluoroalkyl acids (PFAAs) vs Other PFAS

OTHER PFAS: PFAA

Precursors

In soils, during composting, in WWTP processes, etc.

PFAS Intermediates (multiple steps)

PFAAs

Persistent

Anionic (-), low pK_a

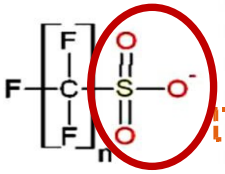
More soluble

More mobile

PFAAs = PFCAs + PFSAs

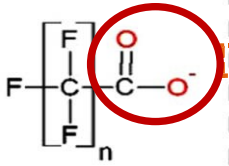
terminal microbial metabolites

Perfluoroalkylsulfonic acids



PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

Perfluoroalkylcarboxlic acids



PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

C1 **M**ethane
C2 **E**thane
C3 **P**ropane
C4 **B**utane
C5 **Pe**ntane
C6 **Hex**ane
C7 **Hep**tane
C8 **Oct**ane
C9 **N**onane
C10 **D**ecane
C11 **Un**odecane
C12 **Do**decane
C13 **Tri**decane
C14 **Te**tradecane

Source: Backe et al., 2013

➢ **Short vs long** terminology (**perfluoroalkyl chain** not just carbon number)

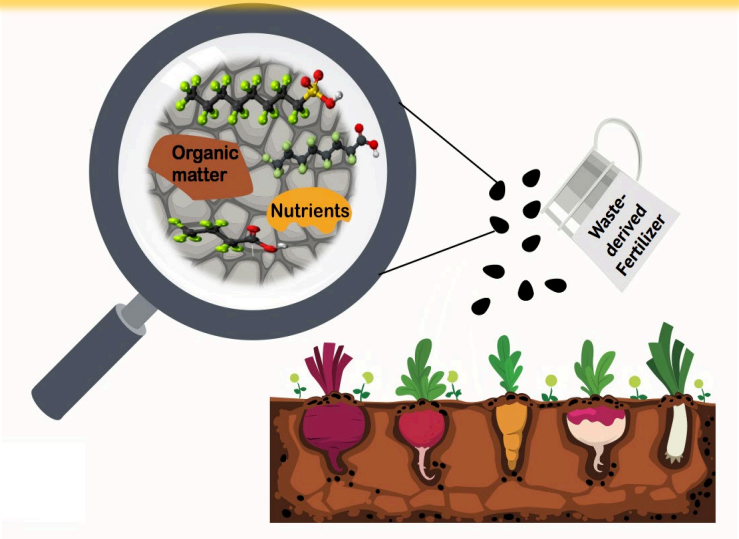
Long-chain PFCAs: ≥ C7 **Long-chain PFSAs: ≥ C6**

Organic Waste-based Soil Amendments

- **Benefits:**

Recycling wastes for plant nutrients and improving soil health

- **Current challenge:** Potential leaching of PFAAs to water sources



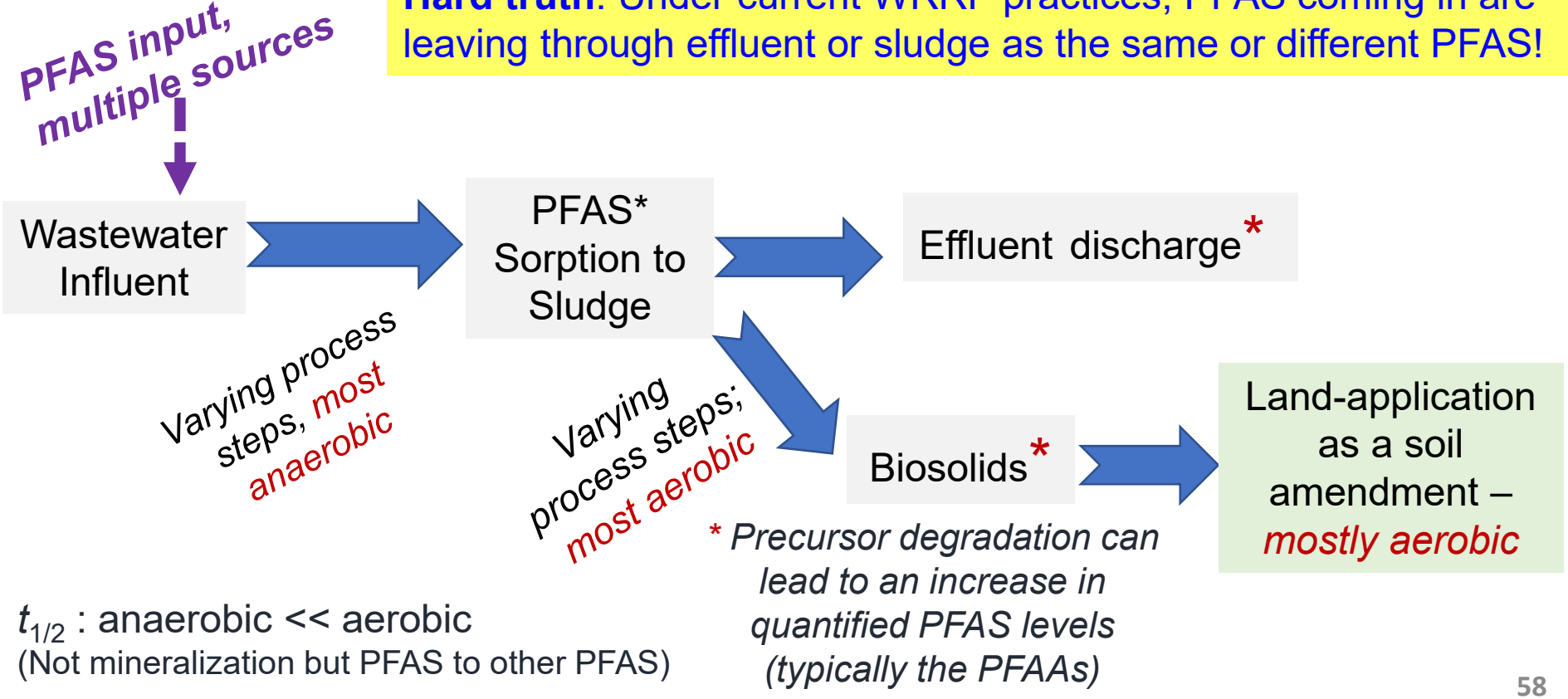
- **Question being addressed:**

What PFAAs are present?

- **At Purdue:** We have been quantifying PFAAs concentrations in different types of waste-derived and commercially available organic products

PFAS Fate in Water Resource & Recovery Facilities (WRRFs)

Hard truth: Under current WRRF practices, PFAS coming in are leaving through effluent or sludge as the same or different PFAS!

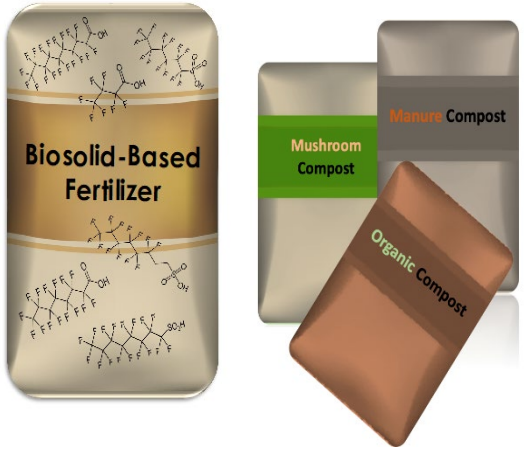


$t_{1/2}$: anaerobic << aerobic
(Not mineralization but PFAS to other PFAS)

PFAS in Composts and Biosolids-based Products

Occurrence

Commercially Available Organic Products



Municipal Organic Solid Wastes (OFMSW)

Landfilling

Compost

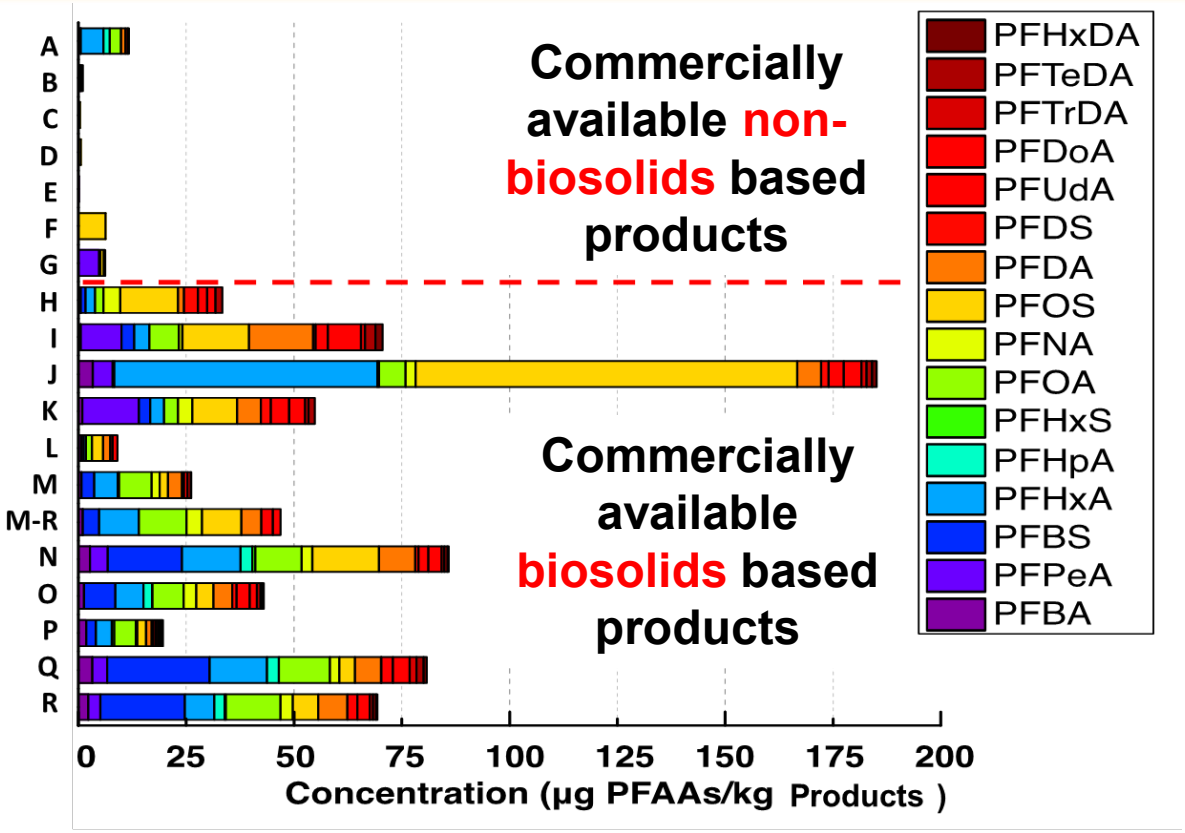
What PFAAs and other PFAS are present in commercially available waste-derived products ?

Commercially Available Organic Products & OFMSW Composts Investigated

Commercially Available Products (2014)
A) Food and yard compost
B) Compost with untreated wood products
C) Manure compost
D) Manure and peat compost
E) Mushroom compost
F) Mushroom compost
G) Peat/compost based growing mix
H) Heat-dried granular biosolids
I) Heat-dried granular biosolids
J) Heat-dried granular biosolids
K) Heat-dried granular biosolids
L) Heat-dried granular biosolids
M) Biosolids blended with maple sawdust and aged bark
N) Composted biosolids with woodchips
O) Composted biosolids with woodchips
P) Composted biosolids with municipal solid waste
Q) Composted biosolids with residential yard trimmings
R) Composted biosolids with plant materials

Municipal Organic Solid Wastes (OFMSW) Composts (Obtained through Zero Waste Washington in 2017)
1) Residential and commercial food waste and yard waste. **Allows compostable food packaging**.
2) Municipal food and yard waste and wood products. **Allows compostable food packaging.**
3) Residential and commercial food waste and yard waste. **Allows compostable food packaging.**
4) Residential and commercial food waste and yard waste. **Allows compostable food packaging.**
5) Residential and commercial food waste and yard waste. **Allows compostable food packaging.**
6) Residential and commercial food waste and yard waste. **Allows compostable food packaging.**
7) Primarily commercial food waste (food scraps, coffee grounds, lobster shells), horse manure and wood shavings. **Allows compostable food packaging.**
8) Leaves and grass from municipalities.
9) Backyard Waste Compost Bin. Includes yard trimmings, food waste and unbleached coffee filters. No compostable serviceware or other paper products.
10) Primarily leaves from municipalities.

PFAS in **2014** Commercially Available Organic Products

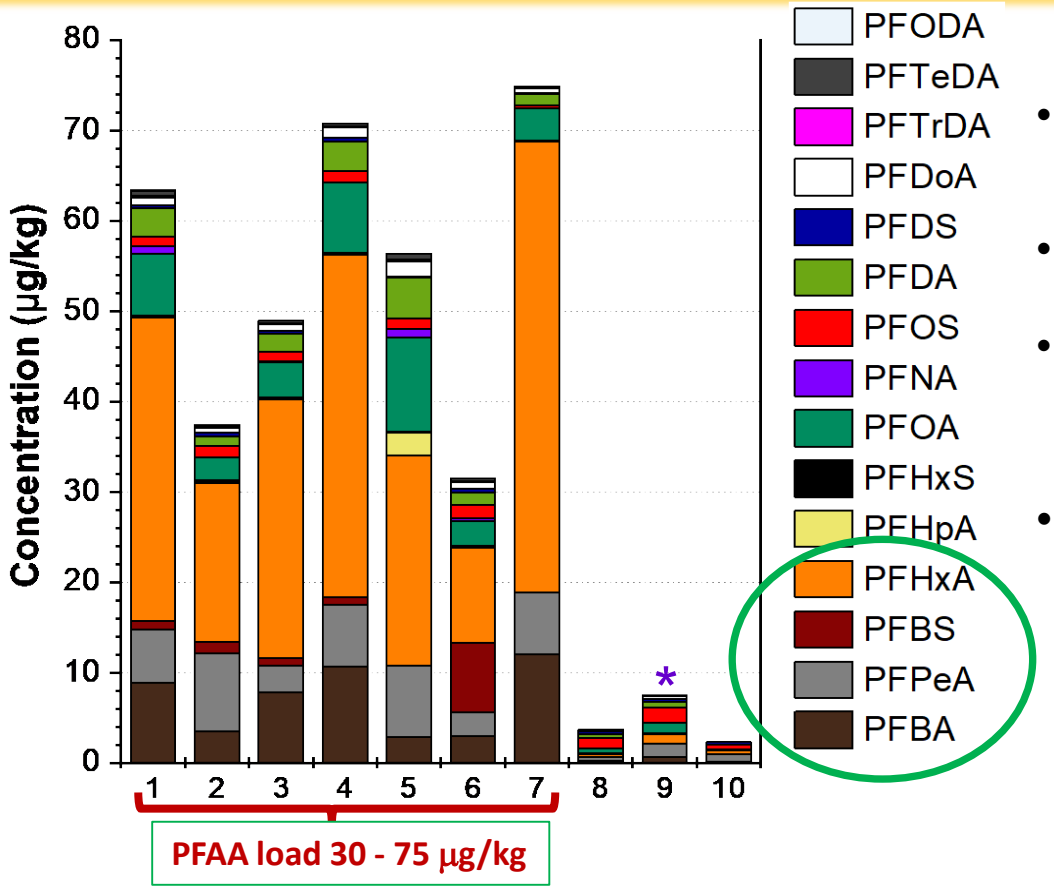


- Higher PFAA loads in **biosolids** based products
- For most of the **biosolids** based products the concentration ranged between 30 – 80 µg/kg
- Longer chains C ≥ 6 dominant
- For one product, the PFAAs concentration was 185 µg/kg
- QToF screening revealed several PFAA precursors (sulfonamides, fluorotelomer sulfonates, PAPs/diPAPs)

*PFAA conc. in < 2 mm fraction (36-80%) normalized to total products (negligible PFAA conc. in the > 2 mm fraction)

(Kim Lazcano et al., *in preparation*)

PFAAs in 2017 OFMSW Composts



Choi, Lee et al., ES&T Letters,
https://doi.org/10.1021/acs.estlett.9b00280

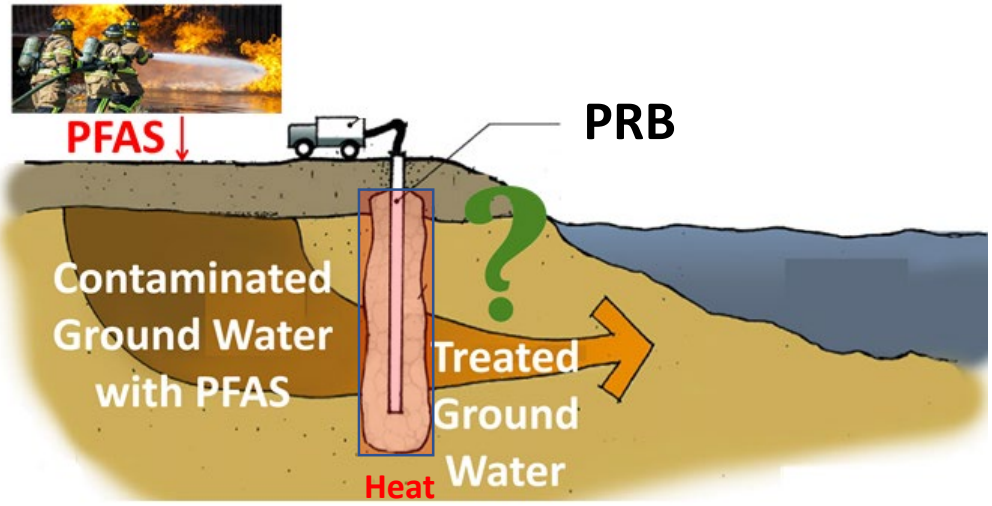
- Higher PFAA loads in OFMSW #1-7 with compostable food packaging
- Shorter chains C ≤ 6 dominant
- #9* included food wastes, coffee grounds, unbleached coffee filters
- PFAA precursors identified similar to biosolid-base products

Data led to Washington's Healthy Food Packaging Act:
HB 2658 - 2017-18: Concerning the use of PFAS in food packaging.

PFAS Contaminated Groundwater

Plume generation from aqueous film forming foams (AFFFs)

- Substantial soil and groundwater contamination has been observed in the vicinity of firefighter training areas.
- Effective in-site technologies are needed
- We chose an Fe-based bimetal that has potential to be used in a permeable reactive barrier (PRB) to intercept PFAS-contaminated groundwater



PFAS Remedial Technique

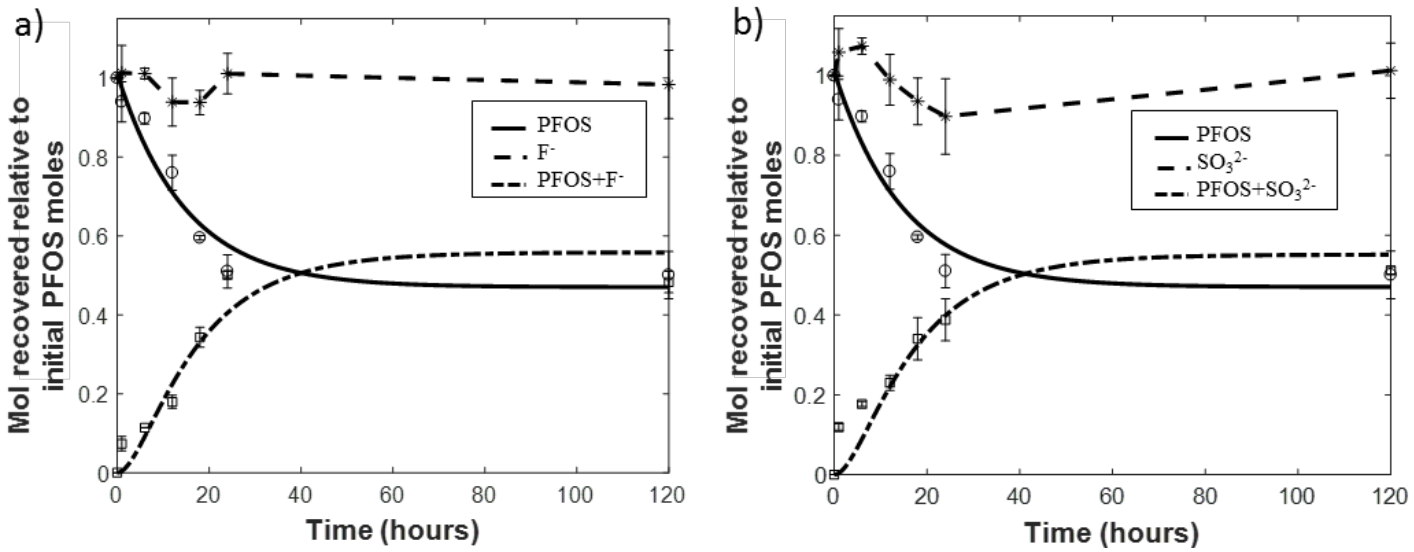
$NiFe^0$ nanoparticles Synthesized onto Activated Carbon ($nNiFe^0$-AC)

SERDP DOD • EPA • DOE ER-2426

- **Benefits:**
  - Effective in transforming PFAS more resistant to chemical oxidation
  - Amenable for use in-situ, e.g., permeable reactive barrier (PRBs)
- **Questions being addressed:**
  - What are the major products of PFOS transformation by $nNiFe^0$-AC?
  - How does PFAA structure affect transformation by $nNiFe^0$-AC?
  - What is the effect of temperature on $nNiFe^0$-AC transformation magnitude?
  - Is $nNiFe^0$-AC effective in removing PFAAs under flow-conditions?
- **At Purdue:** We have been conducting batch and column experiments investigating the efficiency of $nNiFe^0$-AC in remedial of PFAS in batch reactors (static) and column systems under different flow conditions at different temperatures

Reductive Decomposition of PFAS with nNiFe^0-AC
PFOS Batch Experiments

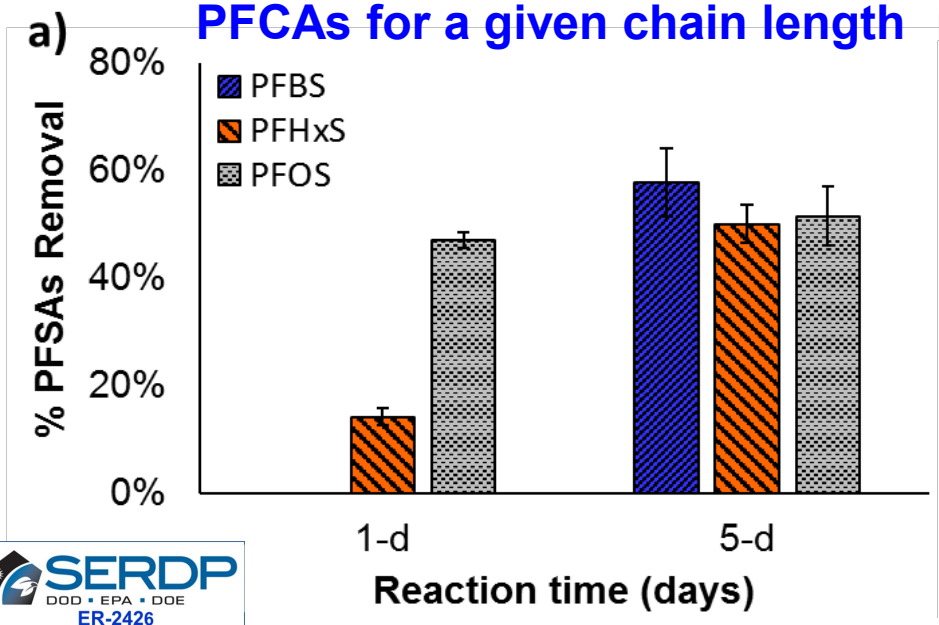
- Fluoride (F^-) and sulfite (measured as sulfate, SO_3^{2-}) are major products
  - Mol ratio of total PFOS recovery and F^- and SO_3^{2-} generated relative to initial PFOS (6 µM) over time in a reaction at 60 °C was close to unity.
    - ➢ **Supports the transformed PFOS has been converted to F^- and SO_3^{2-}**

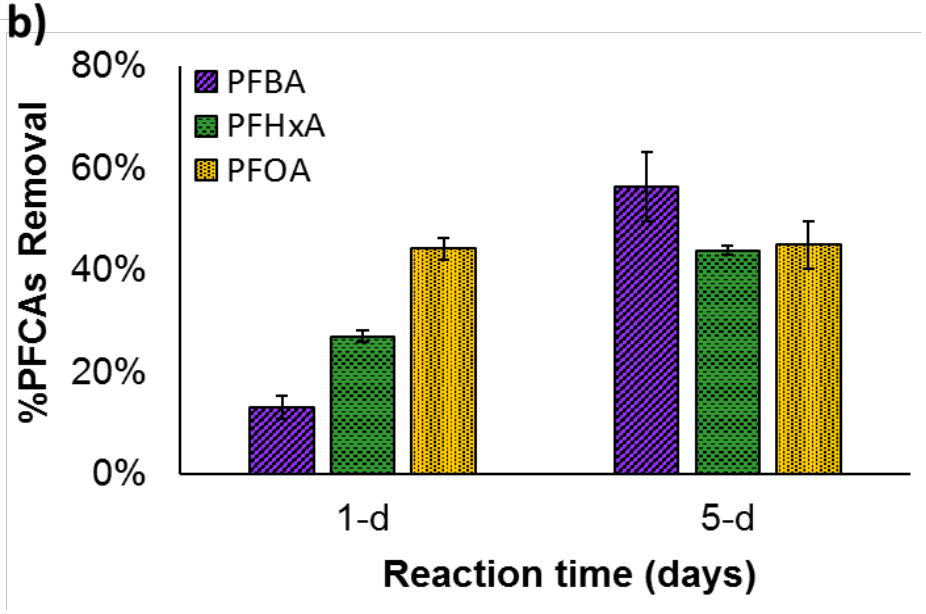


Adapted from Jenny E. Zenobio (2019), Abiotic reduction of perfluoroalkyl acids by NiFe^0-activated carbon, Purdue University, IN, USA

Reductive Decomposition of PFAS with nNiFe^0-AC
Carbon-chain Length and Functional Group Effects

- Greater contact times required to transform shorter chain PFAAs
- Transformation magnitude somewhat greater for PFSAs vs PFCAs for a given chain length





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Adapted from Jenny E. Zenobio (2019), Abiotic reduction of perfluoroalkyl acids by NiFe^0-activated carbon, Purdue University, IN, USA

Reductive Decomposition of PFAS with nNiFe^0-AC
Effect of Temperature

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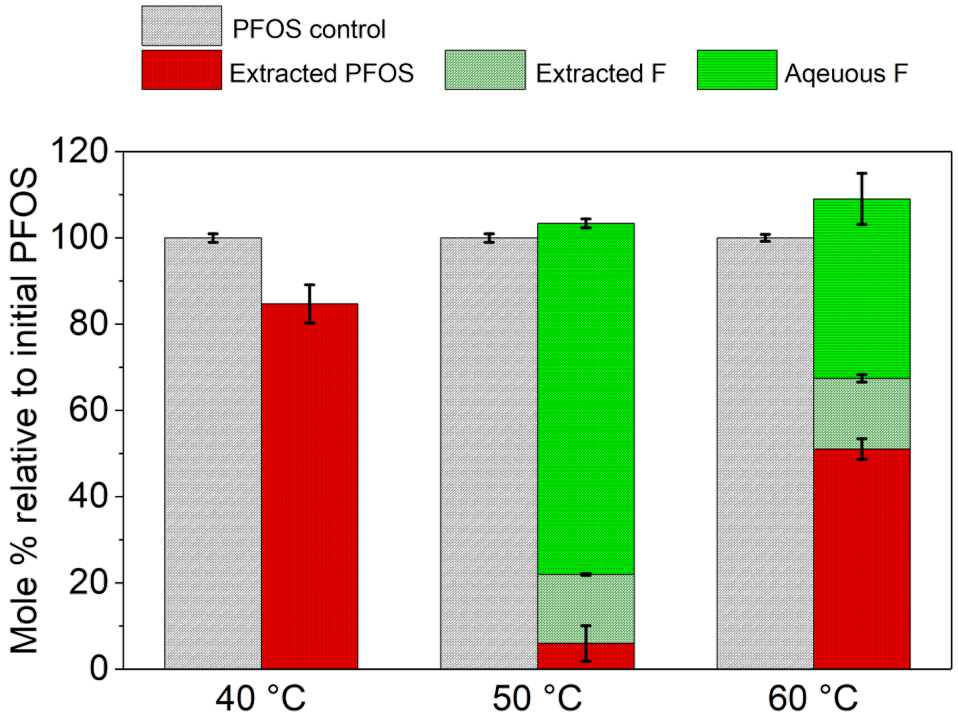
Geosyntec

➢ **Highest transformation happened with 50 °C**



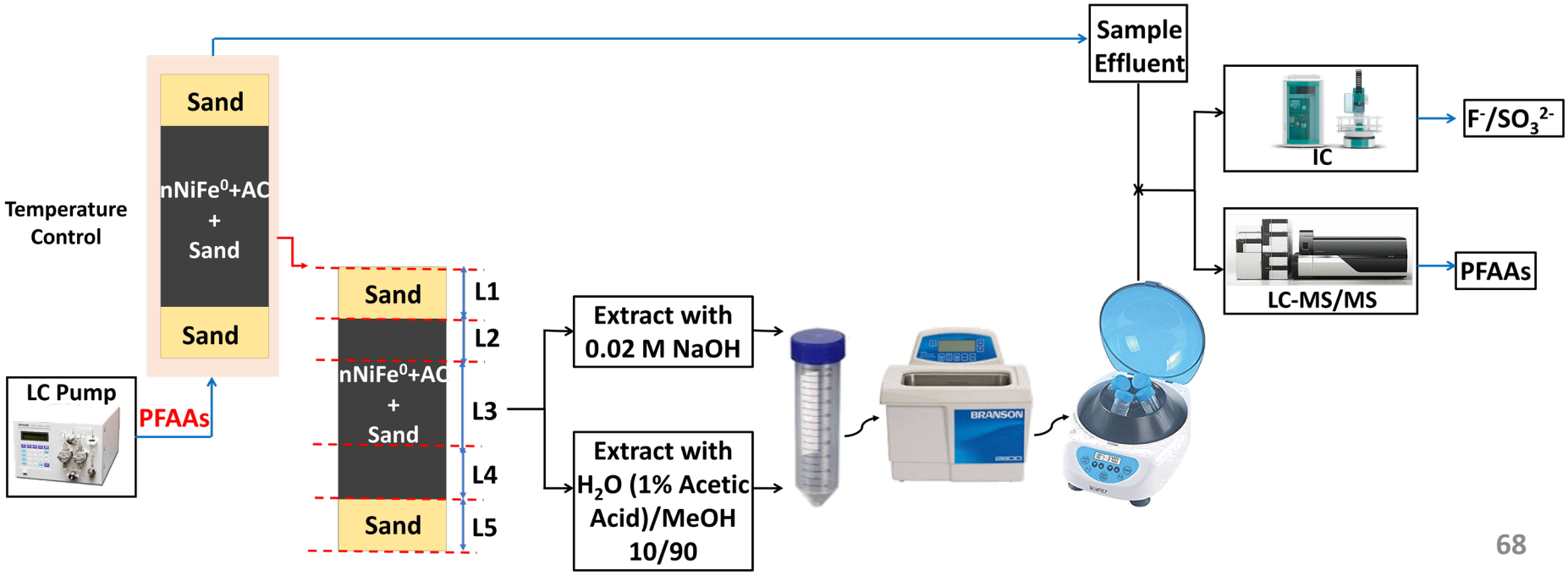
Temp. (°C)	F content (%)		Total F content (%)
	PFOS Recovered	F^-	
40	84%	0%	84%
50	51%	54%	104 %
60	6 %	91%	97 %

Reductive Decomposition of Individual PFAS and PFAS Mixture with nNiFe^0-AC Column Experiments

Geosyntec

SERDP DOD • EPA • DOE ER-2426

- **Mix PFAA Influent in a bicarbonate background at 1.8 cm/hr: 58% Total PFAA transformed**



Summary Highlights

- PFAS Occurrence in Organic Waste Products
  - Total PFAA loads were similar (30 – 80 μg/kg) between biosolids-based products and composted OFMSWs, except for one biosolid-based product (~185 μg/kg)
  - Several PFAA precursors were present that can lead to PFAA generation
- **Remediation** of PFAS with **nNiFe^0-AC**
  - **F^- and SO_3^{2-}** are the major products of PFOS transformation.
  - **Shorter chain PFAAs** need longer contact time to transform
  - **Temperature** affects PFOS transformation, but not linearly:
    - Highest transformation occurred with 50°C in 3 days
    - No transformation at 40°C in 3 days
  - Results of 58% PFAA removal from a PFAA mixture in bench scale PRB column studies is encouraging
  - Additional PRB column studies ongoing

Acknowledgements

- Dr. Jenny Zenobia (Post doc., University of California-Irvine, Irvine)
- Dr. Rooney Kim Lazcano (Ph.D. Procter & Gamble)
- Dr. Michael L. Mashtare (Assist. Prof., Purdue Univ.)
- Dr. Youn Jeong Choi (Post doc., Univ. of Colorado)
- Dr. Chloe de Perre (analytical chemist, Purdue Univ.)
- Geosyntec
- SERDP ER-2426

Cheryl Murphy

Cheryl Murphy is an Associate Professor of Ecotoxicology in the Department of Fisheries and Wildlife. Her research is focused on interpreting the sublethal effects of contaminants and stressors in terms of population impacts on fish and wildlife species, and improving the science of toxicology using novel in vitro and computational methods.

PFAS Chemicals: Ecological and Agricultural Risk Assessment

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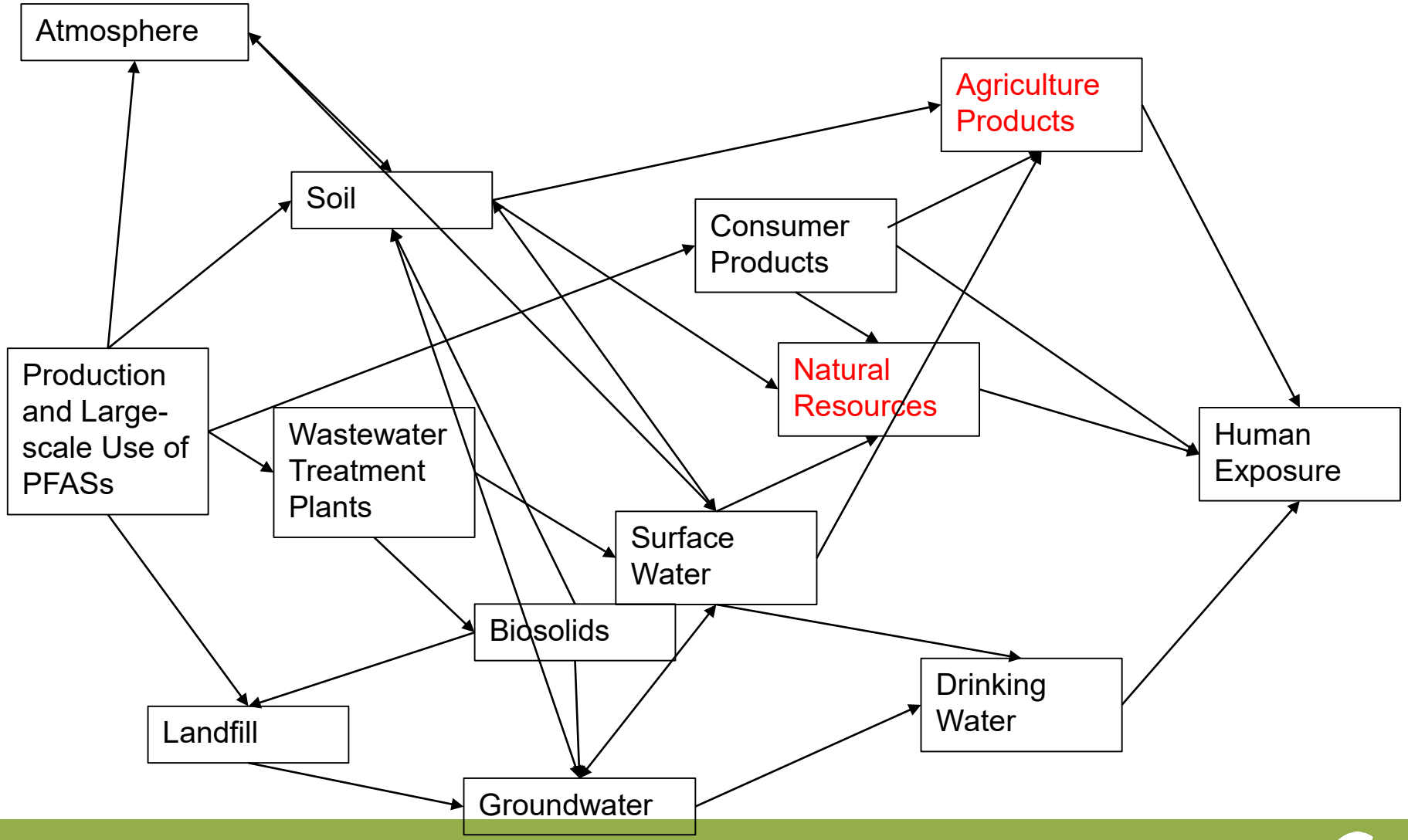
Department of Fisheries and Wildlife
Michigan State University
East Lansing, MI, 48824

The Current, November 2019

Environmental Transport of PFAS



Example of Eat Safe Fish Guidelines (MDNR)

Au Sable River

(downstream of Foote Dam; includes Van Etten Creek)

Type of Fish	Chemicals of Concern	Size of Fish (length in inches)	MI Servings per Month*
Brown Trout	PCBs	Any	6 Per Year[2x]
Carp	PFOS	Any	Do Not Eat▲
Chinook Salmon	PCBs	Any	6 Per Year[2x]
Coho Salmon	PCBs	Any	6 Per Year[2x]
Largemouth Bass	PFOS	Any	Do Not Eat▲
Rainbow Trout	PCBs	Any	6 Per Year[2x]
Rock Bass	Mercury & PFOS	Any	Do Not Eat▲
Smallmouth Bass	PFOS	Any	Do Not Eat▲
Steelhead	PCBs	Any	6 Per Year[2x]
Suckers	PFOS	Any	Do Not Eat▲
Walleye	Dioxins	Any	6 Per Year[2x]
All Other Species	PFOS	Any	Do Not Eat▲

PFOS can't be reduced by trimming and cooking. Do not double MI Servings.

Fish and Wildlife Consumption Advisory Committee (FAWCAC)

PFAS RESPONSE

TAKING ACTION, PROTECTING MICHIGAN

PFAS in Deer

PFAS IN DEER FAQS ➤ | MAP OF ADVISORY AREA ➤

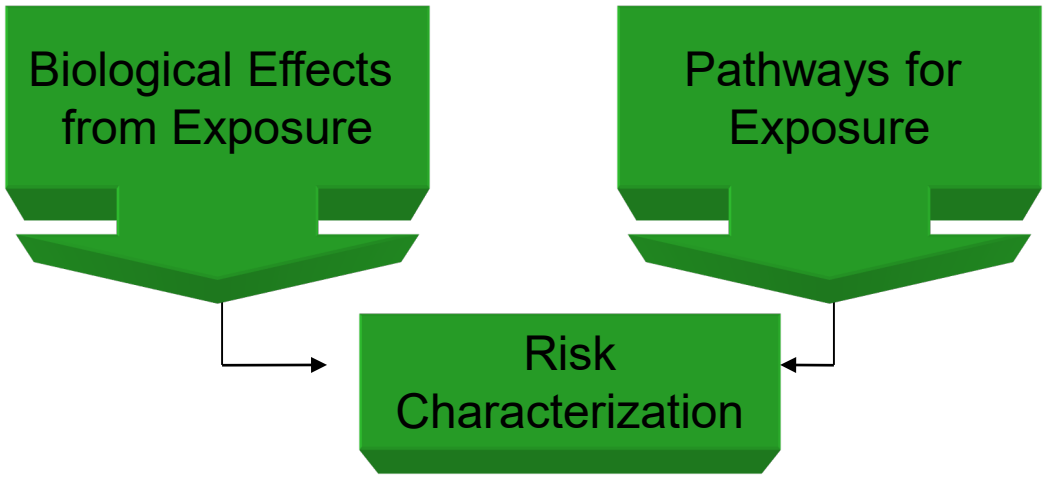
As part of Michigan's efforts to identify PFAS in Michigan, deer were tested from areas known to have PFAS contamination in lakes or rivers. In October of 2018, MDHHS and DNR issued a 'Do Not Eat' advisory for deer taken within five miles of Clark's Marsh in Oscoda Township. The advisory is due to high levels of PFAS chemicals found in deer taken within five miles of the Marsh.

https://www.michigan.gov/pfasresponse

What is Unknown about PFAS in Fish, Wildlife and Agriculture

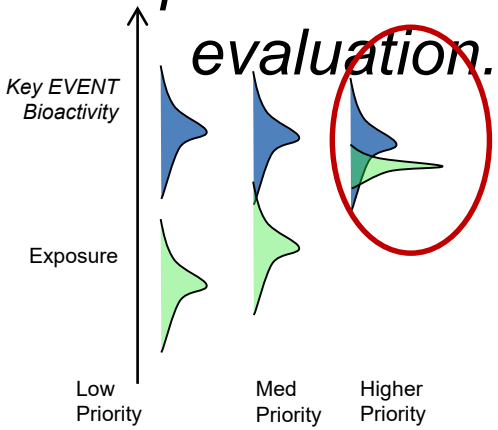
- Exposure pathways
- Biomagnification in food web
- Biological effects on different taxa
- Understanding of risk

Assessing Risk to Fisheries/Wildlife and Agriculture Populations Through Risk Assessment



Ecological Risk Assessment

A combination of biological effects and exposure determines risk, and this risk can be used to prioritize monitoring and evaluation.



High Risk when exposure and bioactivity combine

Exposure Assessment and Characterization

- How these chemicals bioaccumulate, bioconcentrate, biomagnify is uncertain. They are unusual because:
  - Bind to proteins (albumin), and membrane phospholipids, instead of storage lipids
  - Can be metabolized, but mechanism and rates are uncertain
- Next generation of PFAS have not been studied (1000's of them)
  - Trend towards increasing bioconcentration and biomagnification with increasing carbon chain length of the molecule
- Toxicity occurs after exposure to contaminated water, soils and food

Exposure Assessment and Characterization

What is needed:

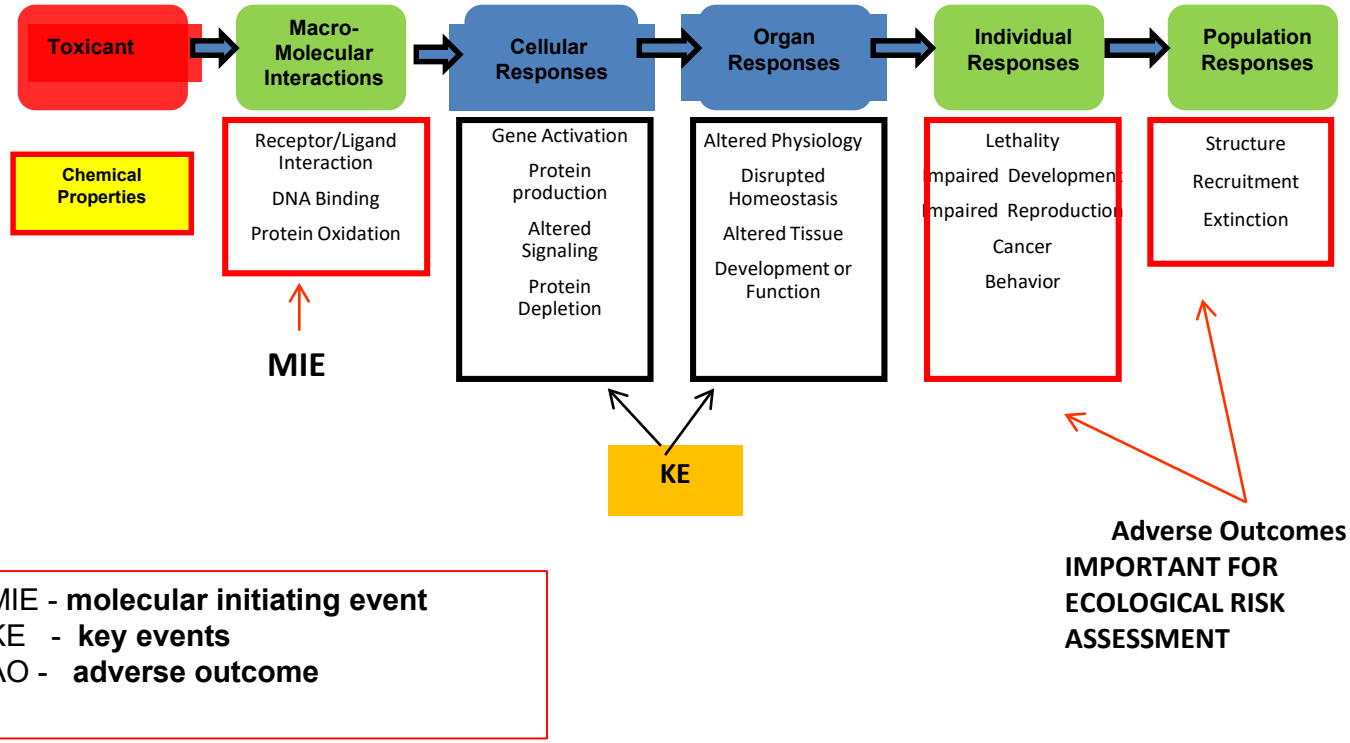
- Standards for PFAS, and identification of “unknowns”
- Controlled laboratory or “semi-field” dietary biomagnification studies on fish, mammals, avian species and various plants
- Laboratory studies in which fish are exposed to contaminants solely through their diet, and not by respiratory uptake from water through their gills, can provide useful information on biomagnification
- Controlled experiments that expose mammals (deer, mink, others) to background levels of PFAS in drinking water and feed
- Similar experiments on birds
- Determine the elimination half-life for the different PFAS
- Trophic structure studies for specific impacted areas (stable isotopes)
- Incorporate data into exposure **MODELS** developed for contaminant fate and transport

Biological Effects from exposure – dose response

- This is the “hazard” of Ecological Risk Assessment, and need to determine the hazard to biological life
- Many of the effects are non lethal but could impact long term population health because of effects on reproduction, growth and immune function
- PFAS rarely occur in isolation and usually occur with other legacy contaminants such as MeHg and PCBs.
- PFAS could amplify the effects of the legacy contaminants because it interferes with cell membranes and protein function

AOP (Adverse Outcome Pathways) Components

Conserved between taxonomic groupings (eg. bird, fish, mammal)



MIE - **molecular initiating event**
KE - **key events**
AO - **adverse outcome**

Modified from Ankley et al (2010)

Adverse outcome pathways

Need to test on molecular and cellular levels of biological organization to determine potential toxicity pathways

- Relatively inexpensive and can use *in vitro, in silico* approaches

Mechanistic information will help inform interactions with other contaminants and stressors

- Many of the organisms will also have other contaminants and diseases

Eventually need to link to adverse outcomes that can be interpreted at the population level for ecological risk assessment

- Whole population studies are expensive and time consuming

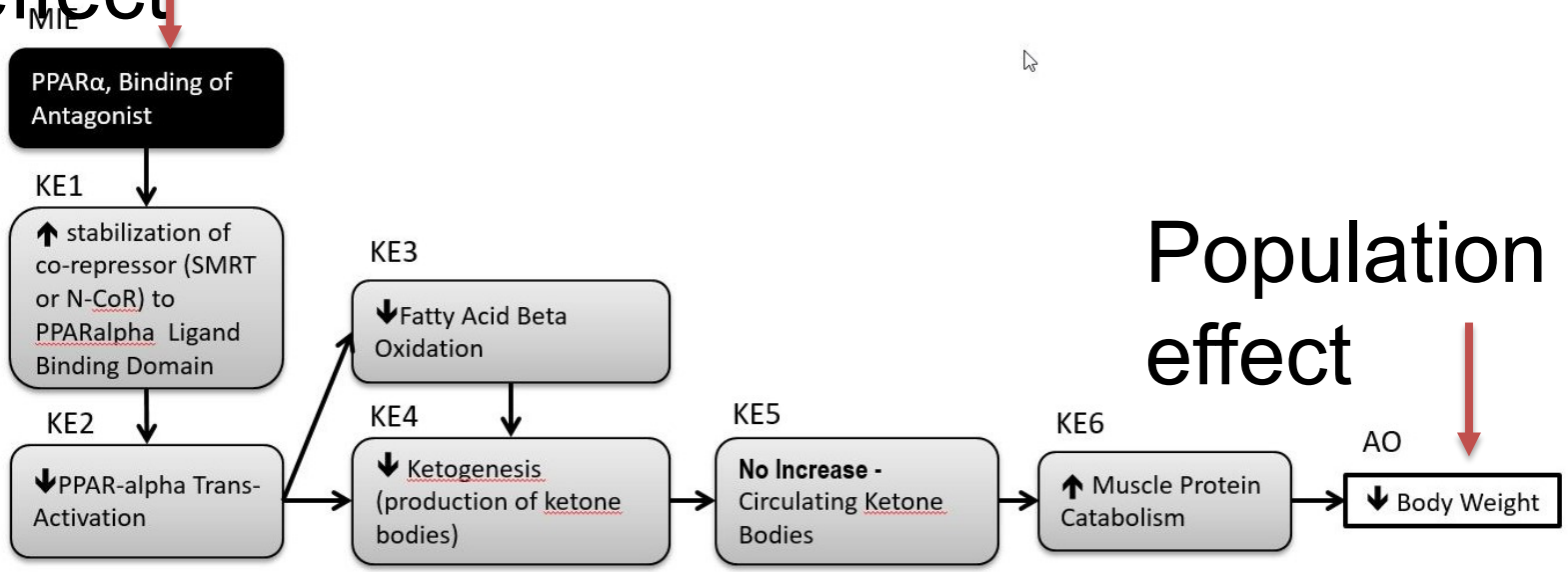
What has to be done

- Many of the PFAS are being run through EPA's ToxCast to determine molecular responses and cellular response
- Molecular level effect will have to inform population models calibrated for Michigan Fish, Wildlife and Agricultural Resources through AOP models.
- We will need representative fish, amphibian, avian and mammalian models
- Thousands of PFAS have to be assessed

Once framework is setup it can be used to respond to any future stressor and multiple stressors

Example:
PPAR α - Peroxisome proliferator-activated receptor

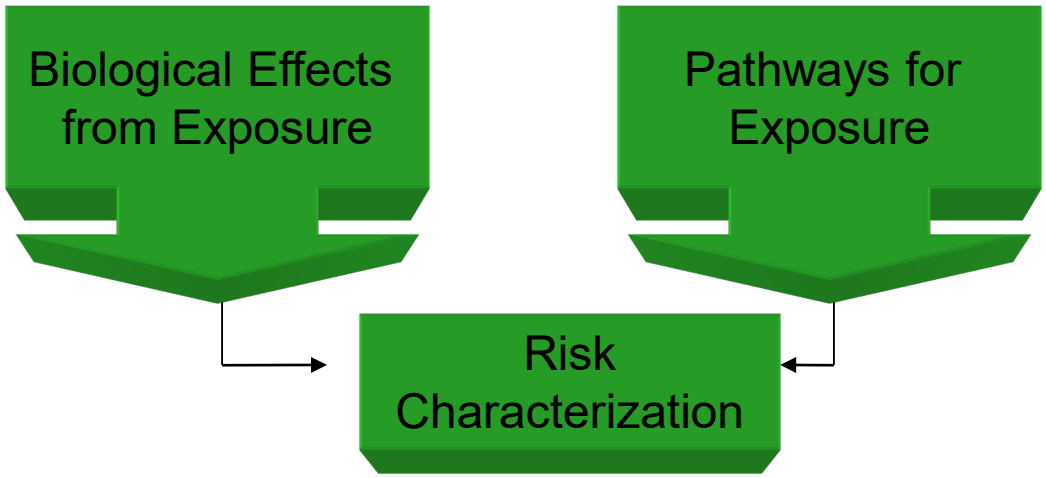
Molecular level effect



Population level effect

https://aopwiki.org/aops/6

Assessing Risk to Fisheries/Wildlife and Agriculture Populations Through Risk Assessment



New Project to study exposure – MDNR

Fate, transport and bioaccumulation of PFASs in the Huron River Watershe

Fate and Transport Model of PFAS in River

Toxicokinetic model of PFAS in Blueg

Acknowledgements

- PFAS AgBioResearch Working Group: Lori Ivan, Dan Jones, Hui Le, Brian Teppen, Jade Mitchell, Courtney Carignan, Matt Zwiernik
- Dr. Tammy Newcomb (MDNR)
- AgBioResearch

Thank-you!

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Question and Answer Session

We will draw initial questions and comments from those submitted via the chat box during the presentations.

Today's Speakers

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Cheryl Murphy – camurphy@msu.edu

Thank you for participating in today's *The Current*!

Visit our website, northcentralwater.org, to access the recording and our webinar archive!