PFAS and Other Emerging Contaminants Conference

PFAS's Ripple Effect of Uncertainty

ACEC
American Council of Engineering Companies of North Carolina

GWPNC
Groundwater Professionals of North Carolina
www.gwpnc.org

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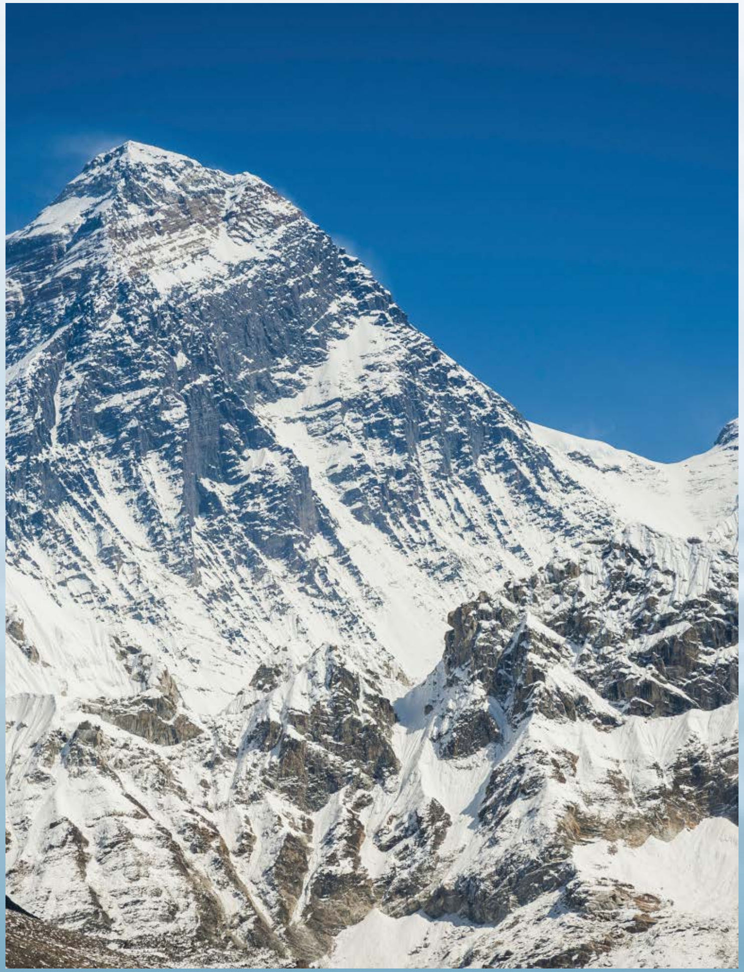
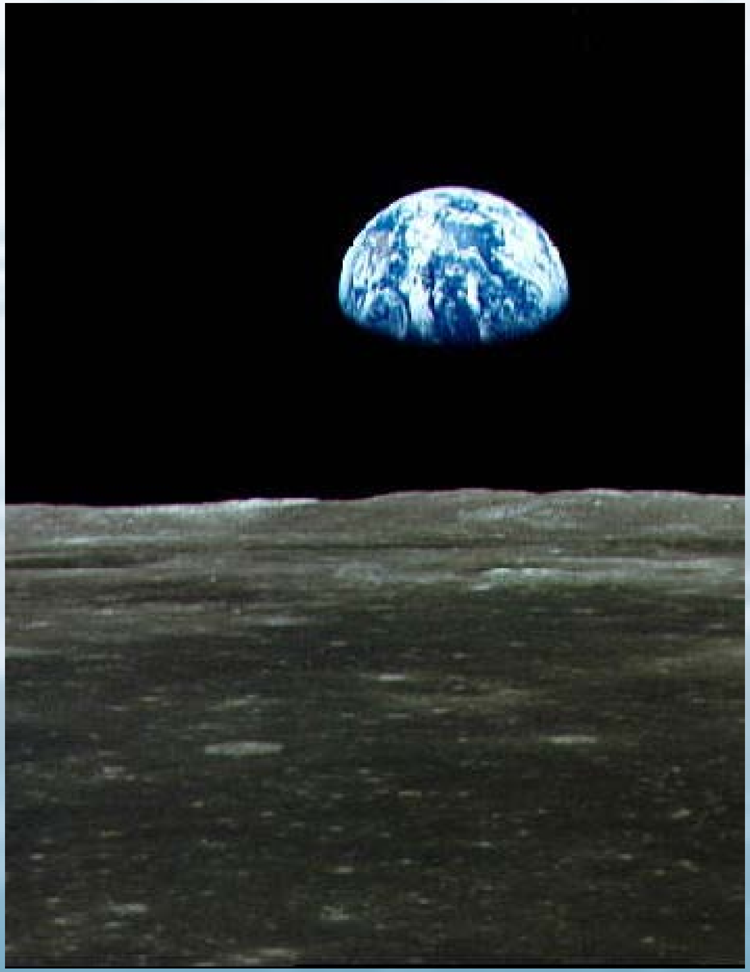
Environmental Assistant Service Line Director
Terracon Consultants, Inc

UNCERTAINTY

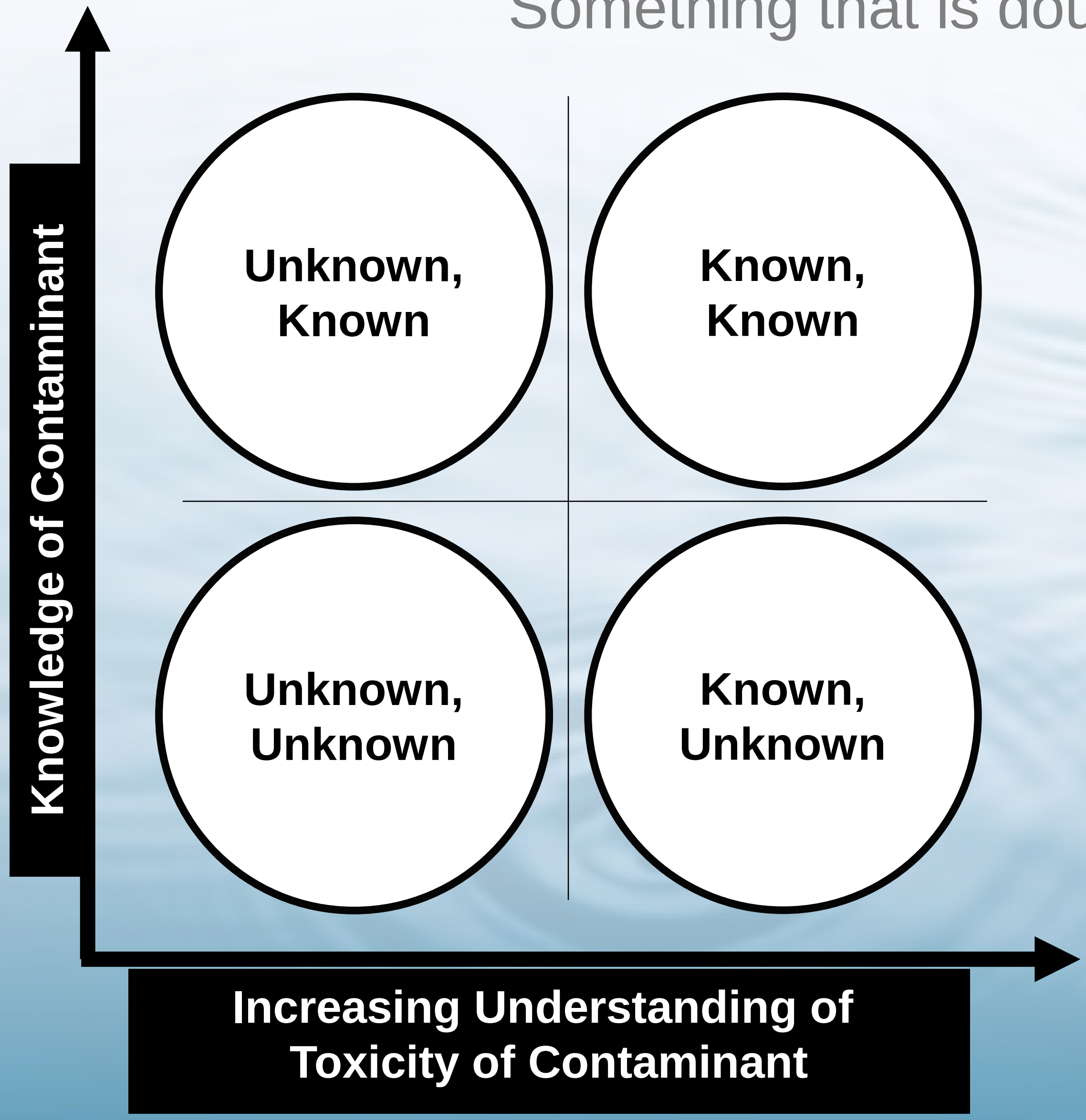
Something that is doubtful or unknown





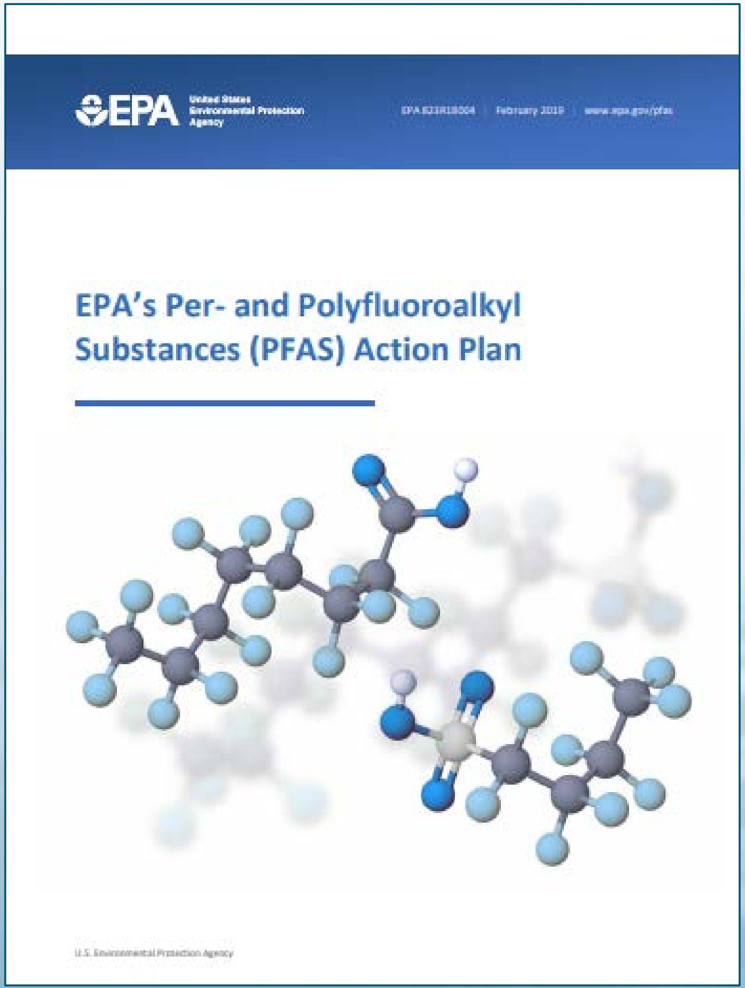
UNCERTAINTY

Something that is doubtful or unknown



Current body of chemicals and compounds we deal with routinely

Current body of Emerging Contaminants we are aware of including PFAS

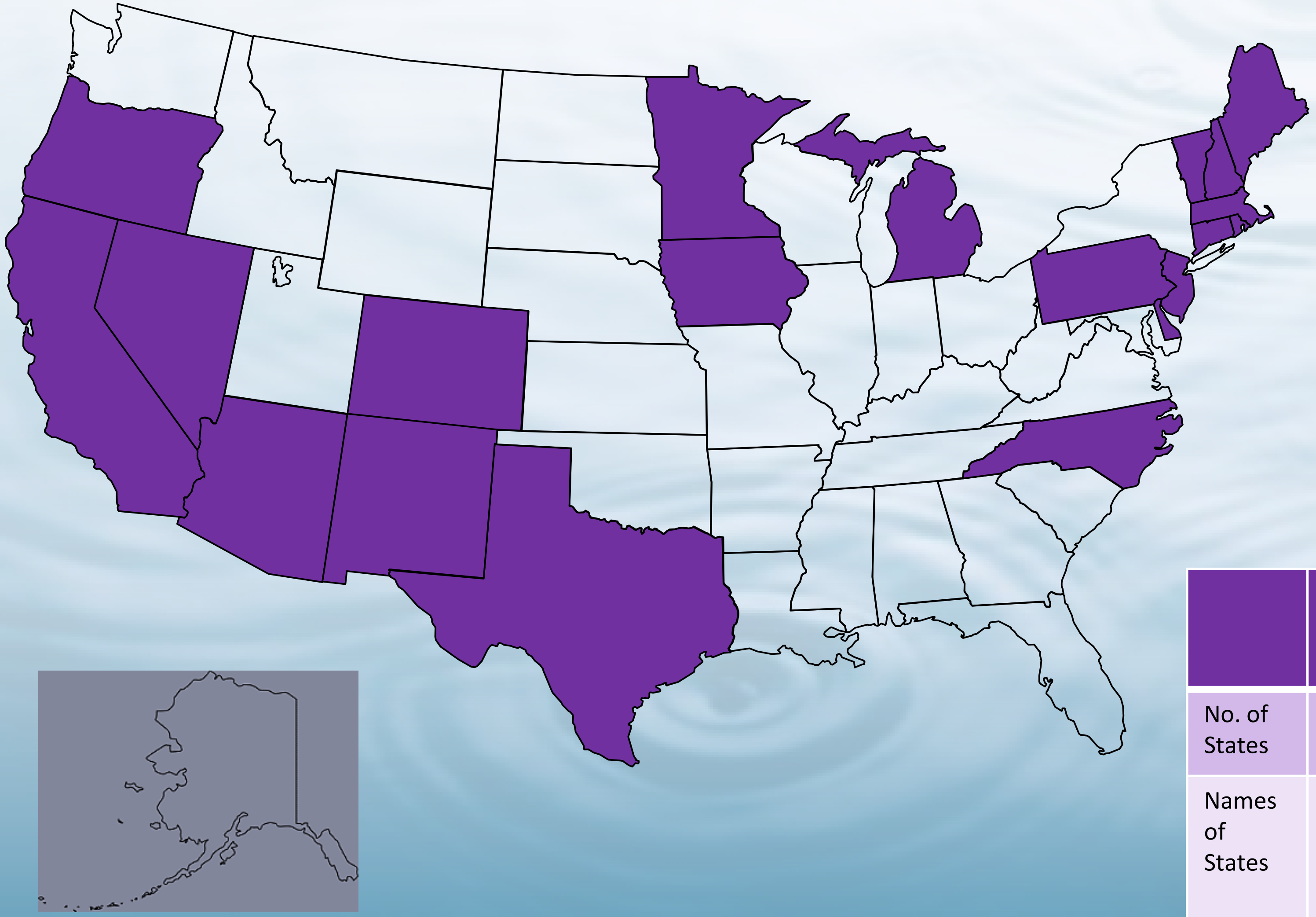


- **Progressing toward a CERCLA Hazardous Substance (2019)**
- **Moving towards establishing MCL of PFOA and PFOS under SDWA (2020)**
- **Toxicity of very limited no. of compounds (PFBS, GenX 2019)(5 additional PFAS in 2020)**
- **Laboratory testing method accepted for "broader suite" of PFAS and precursors including GenX) (2019) and for soil, groundwater, and surface water media (2019-2021)**
- **Next UCMR to include expanded PFAS analytes (2020)**

https://www.epa.gov/sites/production/files/2019-02/documents/pfas_action_plan_021319_508compliant_1.pdf

Water Standards

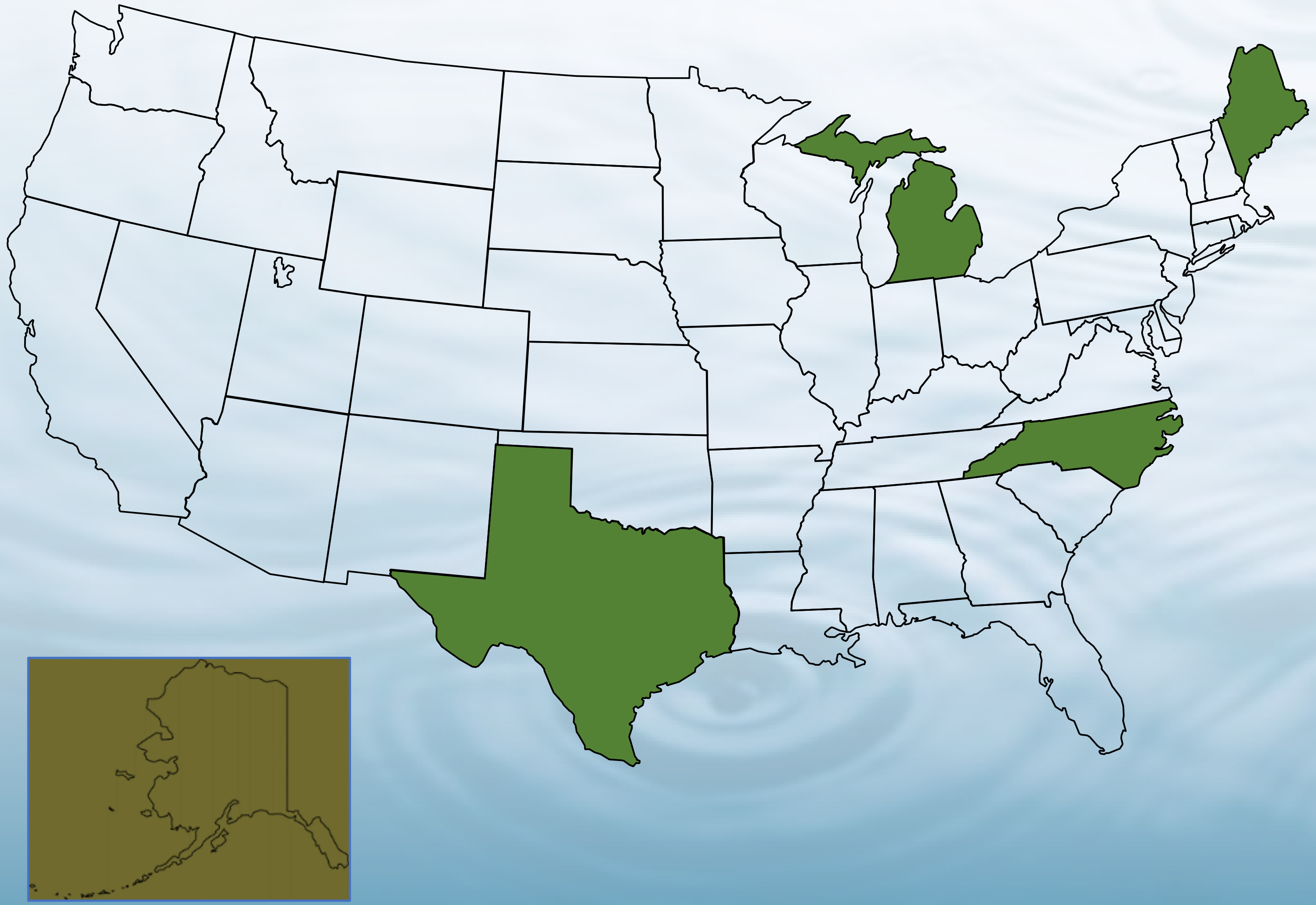
19 States have PFAS Water Standards (LHAs)



	DW	DW/GW	DW/GW/SW	GW	NP GW	P GW	SW	SW/RW
No. of States	4	4	1	10	1	1	2	1
Names of States	CA,ME, MA, NV, NJ, NC	MN, ME. CT, VT	AK	AK, CO, DE, ME, NH, NJ, NC, PA, TX, VT	IA	IA	MI, OR	ME

Soil Screening Levels Protective of Ground Water

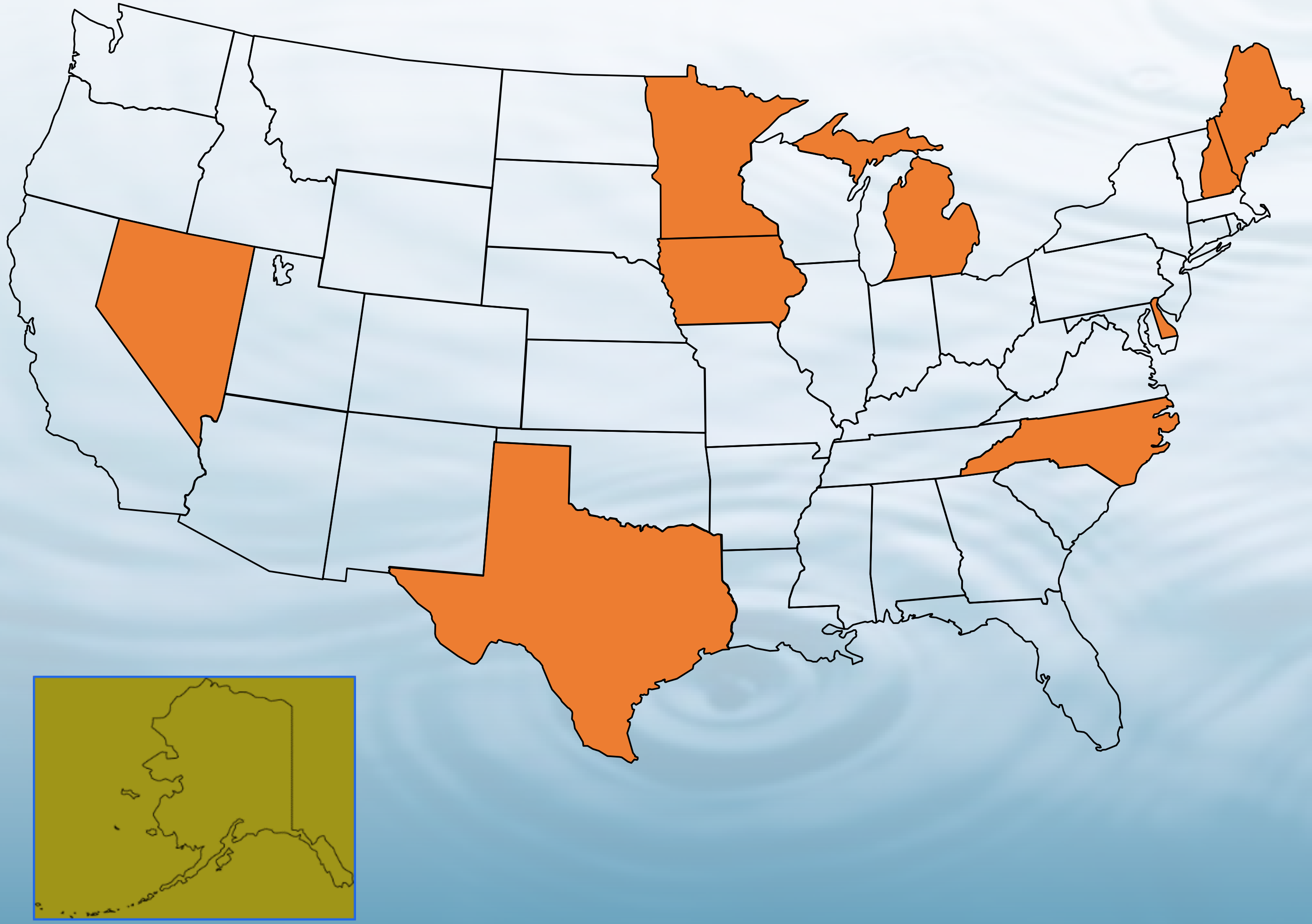
5 States have Soil Screening Levels for Groundwater Protection



	ITRC Table 4.2 (Feb 2019)
No. of States	5
Names of States	AK, ME, MI, NC, TX

Human Health Soil Screening Levels

10 States have Soil Screening Levels



	ITRC Table 4.2 (Feb 2019)
No. of States	10
Names of States	AK, ME, MI, NC, TX, NV, IA, MN, DE, VT

https://pfas-1.itrcweb.org/fact-sheets/

Printed from: Interstate Technology & Regulatory Council (ITRC). 2018. PFAS Fact Sheets PFAS-1. Washington, D.C.: Interstate Technology & Regulatory Council, PFAS Team. http://pfas-1.itrcweb.org

PFAS Fact Sheets

This page includes in the links for the ITRC PFAS fact sheets. The fact sheets are available as PDF files. Several tables of supporting information are published separately so that they can be updated periodically by ITRC. The fact sheet user should visit this page to access the current versions of the files.

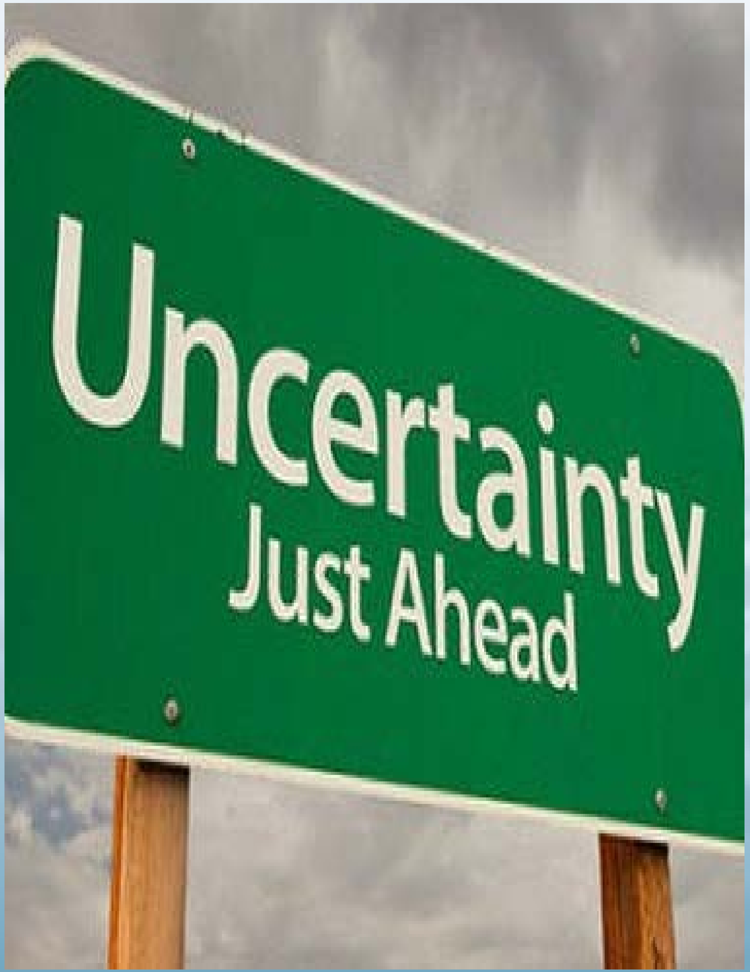
An Introductory document (Spanish Version) has been prepared that briefly describes the contents of each of the fact sheets. An Introductory document has been prepared that briefly describes the contents of each of the fact sheets. This web site also includes a combined references list and acronyms list.

- Naming Conventions and Physical and Chemical Properties (updated 3-16-18)
- Naming Conventions and Physical and Chemical Properties (Spanish Version)
- Regulations, Guidance, and Advisories (updated 1-4-18)
  - Section 4 Tables Excel file – (updated February 2019)
    - Table 4-1 presents the available PFAS water values established by the USEPA, each pertinent state, or country (Australia, Canada and Western European countries)
    - Table 4-2 presents the available PFAS soil values established by the USEPA, each pertinent state, or country (Australia, Canada and Western European countries)
  - Section 5 Tables Excel file (updated January 2019)
    - Table 5-1 summarizes the differences in the PFOA values for drinking water in the United States.
    - Table 5-2 summarizes the differences in the PFOS values for drinking water in the United States.
- Regulación, Orientación, y Asesoramiento para sustancias Per- y Polifluroalquiladas (PFAS) (Spanish Version)
- History and Use (published 11-13-17)
- Historia y Uso (Spanish Version)
- Environmental Fate and Transport (published 3-16-18)
  - Table 3-1 Log Koc values for select PFAS Excel file (published April 2018)
- Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods (published 3-15-18)
- Remediation Technologies and Methods (published 3-15-18)
  - Remediation Comparison Tables Excel file (published April 2018)
    - Table 1 – Solids Comparison
    - Table 2 – Liquids Comparison
- Aqueous Film-Forming Foam (published October 2018)

“Some of the secret joys of living are not found by rushing from point A to point B, but by inventing some imaginary letters along the way.”

Douglas Pagels, writer

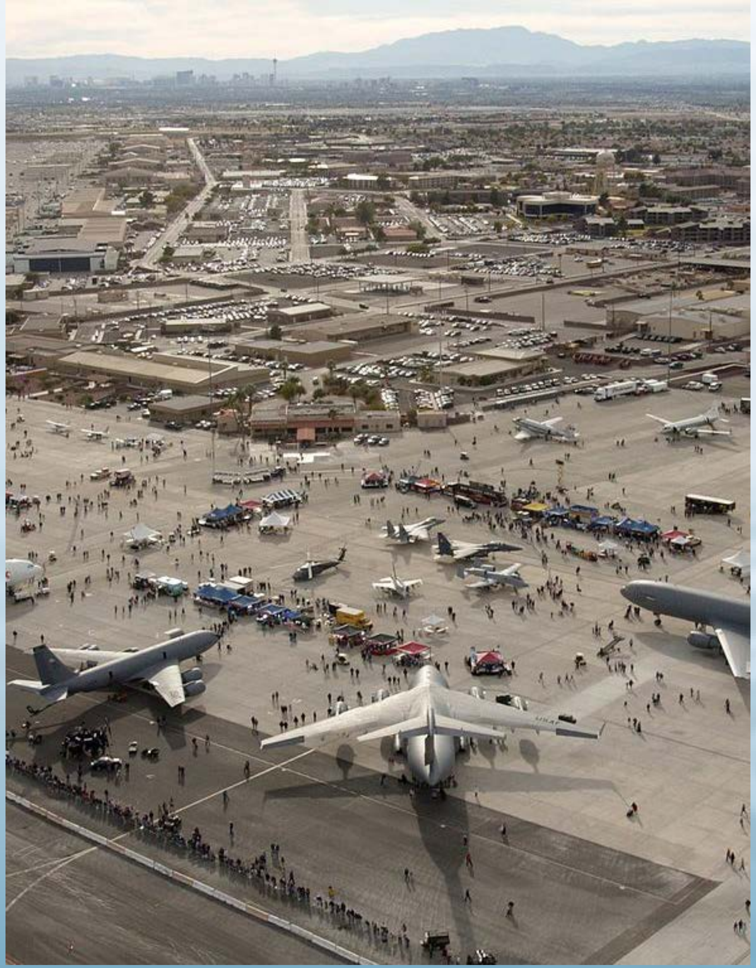
Navigating Uncertainty in Real Estate Transactions



Emerging Contaminants in ASTM 1527-13
Emerging Contaminants in the future ASTM 1527-??

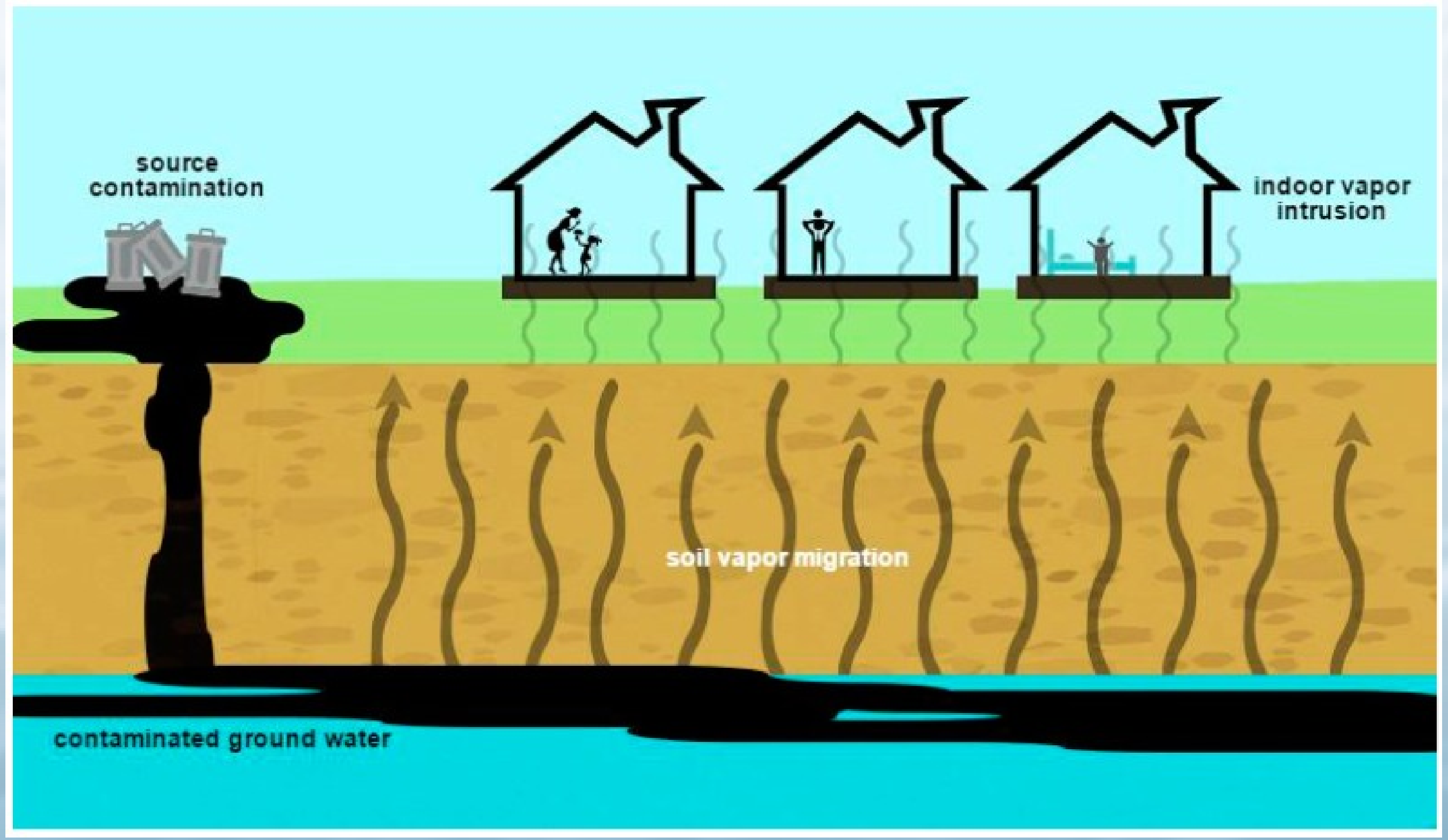
ASTM INTERNATIONAL

Where Does PFAS Contamination Originate?



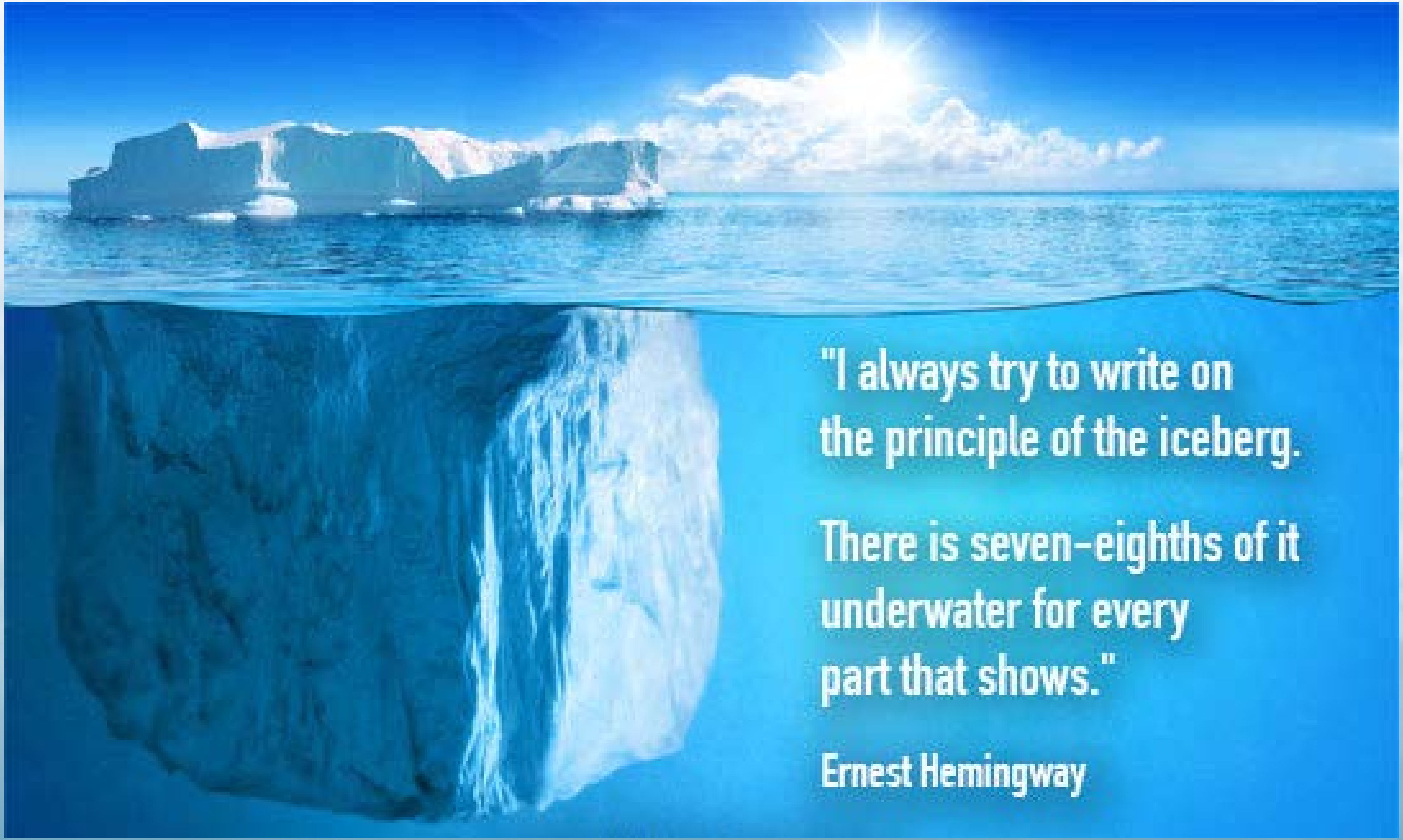
What Do We Do?


RESET


source
contamination
indoor vapor
intrusion
soil vapor migration
contaminated ground water

What Do We Do?

Enjoy the Conference!



INTRODUCTION TO PFAS AND SITES THAT MAY BE OF CONCERN

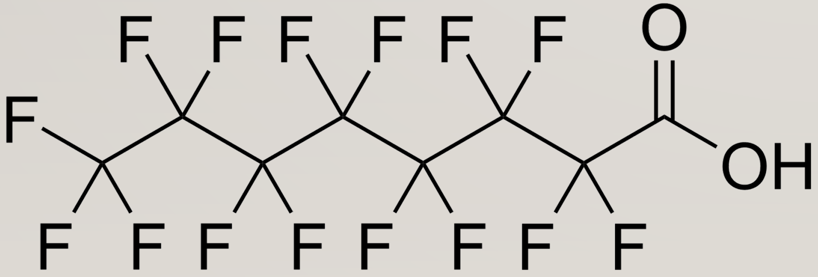
AARYN JONES

RESOURCE CONSERVATION AND RESTORATION DIVISION, EPA REGION 4

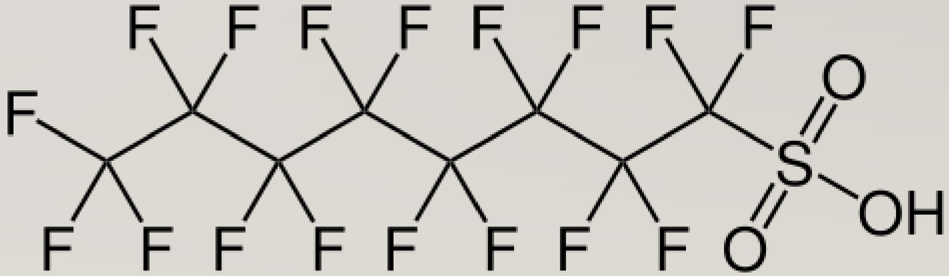
PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

- Umbrella term
- "PFC" no longer used
- Aliphatic carbon chain -- no aromatic rings, no chlorofluorocarbons (refrigerants)
- PFAS are family of more than 5,000 manmade chemicals

PFOA or "C8"

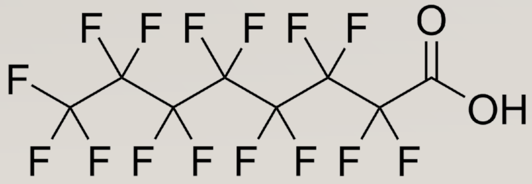


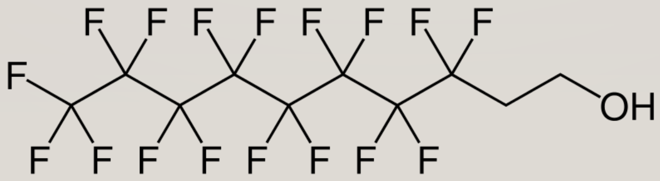
PFOS



PFAS FAMILIES

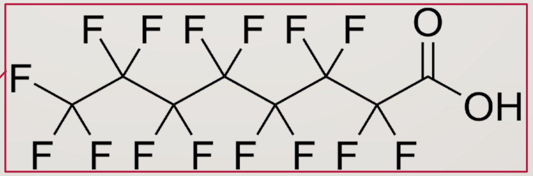
- PFAS
  - Non-polymer
    - Perfluorinated
      - PFAAs
        - PFCAs
        - PFSAs
      - FASAs
    - Polyfluorinated
      - Precursors
        - FTSAs
        - FTCAs
        - FTOHs
        - FASEs
        - FASAAs
  - Polymer
    - Potential precursors



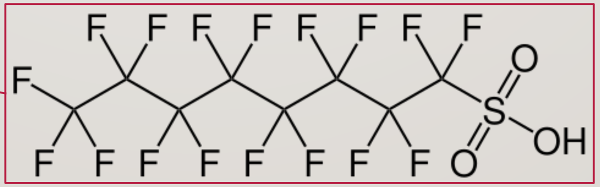


NOMENCLATURE

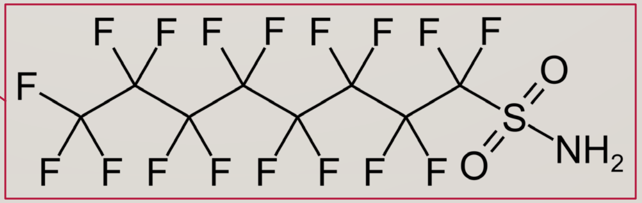
- Perfluorinated Class
  - Perfluoroalkyl Acids (PFAAs)
    - Perfluoroalkyl carboxylic acids (PFCAs)
    - Perfluoroalkyl sulfonic acids (PFSAs)
  - Perfluoroalkane Sulfonamides (FASAs)



Perfluorooctanoic Acid "PFOA"



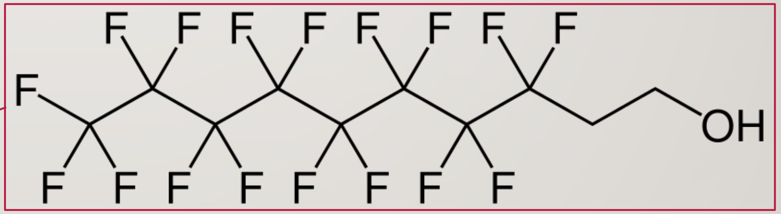
Perfluorooctane Sulfonate "PFOS"



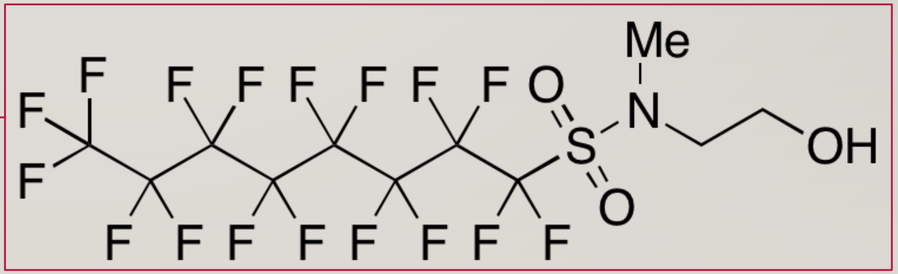
Perfluorooctane Sulfonamide "FOSA"

NOMENCLATURE

- Polyfluorinated Class
  - Fluorotelemer substances
    - n:2 Fluorotelemer alcohols (n:2 FTOHs)
    - n:2 Fluorotelemer sulfonic acids (n:2 FTSAs)
    - n:2 Fluorotelemer carboxylic acids (n:2 FTCAs)
  - Perfluoroalkane sulfonamido substances
    - Perfluoroalkane sulfonamido ethanols (FASEs)
    - Perfluoroalkane sulfonamido acetic acids (FASAAs)



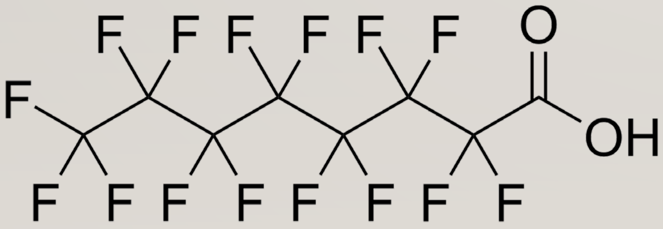
8:2 Fluorotelemer Alcohol "8:2 FTOH"



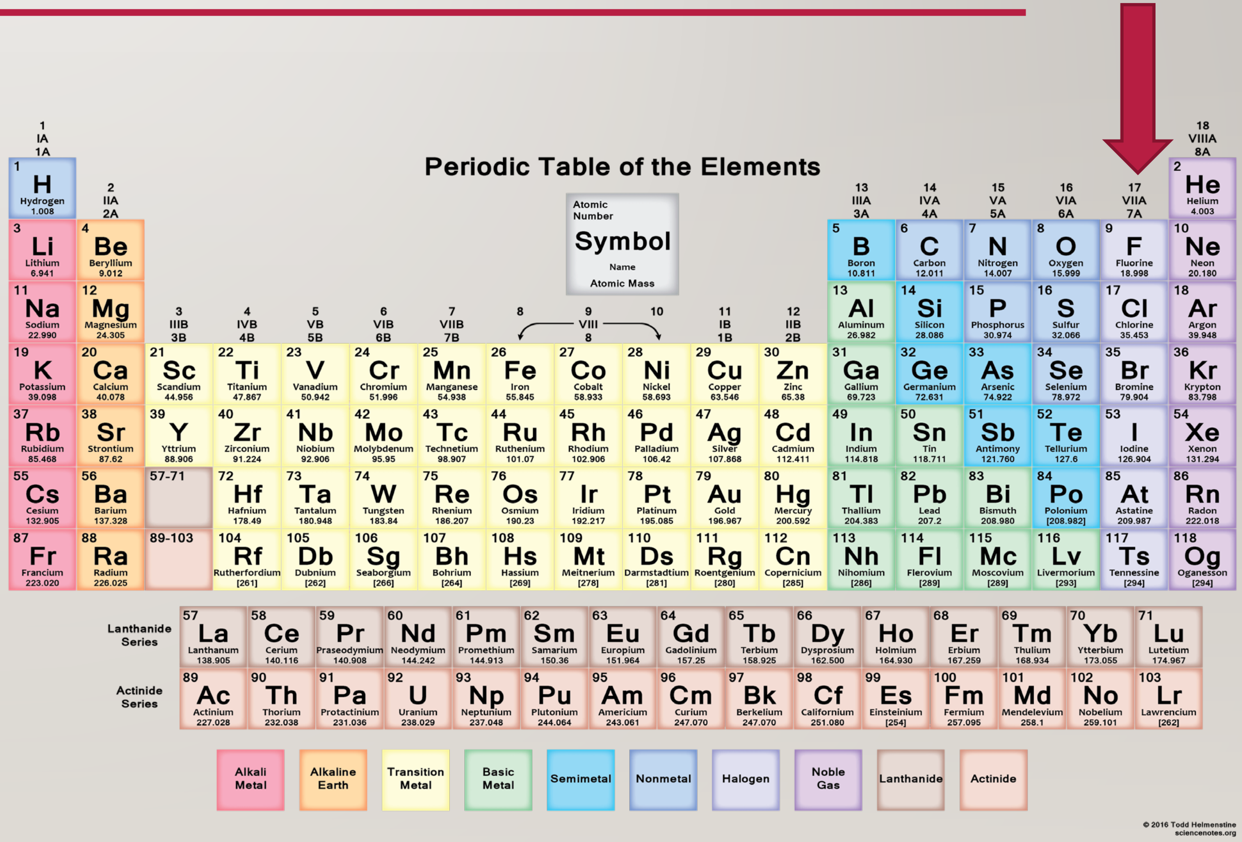
N-methyl perfluorooctane sulfonamido ethanol "N-MeFOSE"

WHAT'S SO SPECIAL ABOUT PFAS?

- Carbon – Fluorine bond is so strong
  - Short bond length (electronegativity of F)
  - Need higher energy to break bond
- Low polarizability of F
- Small size of F
  - Shields carbon

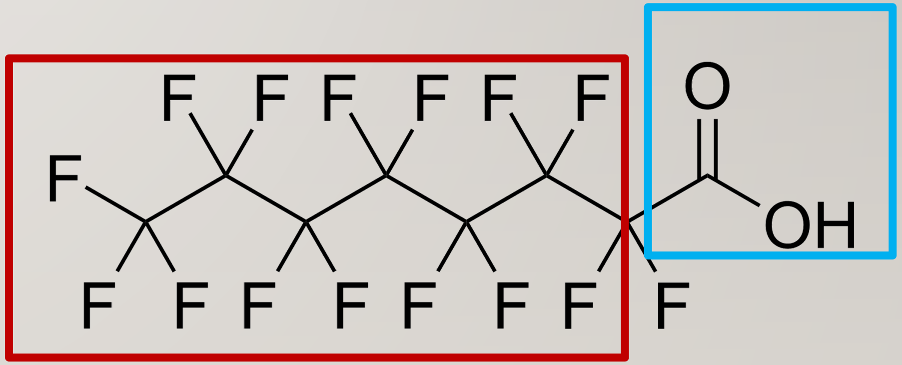


Halogens

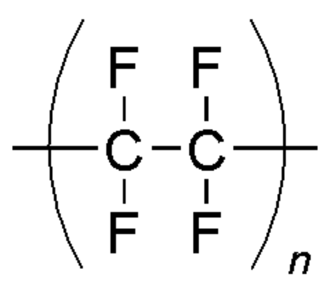


UNIQUE PROPERTIES OF PFAS

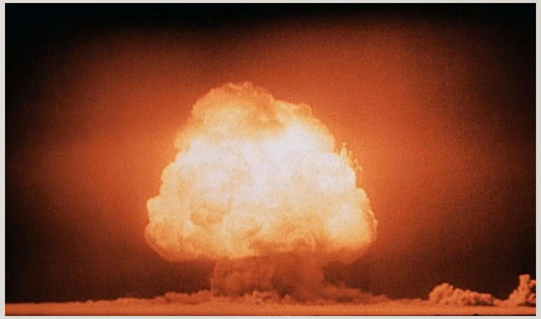
- Thermal stability
- Chemical stability
- When paired with polar functional group
  - Both hydrophobic and lipophobic (surfactant properties)
  - When functional group is acidic – strong acid
- Many unique applications in products – unfortunately also some unique environmental challenges



HISTORY



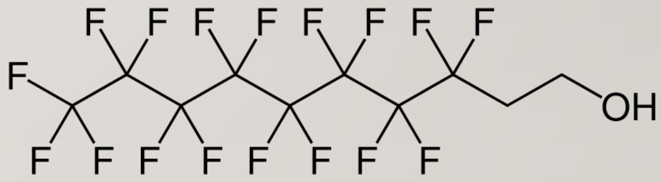
- In 1938, DuPont scientist accidentally discovered polytetrafluoroethylene (PTFE - Teflon)
- DuPont did not find a use for it at the time
- Manhattan Project – 1939-1946
  - Enrichment of U^{235} using gaseous UF_6 (corrosive)
  - Needed highly resistant coolants and solvents
  - DuPont scientists recall PTFE properties
  - Liquid fluorocarbons are used for the first time



- After the war, technology was declassified and commercialization begins in 1949

PRODUCTION

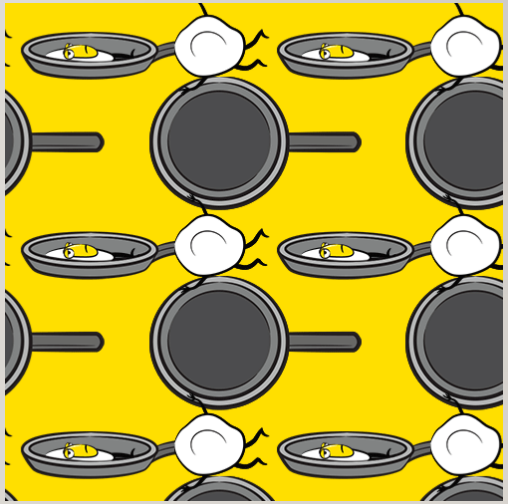
- Electrochemical Fluorination (ECF) – one of the declassified methods for producing fluorinated alkanes
  - Hydrocarbon + HF + e^- → Fluorocarbon
  - Messy synthesis – many impurities (straight and branched chains)
- Telemerization process
  - Building by blocks of "2"
  - Precursor compounds degrade in the environment to more stable perfluorinated compounds

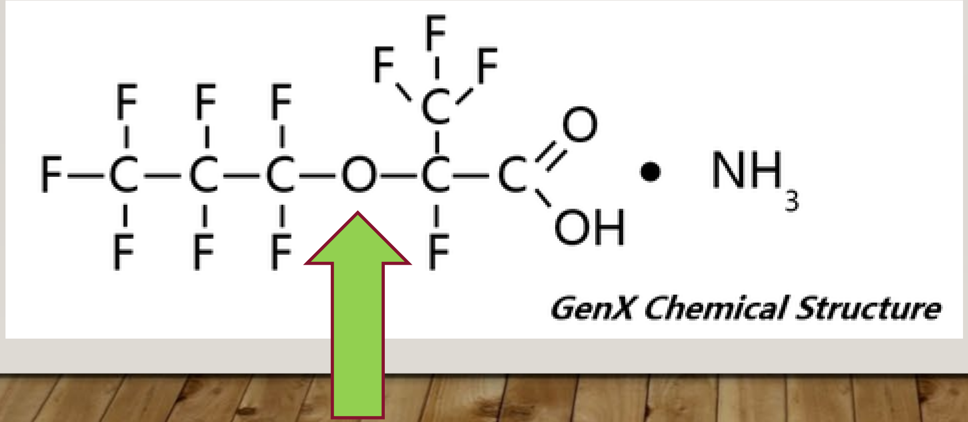


- Hexafluoropropylene Oxide (HFPO) chemistry
  - Readily reacts with nucleophiles
  - Building block for many fluorochemicals (GenX)

REPLACEMENTS FOR PFOA AND PFOS

- GenX (HFPO dimer acid) and ADONA
  - Perfluoroethercarboxylic acids used as fluoropolymer processing aids
- Shorter chain alternatives such as PFHxA (6 perfluorinated carbons) and PFBS (4 perfluorinated carbons)

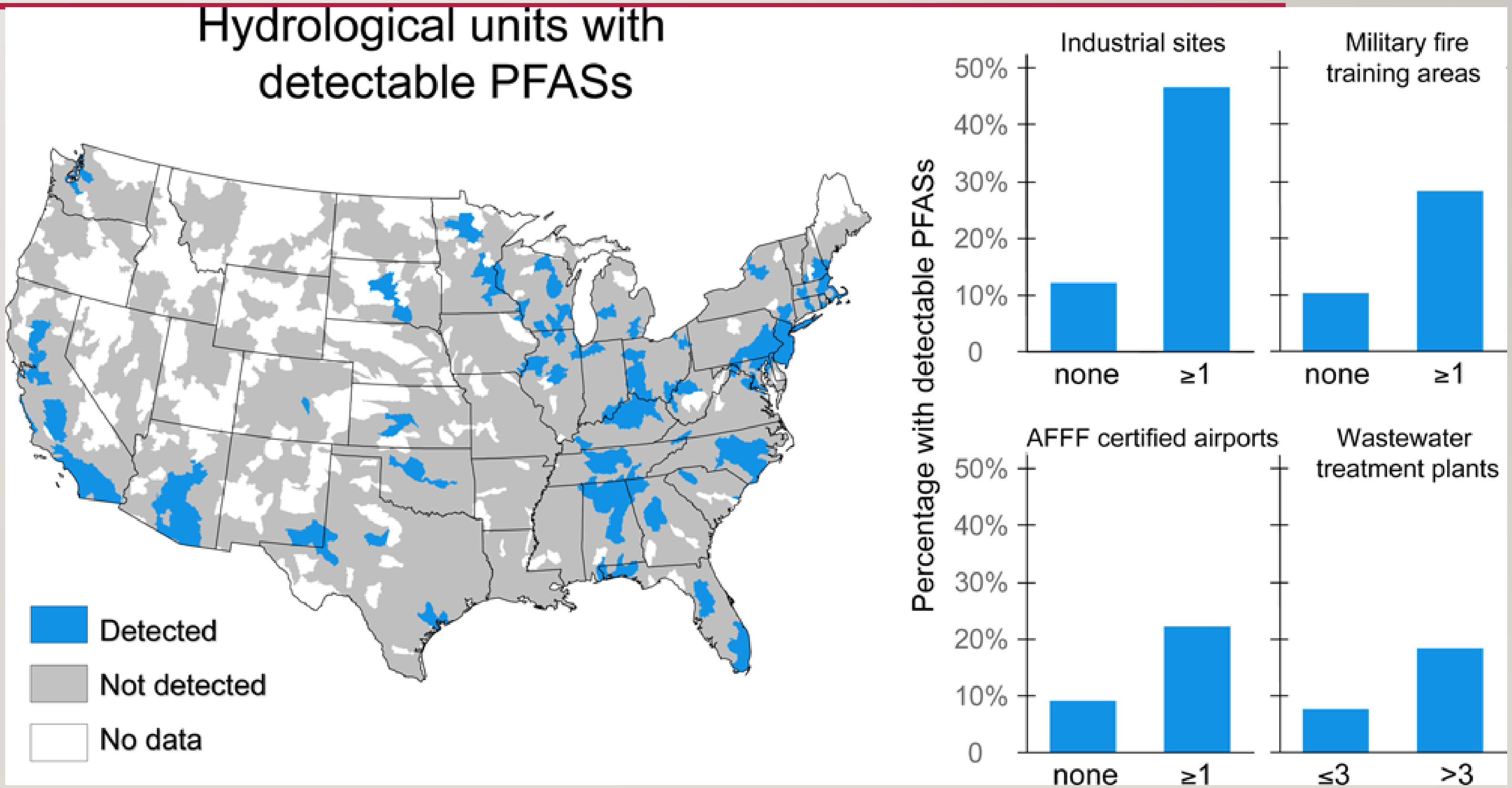




GenX Chemical Structure

PFAS IN PUBLIC WATER SYSTEMS

- 3rd round of Unregulated Contaminant Monitoring Rule (UCMR) sampling of public water systems included 6 PFAS and was conducted between 2013-2015
  - Showed where these PFAS have impacted large public water systems (>10K served) and some smaller systems



https://pubs.acs.org/doi/pdf/10.1021/acs.estlett.6b00260

AQUEOUS FILM FORMING FOAM (AFFF)

- 3 characteristics needed to meet fire fighting requirements for hydrocarbon fuel fires (such as Military Specifications)
  - "Aqueous" – water cools the temperature down
  - "Foam" – foam blanket blocks oxygen from the surface of the fire
  - "Film Forming" – film also forms on the surface of the hydrocarbon fuel to prevent vapors and any subsequent re-ignition
- An example of the hydrophobic and lipophobic PFAS properties
  - PFAS addition to aqueous phase allows the AFFF to quickly spread over the surface of the burning hydrocarbon fuel

https://dyayan.com/en/fire-fighting-foams_20

https://www.nist.gov/sites/default/files/documents/el/fire_research/R0201327.pdf

PFAS AT DOD SITES

- Historical use of AFFF in fire fighting training exercises and responses have resulted in PFAS contamination at many DOD sites
- After the UCMR3 sampling, DOD tested all 524 on-installation drinking water systems
  - 24 had PFOA/PFOS levels above 70 ppt (individually or combined)
  - Additionally, 12 systems where DOD was not the supplier had PFOA/PFOS levels above 70 ppt
- DOD has tested 2,445 off-base public and private drinking water systems
  - 564 of these had PFOA/PFOS levels above 70 ppt
- DOD identified and sampled 401 active and BRAC installations with known/suspected releases of PFOA/PFOS
  - 90 of these had PFOA/PFOS levels above 70 ppt
    - 2,668 groundwater wells sampled in this effort, with 1,621 wells above 70 ppt
- The National Defense Authorization Act was signed in December 2017 and authorizes a 5-year study to be conducted by CDC on PFAS health effects ($7M) and also $72M for Air Force and Navy to address PFAS contamination (In FY19 NDAA, the health study budget increased to $10M)

http://www.oea.gov/resource/addressing-perfluorooctane-sulfonate-pfos-and-perfluorooctanoic-acid-pfoa

WHERE COULD PFAS POTENTIALLY BE FOUND?

- Fire fighting foam
  - There are 535 FAA 14 CFR Part 139 Airports
  - Railyards and oil refineries
  - Often a mix of PFAS in the foams, for example not just PFOS
- Metal plating and finishing
  - Dust suppression, wetting agents, and surfactant use of PFAS
  - Copper, Nickel, and Tin, as well as levelling agent for Zinc electrodepostion
- Waste Water Treatment Plants

WHERE COULD PFAS POTENTIALLY BE FOUND?

- Landfills
- Textiles
  - Fabrics for jackets, shoes, umbrellas, tents
  - Carpets, upholstery, leather
  - Brand names Scotchgard, Zonyl, Foraperle, and Capstone
- Paper and Cardboard Packaging
  - Plates, popcorn bags, pizza boxes, fast food wrappers, oven-safe papers (muffin cups/parchment paper)
  - Many of the PFAS used in food packaging have a phosphate functional group

WHERE COULD PFAS POTENTIALLY BE FOUND?

- Industrial and Household cleaning products
  - Carpet/upholstery spot cleaners, denture cleaners, dishwashing liquids, floor polish, car wash products and waxes, wiper fluids, cleaners for wood, glass, countertops, and flooring
- Surface coating, paint, varnish, inks
  - Ink jet printer inks, ski waxes
- Plastics, resins, and rubber
  - Manufacture of PTFE and PVDF

WHERE COULD PFAS POTENTIALLY BE FOUND?

- Adhesives
- Antifogging
- Cement Additives
- Oil Industry (surfactants in recovery wells)
- Mining Industry
- Photographic Industry
- Electronics Industry
    - Digital cameras, cell phones, printers, scanners, cable and wire insulation, fuel cell membranes (Nafion)

WHERE COULD PFAS POTENTIALLY BE FOUND?

- Semiconductor Industry
- Etching
- Cosmetic and personal care products
  - Cosmetics, hair creams, toothpaste, dental floss
- Pesticides
- Medical Uses
- Oil Spills
- Solar panels

PFAS SAMPLING CONSIDERATIONS

- Sampling personnel/apparel:
  - Cosmetics, lotions, moisturizers
  - Sunscreens and inspect repellents (certain brands are ok)
  - Clothing washed in fabric softeners
  - Waterproof, water-resistant, stain-resistant clothing and boots (no Gore-Tex®)
  - Coated Tyvek® suits
  - Fast Food Wrappers
- Sampling equipment:
  - Fluoropolymer bailers, pump bladders, tubing, valves
  - LPDE HydraSleeves
  - Waterproof field books
  - Sharpies
  - Post-it notes
  - Blue (chemical) ice
  - Aluminum foil

http://www.newmoa.org/events/docs/228/PFAS_Sampling_Chiang_Aug2016.pdf

FEDERAL REGULATIONS

- TSCA – Significant New Use Rules (SNUR) limit use of new chemicals that may pose risk to human health or the environment
  - 271 PFAS under SNURs
  - Section 5e orders can be issued when there is not enough information for EPA to make a determination on health or environmental effects
    - Requires facilities to restrict releases to air, water and land, protect worker exposures, perform toxicity and environmental fate testing, etc.

FEDERAL REGULATIONS

- Safe Drinking Water Act (SDWA) – can require action if "a contaminant present in or likely to enter a public water system or an underground source of drinking water… may present an imminent and substantial endangerment to the health of persons…"
  - Office of Water Health Advisory for PFOA and PFOS is now 70 ppt, individually or in sum
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) – PFAS are not listed hazardous substances but may be addressed as CERCLA pollutants or contaminants, and investigations can include PFAS on a site-specific basis
  - RSL values for PFBS

FEDERAL REGULATIONS – OTHER POTENTIAL AUTHORITIES

- Clean Water Act
  - Pollutants (?)
- RCRA
  - Listed or characteristic hazardous wastes (?)
  - RCRA 7002 (citizen suit) actions have been filed to address PFAS contamination as "solid waste" that "may present an imminent and substantial endangerment"
- Clean Air Act
  - Hazardous Air Pollutants (?)

DUPONT WASHINGTON WORKS – WEST VIRGINIA

- EPA issued combined TSCA and RCRA (3008) order, which settled in December 2005 for $16,500,000 (penalty and SEP combined)
- EPA Regions 3 and 5 issued SDWA 1431 order in 2002 (amended in 2006, 2009, and 2017) for PFOA impacts to groundwater used both in public water supply systems and private wells
- On January 11, 2018, EPA Region 3 issued a letter to Chemours requesting GenX sampling due to concerns about its use at the facility as a replacement chemical for PFOA, citing contamination issues at the Chemours Fayetteville Works site in North Carolina.

WOLVERINE WORLDWIDE - MICHIGAN

- Leather tannery with waste disposal issues (sludges/land application and landfilling)
  - 3M Scotchgard used to waterproof shoe leather
- Private wells impacted as high as 38,000 ppt (PFOA + PFOS)
- State of MI filed a 7002 order under RCRA on January 10, 2018
- EPA filed a CERCLA 106 removal order for metals on January 10, 2018

SAINT GOBAIN PERFORMANCE PLASTICS – NEW YORK

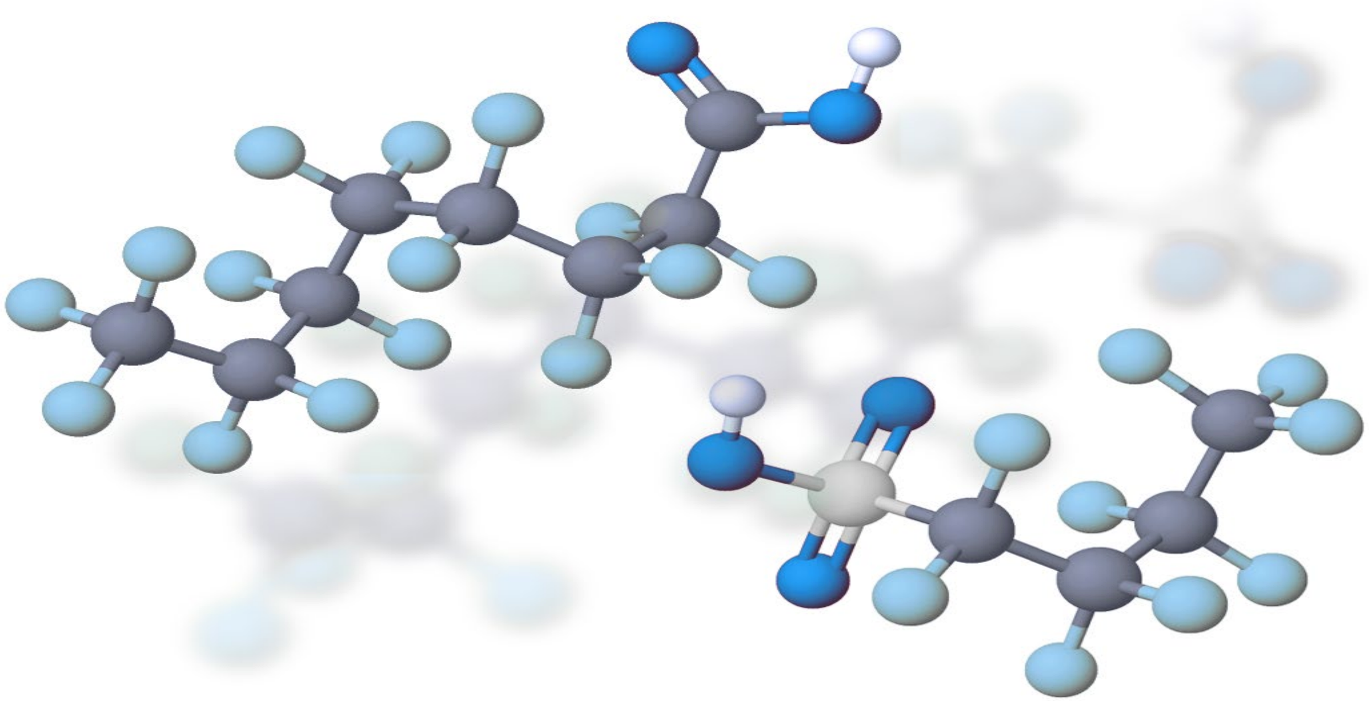
- Facility manufactured extruded tapes, circuit board laminates and PTFE coated fiberglass dating back to the1960's
- Saint-Gobain purchased the Site in1999 to manufacture a variety of polymer-based products that utilized PFOA, including high-performance polymeric films and membranes, as well as foams for bonding, sealing, acoustical and vibrational damping, and thermal management
- Site contaminants (in addition to PFOA) – TCE, VC, and PCBs
- Site was added to state SF list in January 2016 and the state requested that EPA add it to the NPL, which occurred on July 31, 2017

CURRENT RESOURCES

- ITRC Fact sheets (seven in total) https://pfas-1.itrcweb.org/fact-sheets/
  - Naming Conventions and Physical and Chemical Properties of PFAS
  - History and Use of PFAS
  - Regulations, Guidance, and Advisories for PFAS (very useful tables of current state regulations)
  - Environmental Fate and Transport
  - Site Characterization Tools, Sampling Techniques, and Laboratory Analytical Methods
  - Remediation Technologies and Methods
  - Aqueous Film-Forming Foam
- CLU-In PFAS Webpage:
  - https://clu-in.org/contaminantfocus/default.focus/sec/Per_and_Polyfluoroalkyl_Substances_(PFASs)/cat/Overview/

PFAS Background and Action Plan

February 22, 2019



What are PFAS?

- Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that have been in use since the 1940s.

- There are many PFAS chemicals, including the chemicals perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and GenX chemicals (HFPO dimer acid and its ammonium salt).

What are PFAS?

- Due to their strong carbon-fluorine bonds, many PFAS can be very persistent in the environment with degradation periods of years, decades, or longer under natural conditions.

- Two of the most studied PFAS are Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS).

Where are PFAS found?

- PFAS are (or have been) found in a wide array of consumer products like cookware, food packaging, and stain and water repellants used in fabrics, carpets and outerwear.
- PFAS manufacturing and processing facilities, and airports and military installations that use firefighting foams which contain PFAS.

How can this impact people?

- Because of their widespread use and environmental persistence, most people have been exposed to PFAS chemicals.
- Some PFAS chemicals can accumulate and can stay in the human body for long periods of time.
- There is evidence that exposure to certain PFAS may lead to adverse health effects.

EPA's Previous Work on PFAS

- Certain PFAS chemicals are no longer manufactured in the United States as a result of the EPA's PFOA Stewardship Program. All companies met the PFOA Stewardship Program goals by 2015.
- Issued various significant new use rules (SNURs).
- Monitored for six PFAS chemicals under the Safe Drinking Water Act to understand the nationwide occurrence of these chemicals in our drinking water systems.
- Issued drinking water lifetime health advisories for PFOA and PFOS of 70 parts per trillion individually or combined.

EPA's Previous Work on PFAS

- Working to advance research on other PFAS chemicals to better understand their health impacts, exposure pathways, options for treatment and removal
- Released draft toxicity assessments for GenX chemicals and PFBS
- Announced the initiation of assessments for five additional PFAS (PFBA, PFHxS, PFHxA, PFNA, PFDA) via the EPA's IRIS Program.
- Issued enforcement orders, provided oversight for federal agency cleanups and assisted state enforcement actions
- Provided technical assistance related to dozens of areas of PFAS contamination around the country.

Action Plan Background

- EPA convened a two-day National Leadership Summit on PFAS in Washington, D.C.
- Following the Summit, the agency hosted a series of visits during the summer of 2018 in communities directly impacted by PFAS where EPA interacted with more than 1,000 people.
- The EPA's PFAS Action Plan was developed based on feedback from these events in addition to information received from approximately 120,000 comments submitted to the public docket.

Action Plan Purpose

- Provides EPA's first multi-media, multi-program, national research, management and risk communication plan to address a challenge like PFAS.
- Responds to the extensive public input the agency has received over the past year during the PFAS National Leadership Summit, multiple community engagements, and through the public docket.
- As a result of this unprecedented outreach, the Action Plan provides the necessary tools to assist states, tribes, and communities in addressing PFAS.

Highlighted Actions

Drinking Water

- The EPA is committed to following the MCL rulemaking process as established by SDWA.
- As a next step, EPA will propose a regulatory determination for PFOA and PFOS by the end of this year.
- The Agency is also gathering and evaluating information to determine if regulation is appropriate for other chemicals in the PFAS family.

Highlighted Actions

Cleanup

- The EPA will facilitate cleanup efforts by providing groundwater cleanup recommendations.
- The EPA is initiating the regulatory development process for listing certain PFAS as hazardous substances.

Highlighted Actions

Monitoring

- The EPA will propose nationwide drinking water monitoring for PFAS under the next UCMR monitoring cycle.

Research

- The EPA is rapidly expanding the scientific foundation for understanding and managing risk from PFAS.
- This research is organized around understanding toxicity, understanding exposure, assessing risk, and identifying effective treatment and remediation actions.

Highlighted Actions

Toxics

- The EPA is considering the addition of PFAS chemicals to the Toxics Release Inventory
- EPA is issuing a supplemental proposal to guard against the unreviewed reintroduction and new use, through domestic production or import, of certain PFAS chemicals in the United States.

Highlighted Actions

Enforcement

- The EPA uses enforcement tools, when appropriate, to address PFAS exposure in the environment and assist states in enforcement activities.

Risk Communications

- The EPA will work collaboratively to develop a risk communication toolbox that includes multi-media materials and messaging for federal, state, tribal, and local partners to use with the public.

Action Plan Next Steps

- To implement the plan, the EPA will continue to work in close coordination with multiple entities, including other federal agencies, states, tribes, local governments, water utilities, industry, and the public.
- The EPA will provide updates on actions outlined in the plan on the Agency's website.

Questions?

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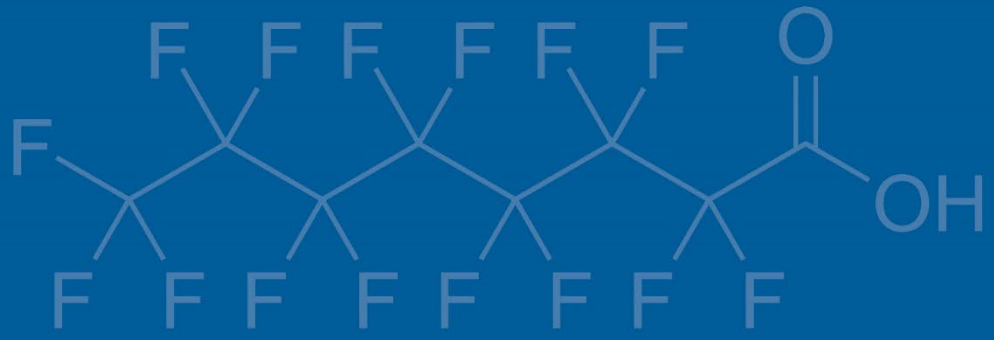
https://www.epa.gov/pfas

TRC
Results you can rely on



PFAS Sampling Techniques & Analysis Methods

PFAS & Other Emerging Contaminants Conference

April 23, 2019

trcsolutions.com |

GWPNC
Groundwater Professionals of North Carolina
www.gwpnc.org

50 1969-2019
ACEC
American Council of Engineering Companies of North Carolina

PFAS Sampling Issues and Quality Control

How Do We Sample PFAS?

Results you can rely on

- Similar to conventional sampling (e.g., low-flow techniques, direct push, etc.)
- Special care required to prevent cross contamination
- Use of and exclusion of specific sampling equipment and materials

DEQ Michigan Department of Environmental Quality

WASTEWATER PFAS SAMPLING

Guidance

PFAS Sampling Dos and Don'ts

WHAT SHOULD I AVOID?	USE INSTEAD
Passive diffusion bags (PDBs)	
LDPE Hydrasleeves	✓ HDPE Hydrasleeves
Post-It notes during sample handling	
Blue Ice® (chemical ice packs)	✓ Regular ice in Ziploc® bags
Waterproof field books, plastic clipboards and spiral bound notebooks	✓ Field notes recorded on loose paper ✓ Field forms maintained in aluminum or Masonite clipboards
Unnecessary handling of items with nitrile gloves	✓ Personnel collecting and handling samples should wear nitrile gloves at all times while collecting and handling samples or sampling equipment

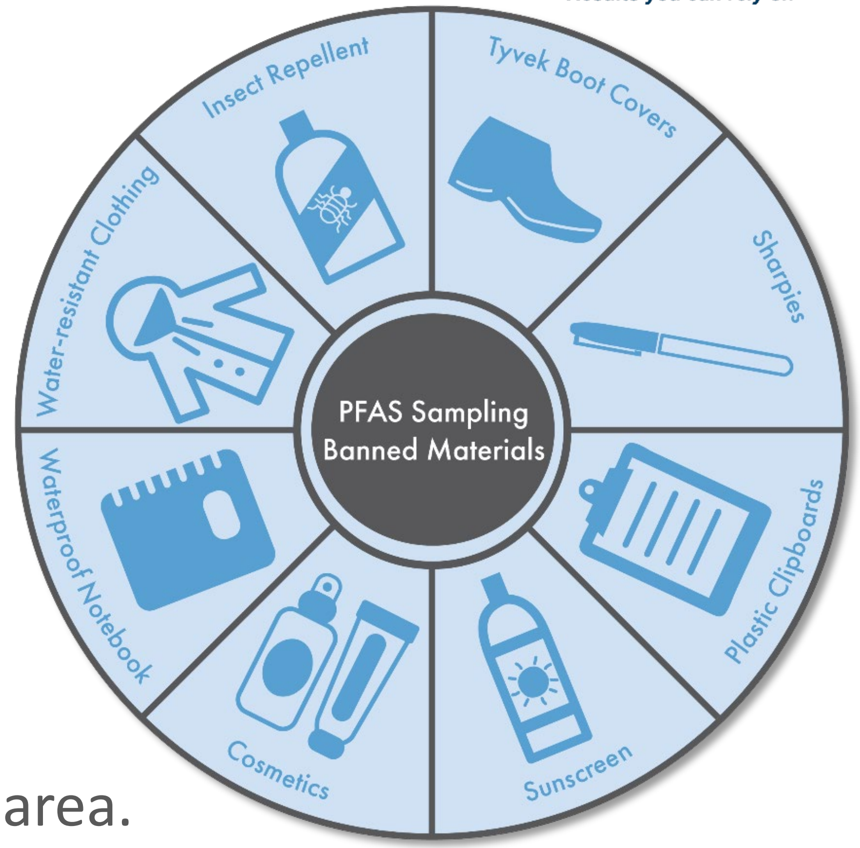
PFAS Sampling Dos and Don'ts

TRC Results you can rely on

WHAT SHOULD I AVOID?	USE INSTEAD
Equipment with **Teflon®** (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization	✓ High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon®
Low-density polyethylene (LDPE) or glass sample containers or containers with Teflon-lined lids	✓ HDPE or polypropylene containers for sample storage ✓ HDPE or polypropylene caps
Tyvek® suits and waterproof boots	✓ Clothing made of cotton preferred ✓ Boots made with polyurethane and polyvinyl chloride (PVC)
Waterproof labels for sample bottles	✓ Paper labels with clear tape
Sunscreens, insect repellants	✓ Products that are 100% natural, DEET
Sharpies	✓ Ballpoint pens
Aluminum foil	✓ Thin HDPE sheeting

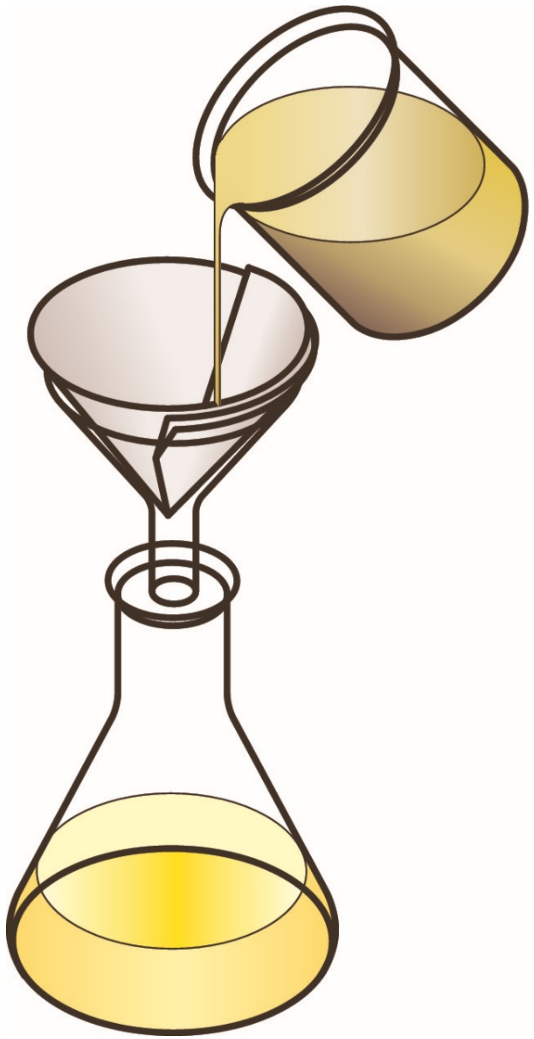
Other Special Considerations

- Field QC
- Decontamination of sampling equipment
- No pre-wrapped food or snacks
- Avoid cosmetics, moisturizers, hand creams on day of sampling.
- Do not filter aqueous samples.
- Visitors to site must remain at least 30 feet from sampling area.
- Wash hands with water after leaving vehicle before setting up on a well.
- **Partitioning of PFAS to surface in wells and reservoirs**



Filtering of Water Samples

- PFAS may sorb onto glass fiber filters
- Filtered/unfiltered data:
  - Is it PFAS sorbed to soil or sediment in the water sample?
  - Is it PFAS sorbed onto the glass fiber filter?
- Preferred method of dealing with particulates: low flow sampling or use of a centrifuge in the lab
- If filtering is required, do not use glass fiber filters



What Should I Wear?

- No clothing with fabric softeners
- No new clothing
- Avoid boots and other field clothing containing waterproof/resistant material
- Cotton is best

Other PFAS Sampling Precautions

- Many PFAS sampling concerns are precautionary and have no scientific data to prove
- HDPE can sorb PFAS as well (evidence of strong 6:2 FTS sorption)
- Laboratory should empty the entire sample bottle for extraction, sub-sampling from the sample bottle must be avoided
  - The empty bottle should be rinsed with methanol to desorb any PFAS on the sample bottle regardless of bottle materials
  - The rinsate should be combined with the sample materials for analysis

PFAS in Sampling Supplies: Fact or Fiction?

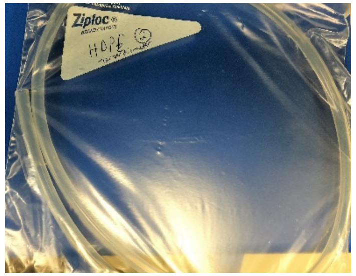
TRC
Results you can rely on

Polyethylene
Tubing - Lab

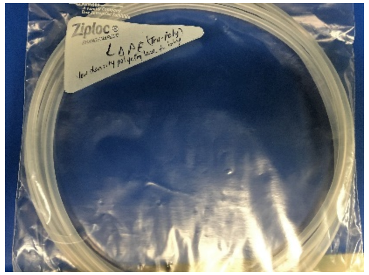
Aluminum Foil

Adhesive note pads

Polyethylene Bladder



HDPE Tubing: 1/8” OD
3/8” OD



LDPE Tubing :
2 Manufacturers

Silastic Tubing

PTFE
Bladder

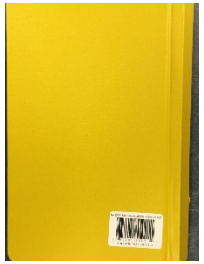
Level C
chemical-
resistant
clothing

PTFE
Tubing

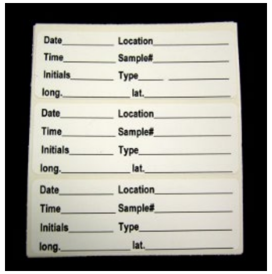
Passive Diffusion Bag

Nitrile Gloves

Bailer Line



Field Book
(cover & pages)



Sample Labels


MONADNOCK
MONADNOCK


SCI SPEC
innova 2300
PLATFORM SHAKER
131
NEW BRUNSWICK SCIENTIFIC

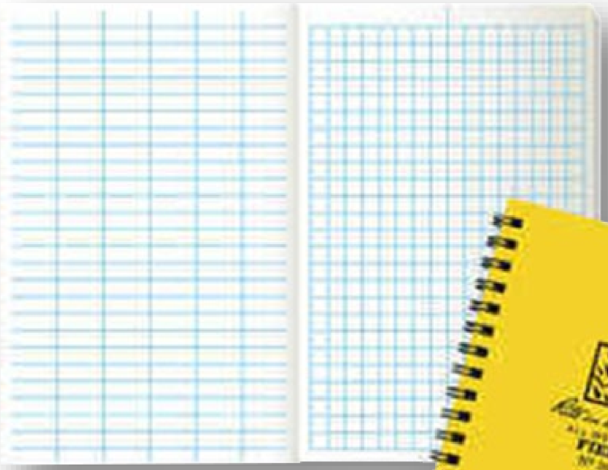
Analyte	Acronym	CAS #
1H,1H,2H,2H-perfluorohexane sulfonate (4:2)	4:2FTS	n/a
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2FTS	27619-97-2
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2FTS	39108-34-4
N-methyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2355-31-9
N-ethyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2991-50-6
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8

PFAS in Sampling Supplies: Fact or Fiction?

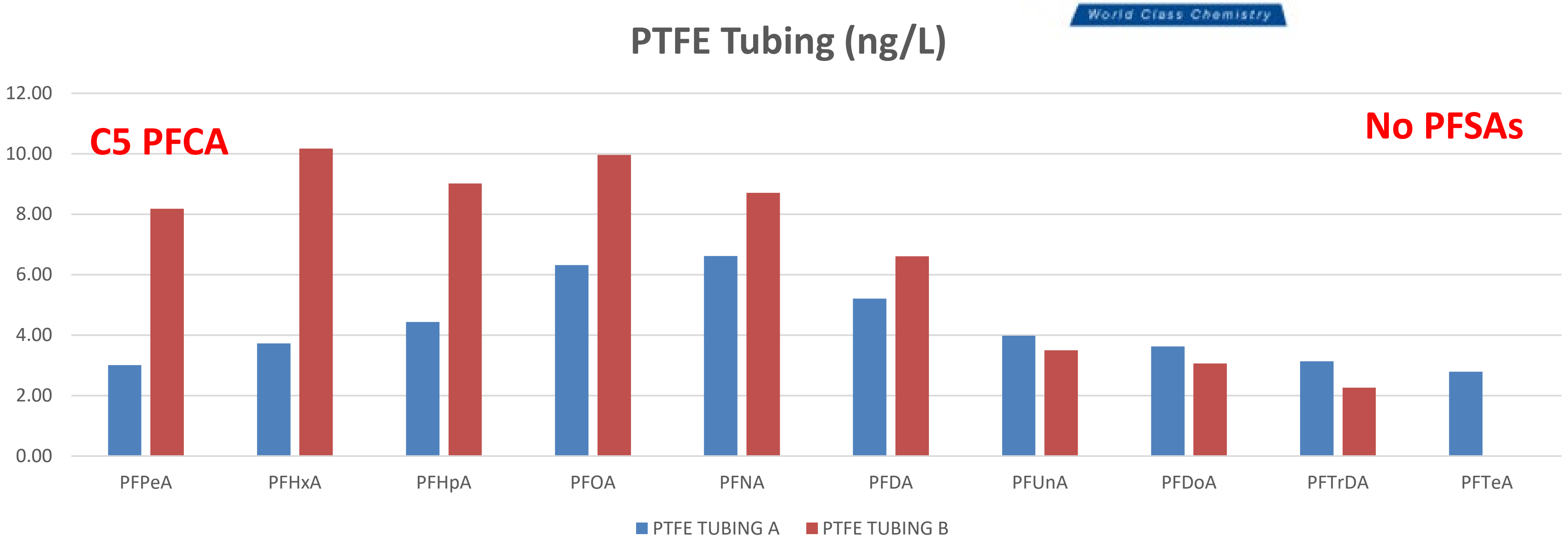
TRC
Results you can rely on

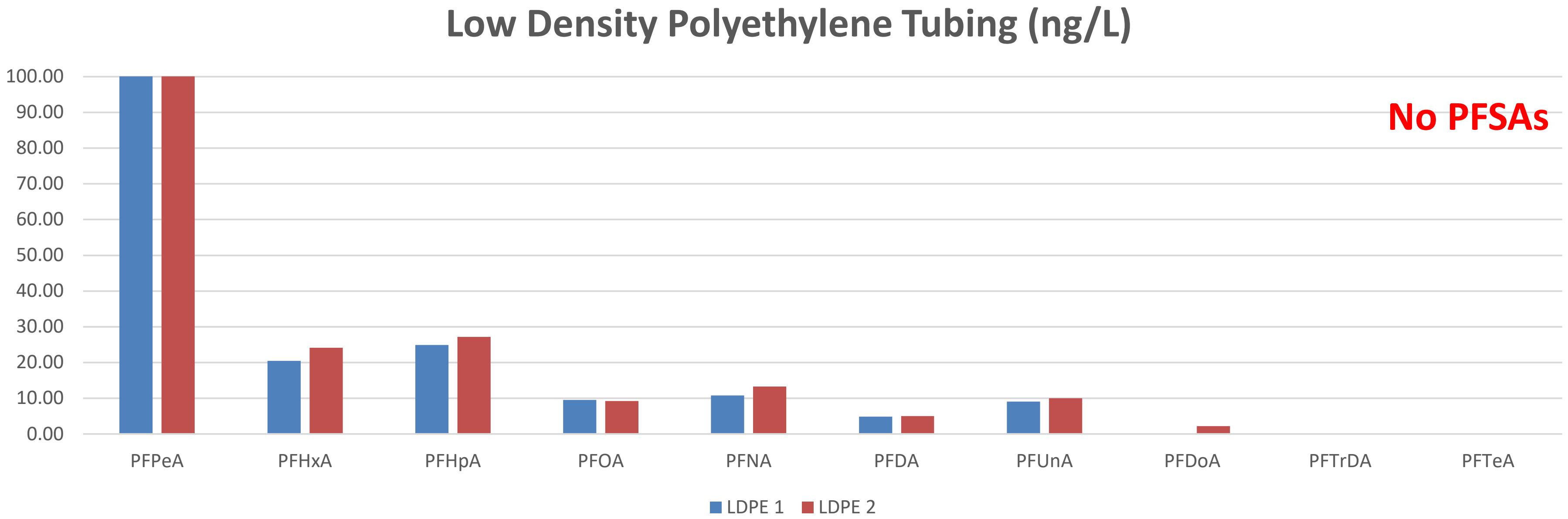
Detections of PFAS:

- PTFE tubing
- LDPE tubing
- Level C chemical-resistant clothing
- String used for bailers
- Field logbook pages
- Field logbook cover
- PTFE bladder
- Sample labels



Tubing Results





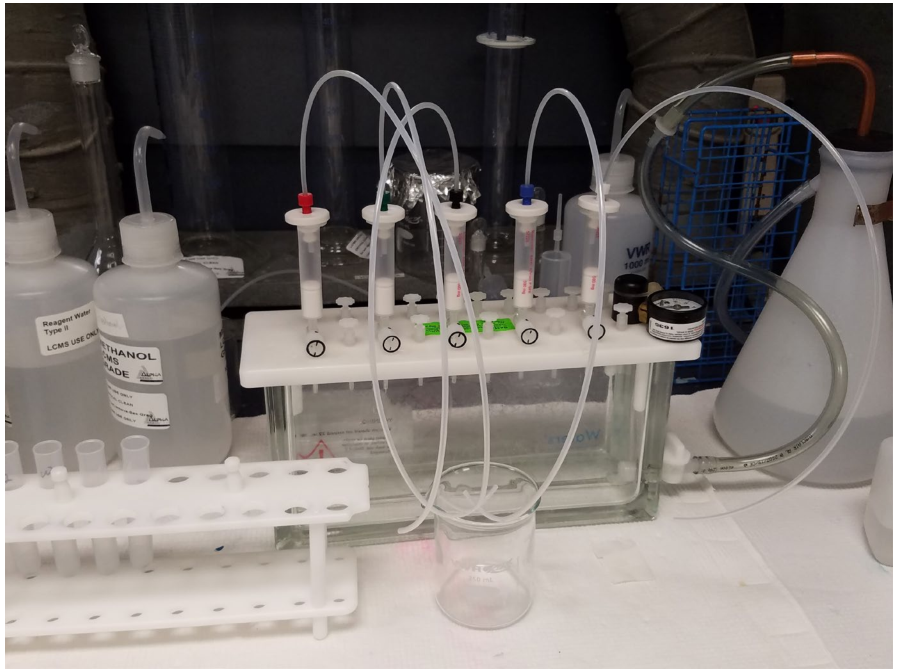
No PFAS Detected

Silastic Tubing	Aluminum Foil
Polyethylene Bladder	Post-its
Passive Diffusion Bag	Zip-locs
High-density polyethylene tubing	

PFAS Analysis Methods

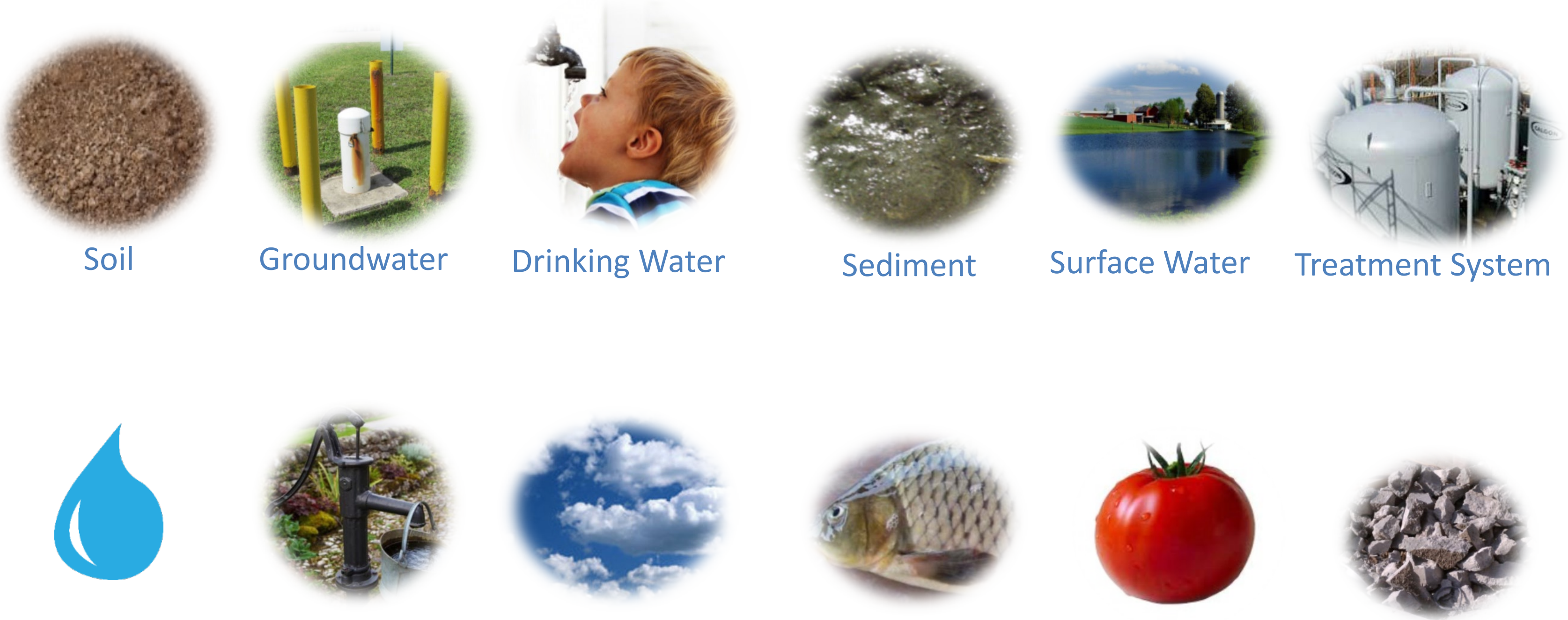
EPA Method 537

- Primary methodology
  - Method 537.1 Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) November 2018 (original Sept 2009)



- Sample preparation
  - Solid phase extraction (SPE), *aqueous samples*
- Analytical Instrumentation
  - Liquid chromatography / tandem mass spectrometry (LC/MS/MS)

Potential PFAS Sampling Media



Soil
Groundwater
Drinking Water
Sediment
Surface Water
Treatment System
Pore Water
Private Well
Ambient Air
Biological Tissues
Vegetables
Concrete

From ITRC PFAS Training, April 2019, Boston, MA

Methods and Analyte Lists

PFAS Methods

Method	Year	Applicable Matrices	# PFAS Analytes
EPA 537 v 1.1	2009	Drinking Water	14 analytes
EPA 537.1	2018	Drinking Water	18 analytes
ASTM D7979-17	2017	Water, Wastewater	21 analytes
ASTM D7968-17	2017	Soil	21 analytes
ISO 25101	2009	Aqueous	PFOA/PFOS
DoD QSM 5.1	2017	Solid & Aqueous	24+ analytes
DoD QSM 5.2	2018	Solid & Aqueous	24+ analytes
EPA 537 "Modified"	Current	All	24+ analytes

Current PFAS Reportable by Analytical Laboratories

Analyte	CAS No.	UCMR3 (6)	537 (14)	NYSDEC (21)	ISO 25101 (2)	MDEQ IPP (24)
Perfluorobutanoic acid (PFBA)	375-22-4			X		X
Perfluoropentanoic acid (PFPeA)	2706-90-3			X		X
Perfluorohexanoic acid (PFHxA)	307-24-4		X	X		X
Perfluoroheptanoic acid (PFHpA)	375-85-9	X	X	X		X
Perfluorooctanoic acid (PFOA)	335-67-1	X	X	X	X	X
Perfluorononanoic acid (PFNA)	375-95-1	X	X	X		X
Perfluorodecanoic acid (PFDA)	335-76-2		X	X		X
Perfluoroundecanoic acid (PFUnA)	2058-94-8		X	X		X
Perfluorododecanoic acid (PFDoA)	307-55-1		X	X		X
Perfluorotridecanoic Acid (PFTrA)	72629-94-8		X	X		X
Perfluorotetradecanoic acid (PFTeA)	376-06-7		X	X		X
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5					
Perfluorooctadecanoic acid (PFODA)	16517-11-6					
Perfluorobutanesulfonic acid (PFBS)	375-73-5	X	X	X		X
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4					X
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	X	X	X		X
Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8			X		X
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	X	X	X	X	X
Perfluorononanesulfonic acid (PFNS)	474511-07-4					X
Perfluorodecanesulfonic acid (PFDS)	335-77-3			X		X
Perfluorooctane Sulfonamide (FOSA)	754-91-6			X		X
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)	2355-31-9		X	X		X
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)	2991-50-6		X	X		X
6:2 Fluorotelomer sulfonic acid (6:2 FTSA)	27619-97-2			X		X
8:2 Fluorotelomer sulfonic acid (8:2 FTSA)	39108-34-4			X		X
4:2 Fluorotelomer sulfonic acid (4:2 FTSA)	757124-72-4					X
10:2 Fluorotelomer sulfonic acid (10:2 FTSA)	120226-60-0					
N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)	24448-09-7					
N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)	1691-99-2					
N-Methyl perfluorooctane sulfonamide (MeFOSA)	31506-32-8					
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	4151-50-2					
HFPO-DA (Gen-X)	62037-80-3		X			
ADONA			X			
F-53B-9Cl			X			
F-53B-11Cl			X			

Analyte lists vary by method, laboratory, and regulatory agency

Determine what list you really need!

“Modified” EPA 537

Results you can rely on

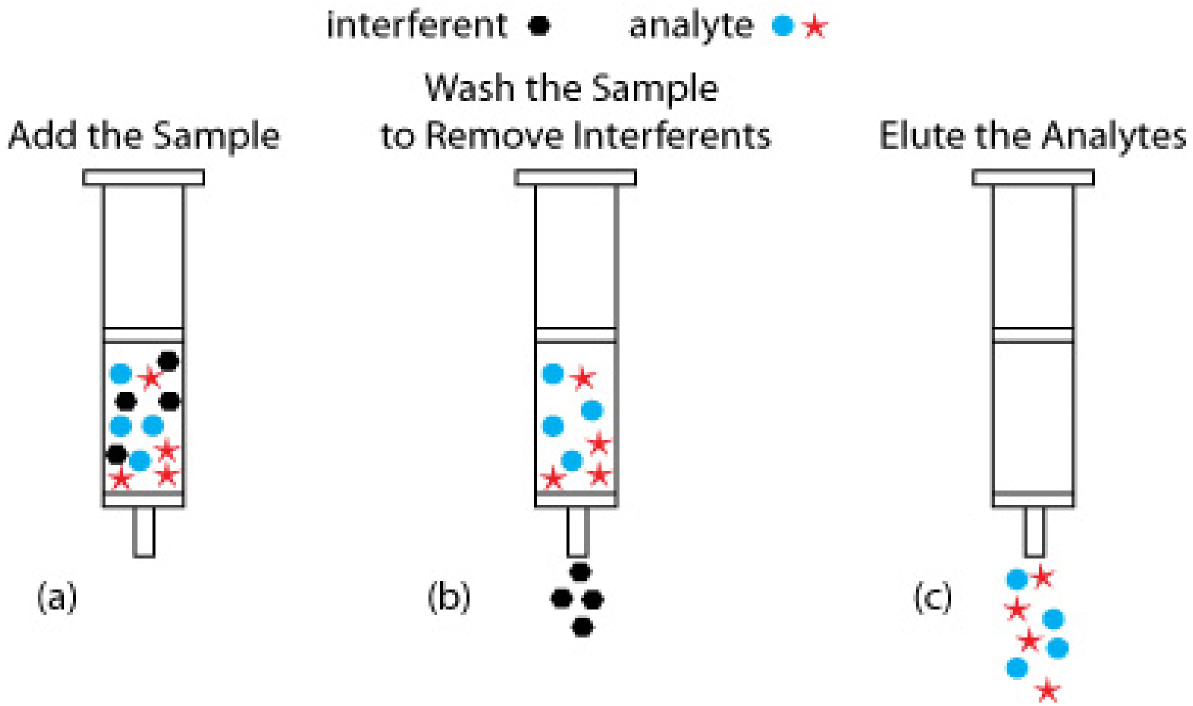
Solid Phase Extraction

- Is the lab extracting the entire sample and rinsing the sample bottle?
- What cartridge is the lab using?
  - *Styrenedivinylbenzene (SDVB) sorbent phase*
  - *Reverse phase copolymer characterized by a weak anion exchange (WAX) sorbent phase*

PFBA, PFPeA poor recoveries

- Is the lab doing washes to remove interferences on the SPE cartridge?

250 mL sample

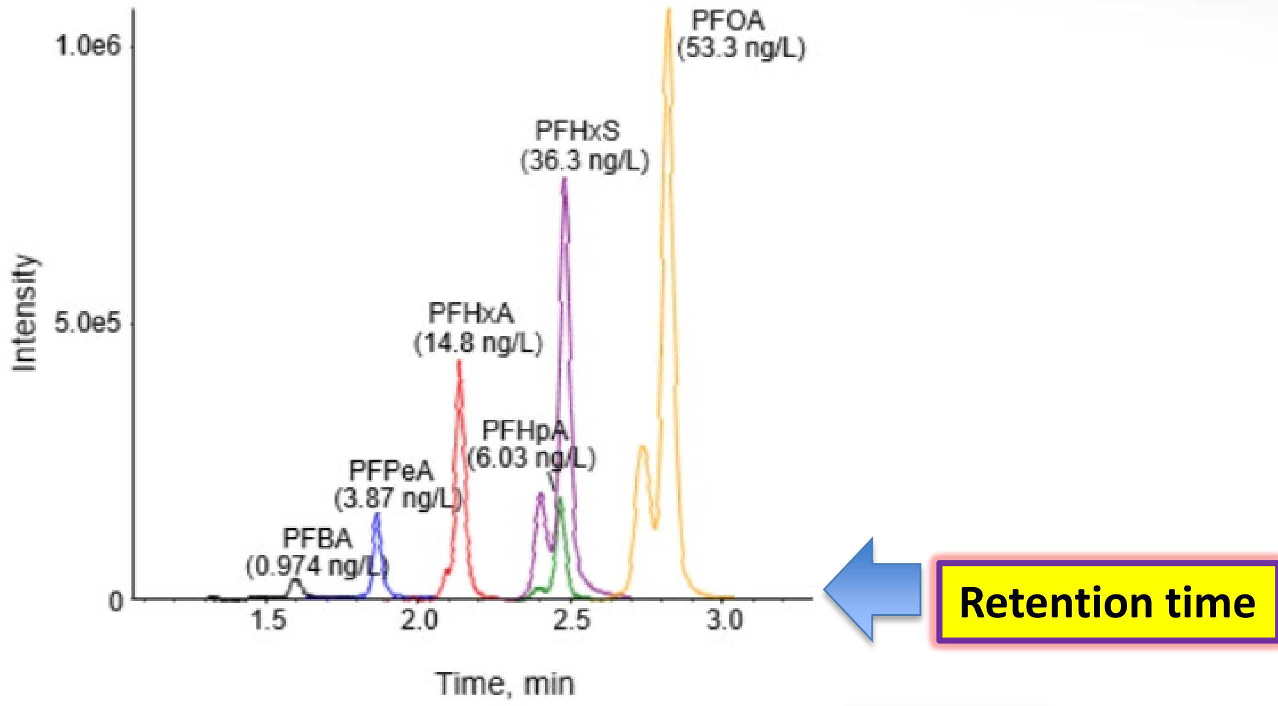


1 mL final extract

Sample Analysis: HPLC Separation (Part 1)

Separates compound mixtures on column. Column has high affinity for PFAS. The affinity of each compound to the column is different based on its solubility.

- Characteristic **retention times**
- **Step 1 in compound identification**: time the compound comes off the column



Analyte	Retention Time (min)
PFBA	1.527
$^{13}C_4$PFBA	1.525
PFOS	3.028
$^{13}C_4$PFOS	3.026

Retention time increases with carbon number

Sample Analysis: MS/MS (Part 2)

- Unique fragmentation patterns **(Step 2 of compound identification)**
- Parent/daughter combinations = definitive ID, more sensitive analysis

Analyte	Retention Time (min)	Parent/Daughter Ions
PFBS	1.754	299/80 299/99
$^{13}C_3$PFBS	1.752	302/83
PFOS	3.028	499/80 499/99
$^{13}C_4$PFOS	3.026	503/80

Transition Ions (Parent/Daughter Ions)

- **Definitive Identification of Compounds**
  - Retention time from HPLC separation
  - Transition to characteristic daughter ions
  - Ion ratios
- **What happens when the ion ratios are outside limits?**
  - What are the limits?
- **What if there is no daughter/confirmation ion?**
  - PFBA
  - PFPeA
  - NMeFOSAA
  - NEtFOSAA

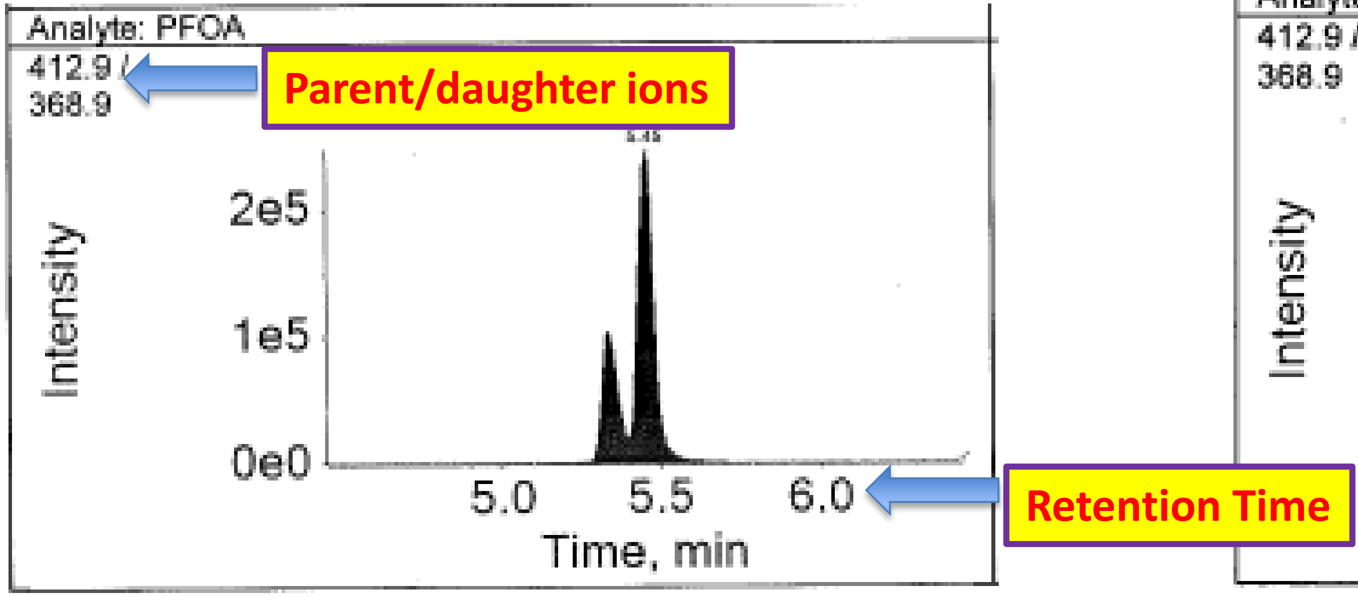
Analyte	Retention Time (min)	Parent/ Daughter Ions	Ion Ratio	Ion Ratio Limit
PFBS	1.754	299/80 299/99	2.91	1.35-4.05
$^{13}C_3$PFBS	1.752	302/83	NA	NA
PFOS	3.028	499/80 499/99	4.19	2.04-6.12
$^{13}C_4$PFOS	3.026	503/80	NA	NA

Linear & Branched Isomers

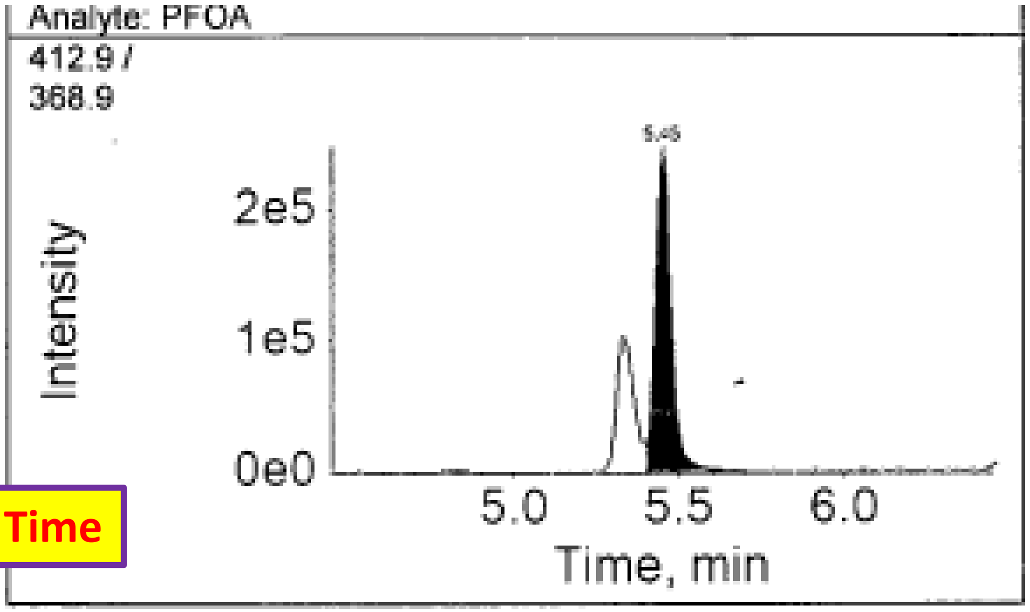
- Before September 2016, some inconsistency in how this performed
- PFHxS, PFOS, PFOA, NMeFOSAA, NEtFOSAA
- If branched isomers not included, result is biased low.

EPA United States Environmental Protection Agency

Technical Advisory- Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) Using EPA Method 537 Rev. 1.1



Correct integration of PFOA



Incorrect integration of PFOA

Isotope Dilution: What is It?

- Sample spiked with KNOWN amount of isotopes (labeled surrogates or extracted internal standards)
- Isotopes match target analytes
  - $^{13}C_4$PFBA is isotope associated with PFBA
  - $^{13}C_4$PFOS is isotope associated with PFOS
  - etc. for each PFAS analyte
- Target PFAS result corrected by proportional amount based on isotope
- **BENEFITS**:
  - Corrects for analytical error associated with matrix
  - Corrects for matrix interferences

EPA 537 and ASTM Method do NOT utilize isotope dilution

DoD QSM requires isotope dilution

$$\text{Concentration Target PFAS} = \frac{\text{Target PFAS Area} * \text{True Concentration Isotope}}{\text{Area Isotope} * \text{Calibration Factor}}$$

How Can Isotope Dilution Vary Between Labs?

- **When** is the lab spiking the isotopic standards?
- **How** is the lab evaluating the recoveries of the isotopic standards?

Surrogate	Lab 1 (%)	Lab 2 (%)	Lab 3 (%)	Lab 4 (%)	DoD (%)
13C3-PFBS	25-150	50-150	26-148	31-159	50-150
13C3-PFHxS	25-150	50-150	34-126	47-153	50-150
13C4-PFHpA	25-150	50-150	35-126	30-139	50-150
13C8-PFOA	25-150	50-150	43-112	36-149	50-150
13C8-PFOS	25-150	50-150	43-115	42-146	50-150
13C9-PFNA	25-150	50-150	32-134	34-146	50-150

- If >10% recovery, results most likely not significantly affected.
- If <10% recovery, higher probability that results may be affected.
  - Some data validation guidelines recommend rejecting nondetect results if <10%.
  - Detected results: potential low bias
  - Only associated target PFAS affected

Example:
If 13C3-PFBS exhibits low %R, only affects PFBS.

PFAS Analytical Reports

Typical sample result summary form

- Number of PFAS reported
- Results, R
- Dilution r
- Collectio
- Percent solids (dry weight)
- Isotope Dilution recoveries

Isotope Dilution	%Recovery	Qualifier	Limits
13C8 FOSA	9	*	25 - 150
13C4 PFBA	27		25 - 150
13C2 PFHxA	49		25 - 150
13C4 PFOA	48		25 - 150

Client Sample Results

Client: xxxx
Project/Site: xxxxx Site

Lab Job ID: xxxxx

Client Sample ID: xxxx-08
Date Collected: 05/18/17 11:20
Date Received: 05/20/17 11:50

Lab Sample ID: xxxxx-19
Matrix: Solid
Percent Solids: 15.8

Method: 537 (modified) - Fluorinated Alkyl Substances

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Perfluorobutanoic acid (PFBA)	ND		1.3	0.41	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.83	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.45	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.56	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.65	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.53	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.36	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.68	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	
			.3	0.77	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	
			3	0.59	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			3	0.37	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			3	0.66	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			3	0.75	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
(PFHpS)			3	0.75	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorodecanesulfonic acid (PFDS)	ND		1.3	0.46	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorooctane Sulfonamide (FOSA)	ND		1.3	0.51	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1

Isotope Dilution	*%Recovery*	*Qualifier*	*Limits*	*Prepared*	*Analyzed*	*Dil Fac*
C8 FOSA	9	*	25 - 150	05/23/17 13:25	05/31/17 03:04	1
C4 PFBA	27		25 - 150	05/23/17 13:25	05/31/17 03:04	1
C2 PFHxA	49		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C4 PFOA	48		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C5 PFNA	43		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C2 PFDA	63		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C2 PFUnA	64		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C2 PFDoA	57		25 - 150	05/23/17 13:25	05/31/17 03:04	1
18O2 PFHxS	65		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C4 PFOS	49		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C4-PFHpA	47		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C5 PFPeA	41		25 - 150	05/23/17 13:25	05/31/17 03:04	1

Method: 537 (modified) - Fluorinated Alkyl Substances - DL

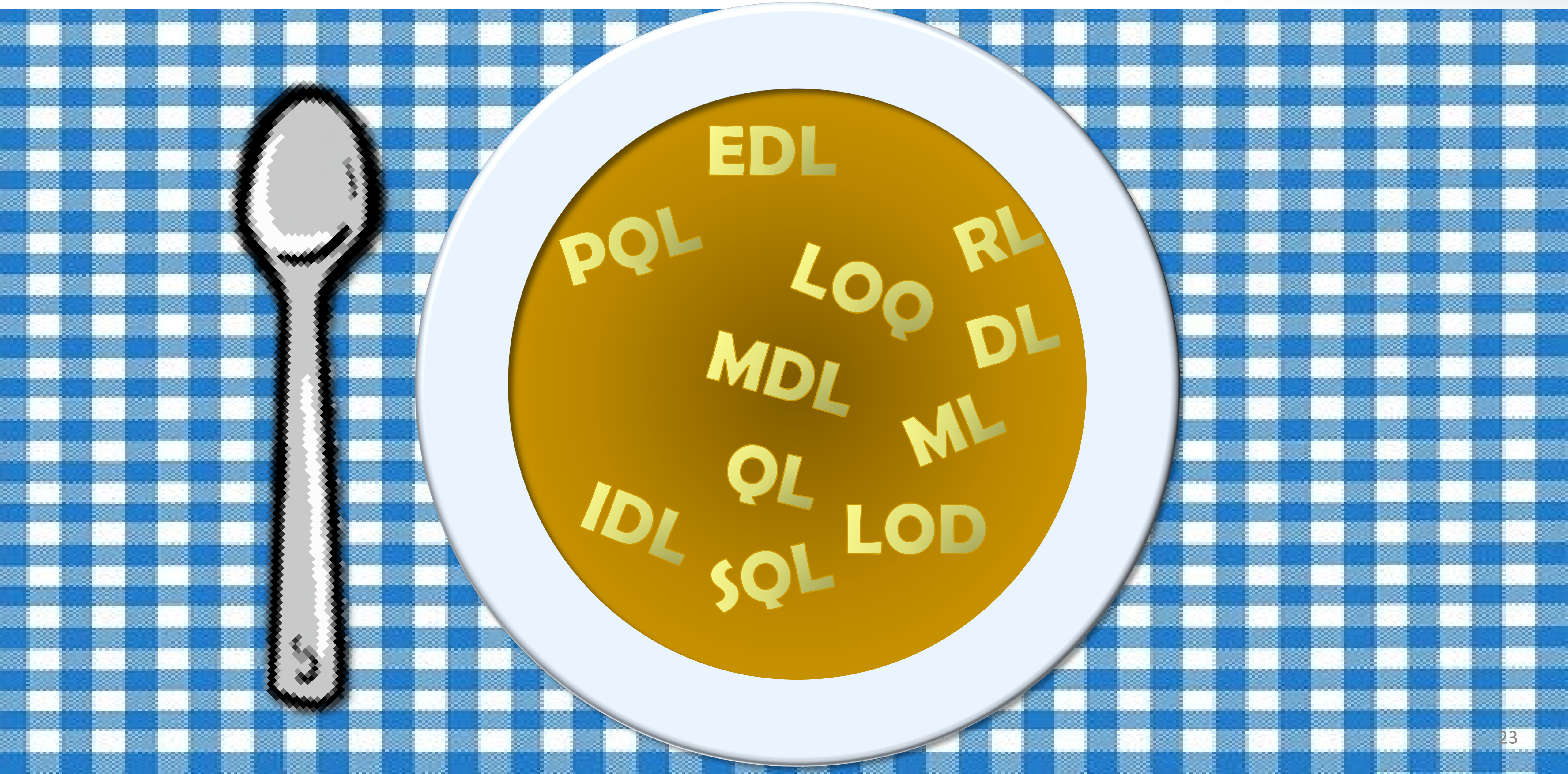
Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Perfluorooctanesulfonic acid (PFOS)	930		13	8.0	ug/Kg	☼	05/23/17 13:25	05/31/17 13:37	10

Isotope Dilution	*%Recovery*	*Qualifier*	*Limits*	*Prepared*	*Analyzed*	*Dil Fac*
13C4 PFOS	76		25 - 150	05/23/17 13:25	05/31/17 13:37	10

Potential Biases from Typical PFAS QC

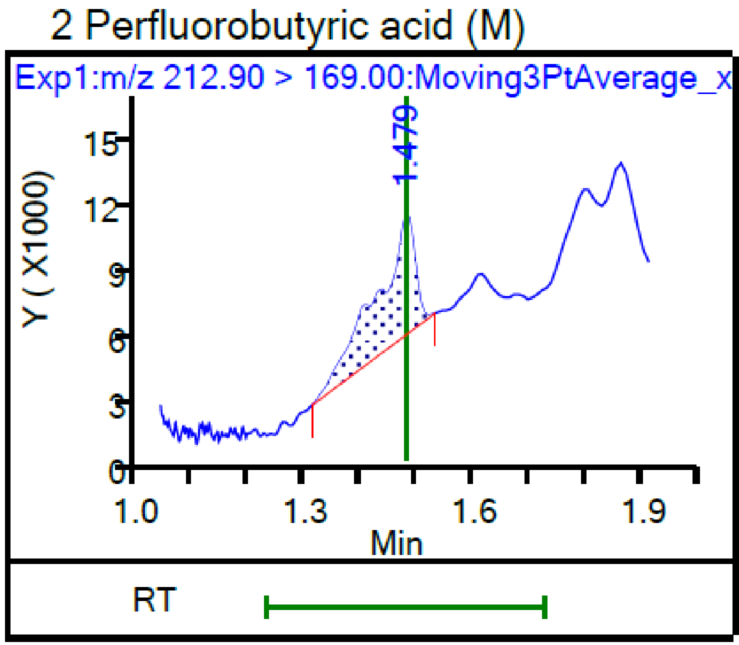
QC	Issue	Bias
Blanks	• *Detected results*	HIGH BIAS } All Associated Samples in Batch
Holding Times	• *Missed holding times*	LOW BIAS } Sample-Specific
LCS	• *Low recoveries* • *High recoveries*	LOW BIAS HIGH BIAS } All Associated Samples in Batch
Labeled Surrogates, Matrix Spikes	• *Low recoveries* • *High recoveries*	LOW BIAS HIGH BIAS } Sample-Specific

Detection Limits

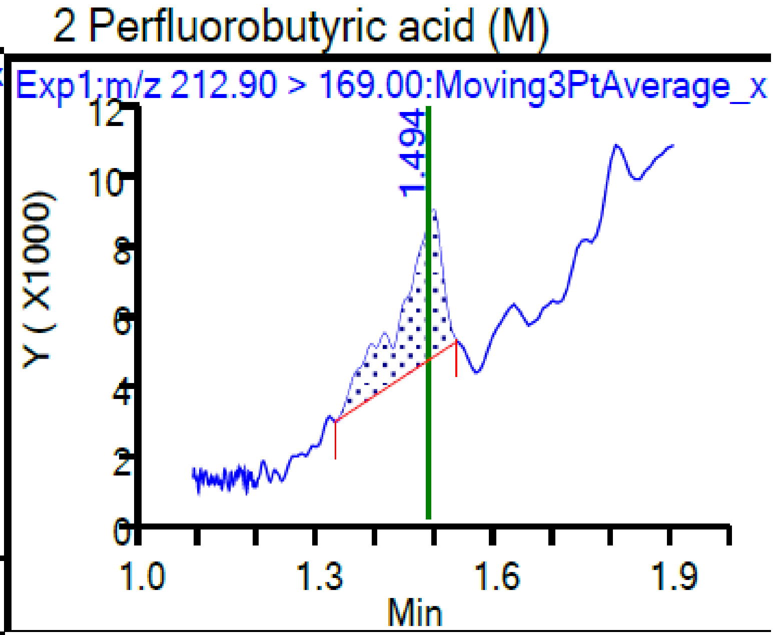


What To Use for PFAS?

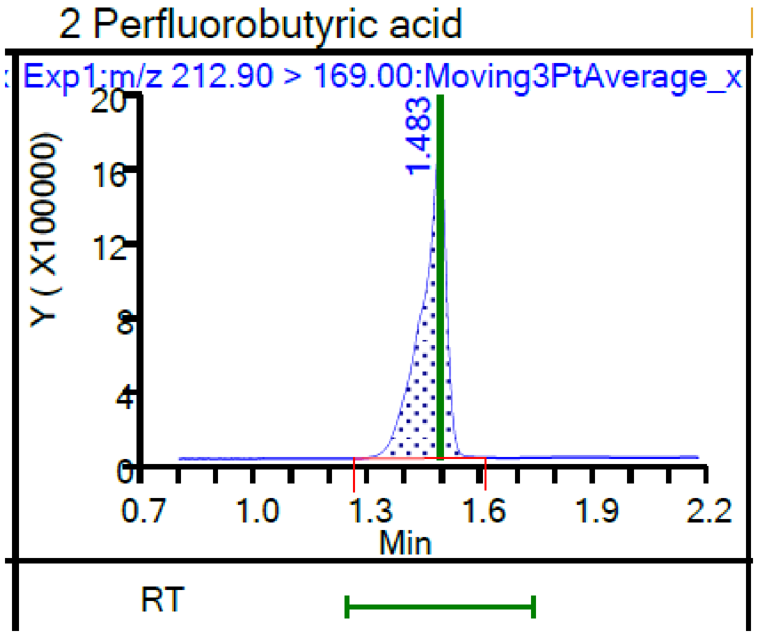
- RLs most reliable value (aka LOQ, QL, SQL, ML, CRQL)
- Most labs RLs 2-10 ng/L, depending on PFAS
- Do not use MDLs as nondetect values
- No J values



PFBA: 0.35 J ng/L

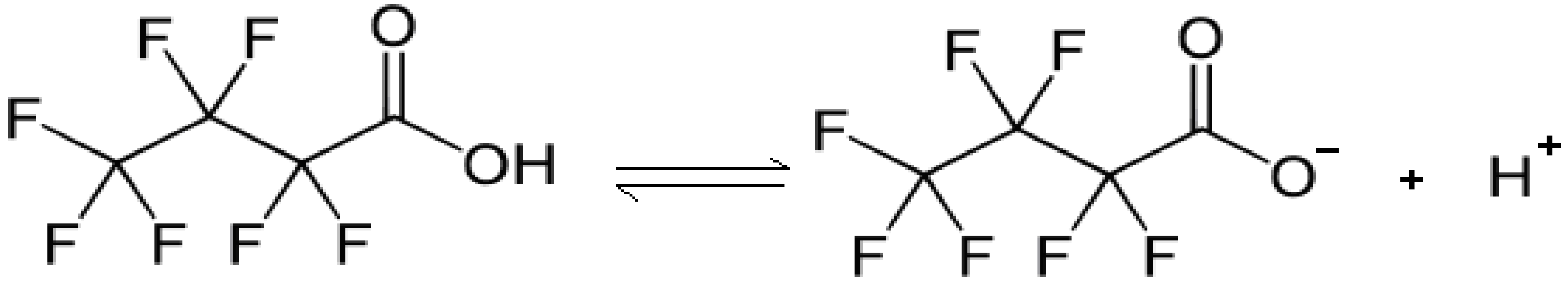


PFBA: <2.0 ng/L



PFBA: 2.5 ng/L

CAS Numbers and PFAS State



	PFAS State		Structure	CAS No.
PFOA	Anion	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
	Acid	Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
PFOS	Anion	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
	Acid	Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1

Labs should report acid form and CAS No. for acid

Standardized Methods in the Future?

Future Method	Matrix	Calibration	Analytes/RLs	When?
SW-846 8327	Aqueous (non-DW)	Direct injection; External standard	24 PFAS; RL 10 ng/L	Out for public comment soon
SW-846 8328	Aqueous and solids	Isotope dilution	24 PFAS in 8327 plus Gen-X; RL 10 ng/L	Spring 2019; EPA collaborating with DoD
SW-846 8329	Solid prep method	NA	NA	Not definite
New Drinking Water Method	Drinking Water	SPE; Internal standard	Shorter chain PFAS	June 2019; EPA ORD & Office of Water

Summary – Take Away Points

- No standard PFAS Analytical Method for non-DW matrix
- SOPs are inconsistent across laboratories
- Evaluate the reported QC results
- Understand what your lab's procedures are

Thank you

Questions?

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Program Director – PFAS Group
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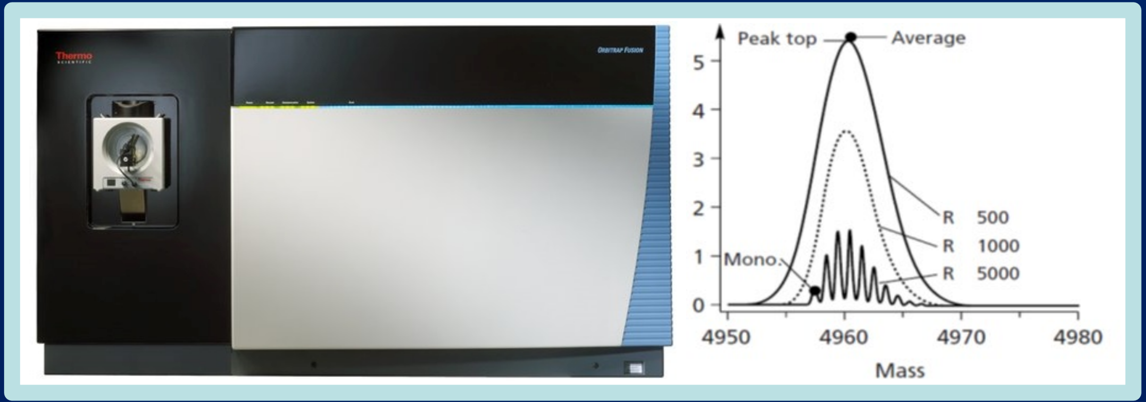
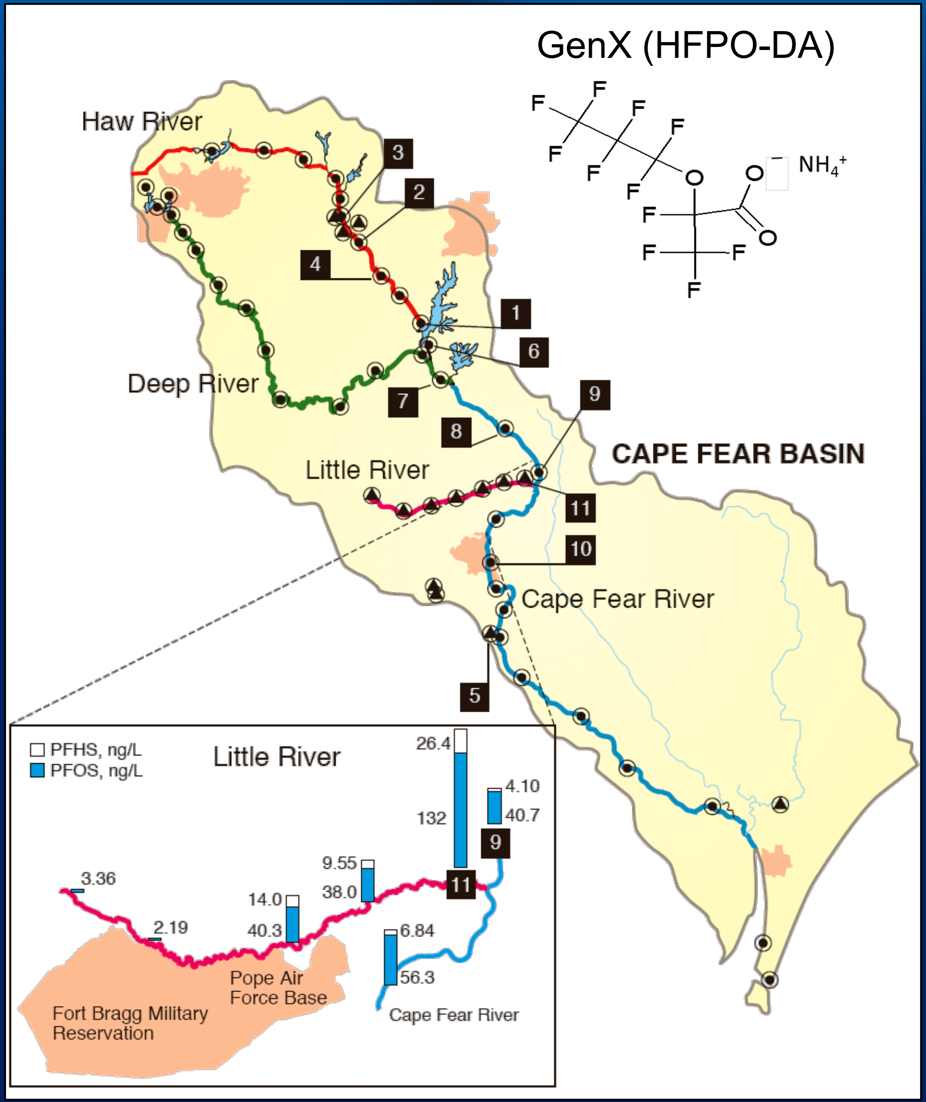
www.trccompanies.com

A Deeper Dive into PFAS Analysis

James McCord ORISE/ORD/NERL/EMMD





April 23rd, 2019
ACEC/NC Seminar

Historical Work: PFAS in the Cape Fear Watershed

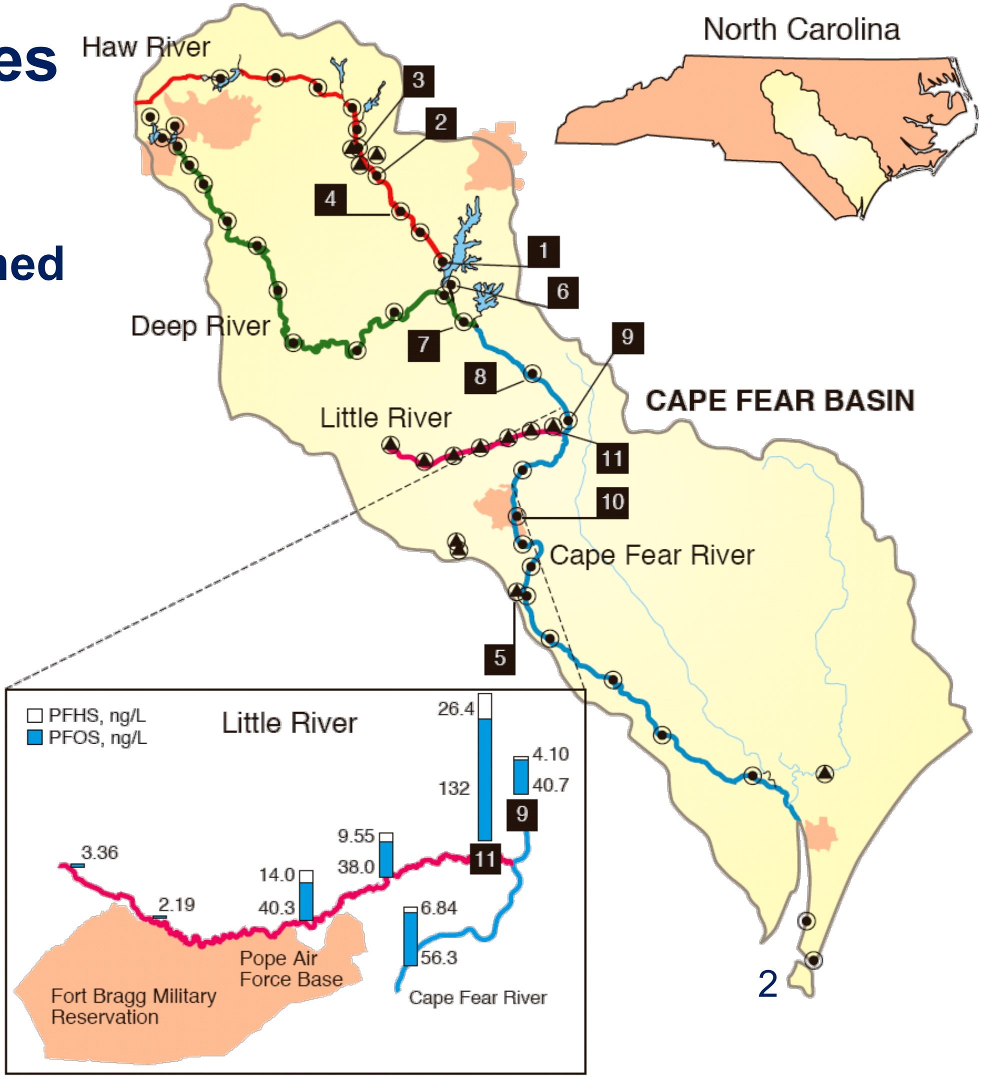
Classic Targeted Analysis for Legacy Analytes

- Analysis against a suite of known compounds with analytical standards PFCAs (C6-12) + PFSAs (C4,6,8)
- Perfluorinated compounds clearly impacting the watershed

TABLE 3. Measured Concentrations at the Eleven Sites with the Highest Total Concentrations of PFCs in the Cape Fear River Basin[a] (See Figure 1 for locations)

no.	river	C12 (ng/L)	C11 (ng/L)	C10 (ng/L)	C9 (ng/L)	C8 (ng/L)	C7 (ng/L)	C6 (ng/L)	PFOS (ng/L)	PFHS (ng/L)	PFBS (ng/L)	total (ng/L)
1	Haw River	*4.46*	*52.1*	*120*	*194*	*287*	118	21.7	127	8.43	*9.41*	942
2	Haw River	3.20	28.7	112	157	200	66.8	14.5	33.4	7.87	2.61	626
3	Haw River	3.29	27.6	109	157	191	59.2	13.7	36.4	9.49	3.04	609
4	Haw River	1.98	20.0	88.2	151	201	58.2	13.2	31.5	7.49	2.88	574
5	tributary to Cape Fear	2.26	15.0	19.6	71.2	58.6	*329*	*23.0*	30.0	3.36	ND	531
6	Haw River	1.18	8.87	31.0	72.1	152	58.3	13.5	31.2	7.70	ND	376
7	Cape Fear River	< LOQ	3.34	13.2	34.8	70.3	24.0	7.84	66.7	5.59	ND	227
8	Cape Fear River	1.14	6.39	17.2	35.7	71.5	26.9	9.35	50.4	4.82	ND	223
9	Cape Fear River	1.23	6.75	17.1	38.0	72.7	23.7	7.05	40.7	4.10	ND	211
10	Cape Fear River	< LOQ	7.55	19.3	31.2	46.8	13.9	4.62	56.3	6.84	2.12	189
11	Little River	< LOQ	< LOQ	2.17	2.24	12.6	3.38	3.23	*132*	*26.4*	3.20	185

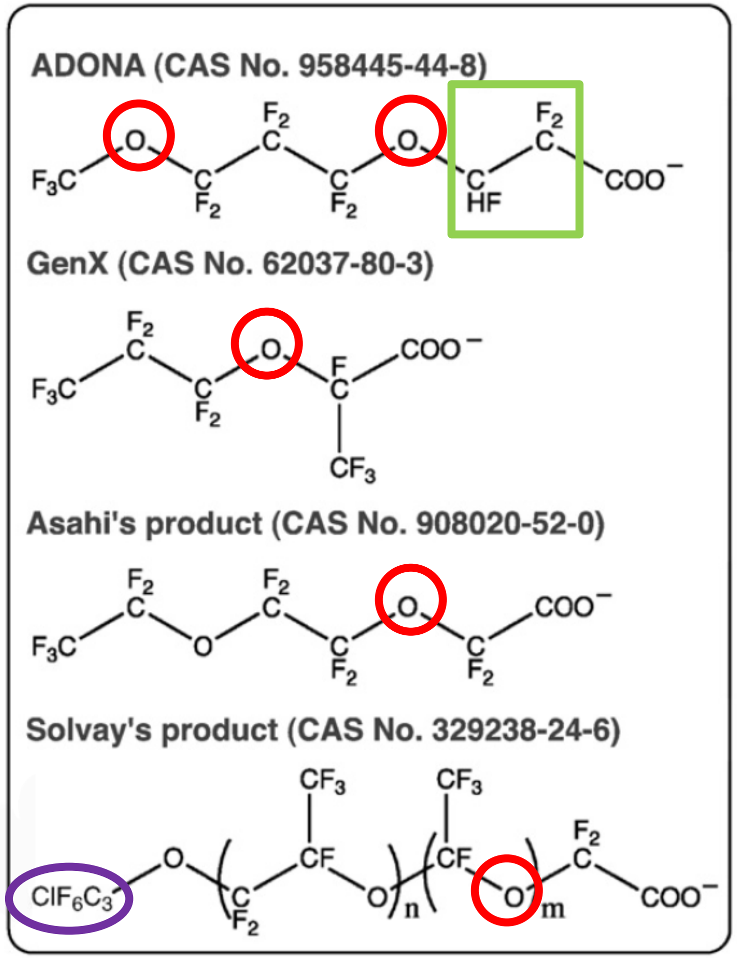
[a] Italicized values show maximal concentrations of each compound.



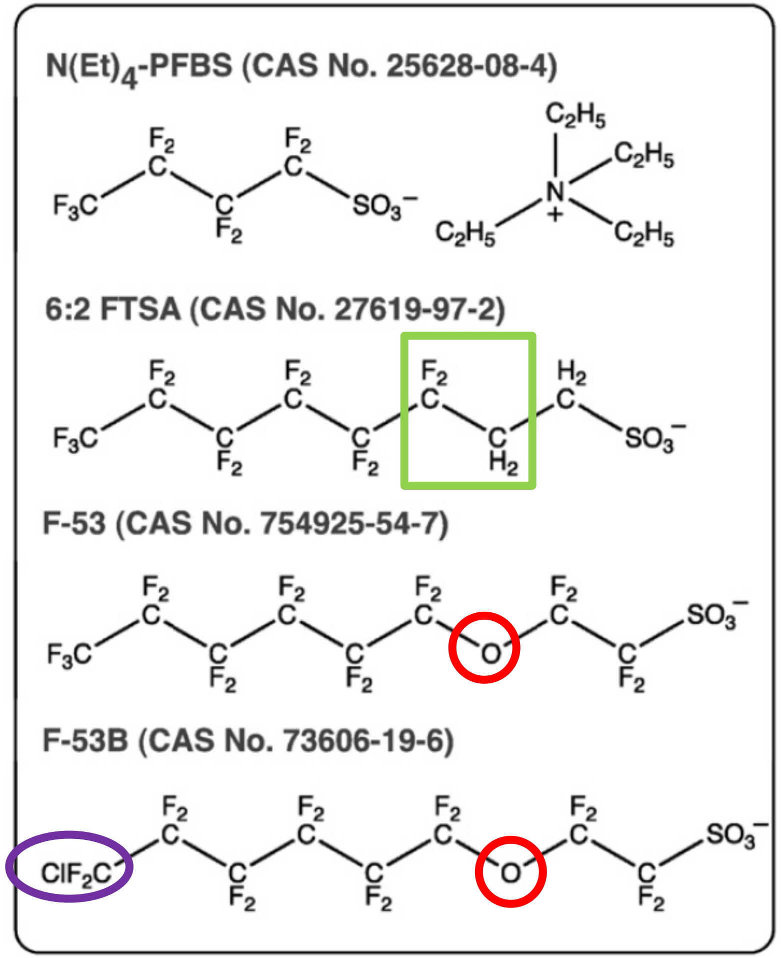
Nakayama et al. 2007 *ES&T* 41:5271-5276

Novel Compounds Post PFOA Stewardship Agreement

Fluoropolymer manufacture



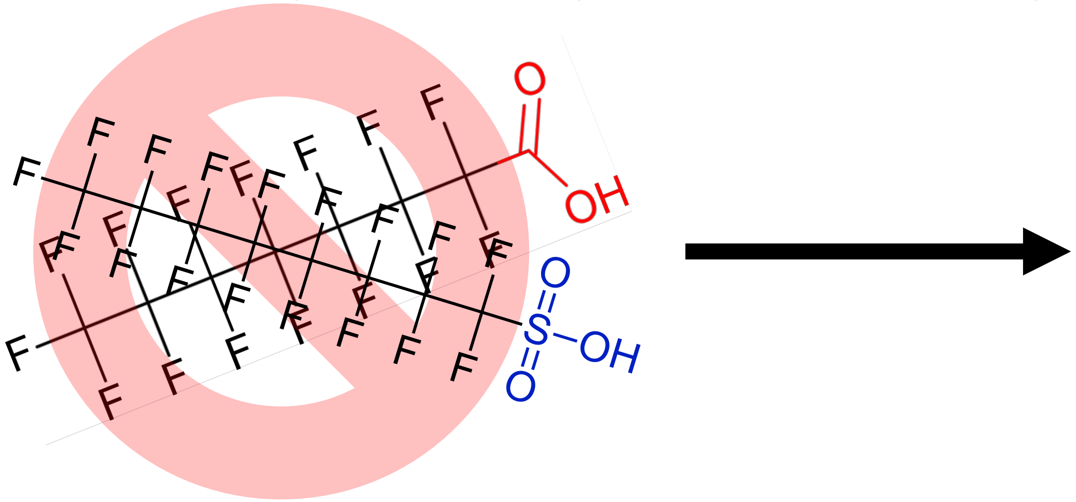
Metal plating



Wang et al. *Environmental International*, **2013,** *60,* pp 242–248

OTHER PFASs: The Era of Non-Targeted Analysis

- How do we find compounds without knowing what they are?
- How do we prioritize unknowns for further analysis?
- How do we identify/quantify without analytical standards?



???

Approaches to Chemical Measurements

	Targeted	Screening	Discovery
Given:	Selected Chemical(s)	Compound Database	No Additional Info
Question:	How much PFOA is in my sample?	Which pesticides from DSSTox are in my sample?	What chemicals are in my sample?

→ Non-Targeted Analysis

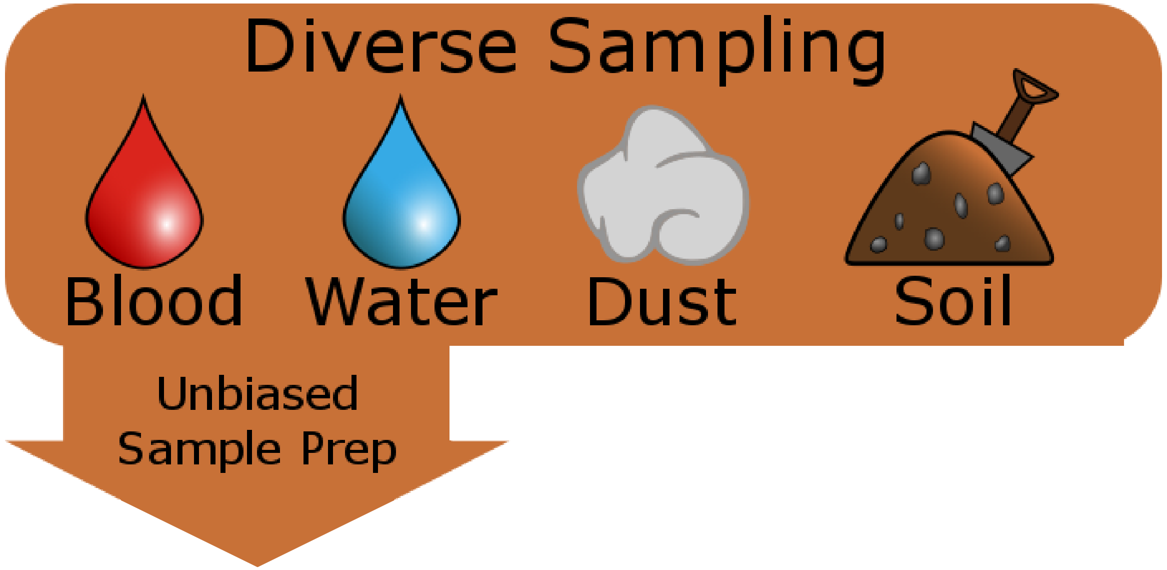
Approaches to Chemical Measurements

	Targeted	Screening	Discovery
Chemical Targets	Few, selected chemicals	100s – 100,000s per library	Any chemical
Method of Analysis	Focused method	Non-Targeted Method	Non-Targeted Method(s)
Chemical Structure	Known	Known in library	Unknown
Reference Data	Available	Some	Some, maybe simulated
Standards	Available	Maybe, for common compounds	Unlikely

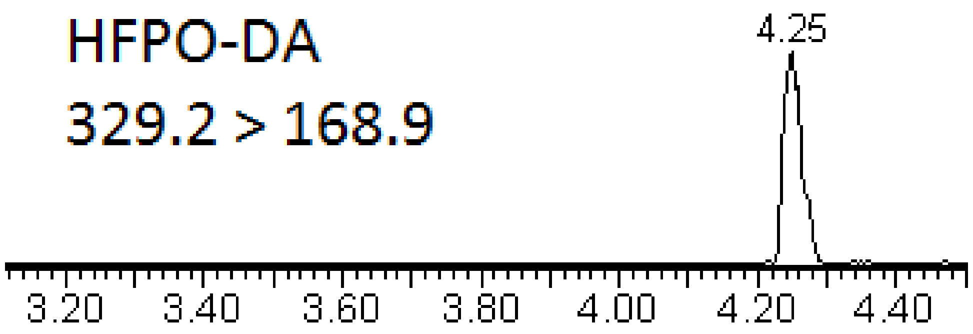
Harder, More Time Consuming Analysis →

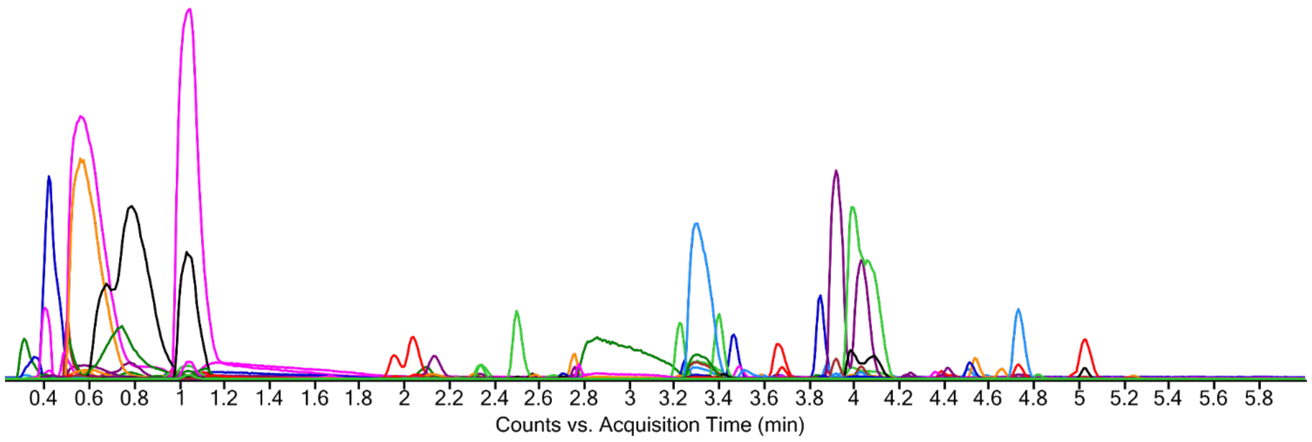
Non-Targeted Data Generation

- Attempts to generate an *unbiased* overview of sample components
- Experimental choices limit observed species and available information
  - Sample (Serum, Tissue, Dust, Water)
  - Extraction (Solvent, SPE)
  - Chromatography (GC, LC, IC)
  - Analyzer (High-Res, Low-Res, MS, MS^n)
- Practicality rules
  - Target rational, probable samples and look for likely “interesting” chemicals



Targeted vs. Non Targeted Data Complexity

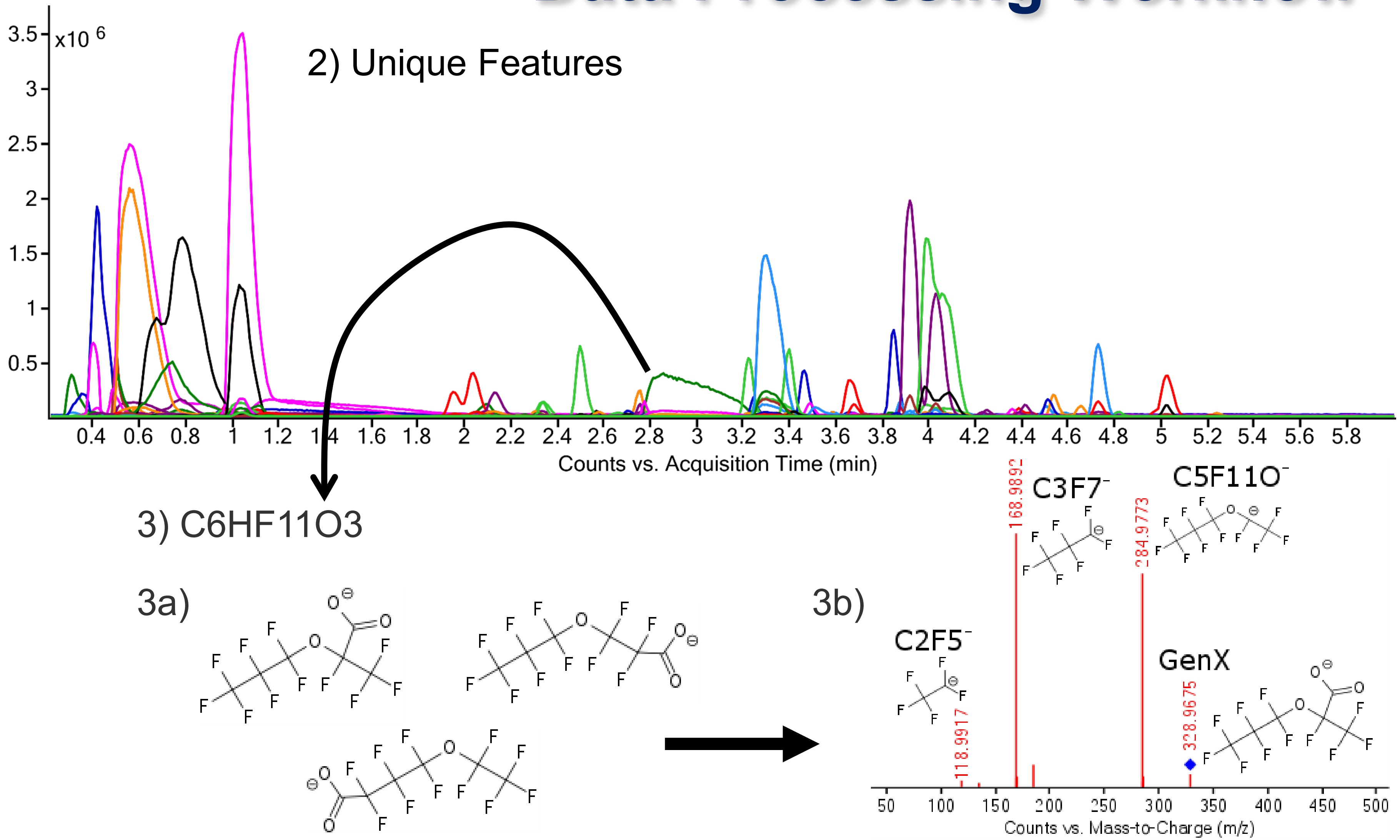




- Predefined mass transitions
- Collect peak area and RT for comparison to standard

- Thousands of detected masses
- Features have RT, isotope patterns, and MS/MS Data
- Information compared against reference info (if available)

Data Processing Workflow



1) Data Generation
2) Feature Finding
3) Formula Assignment
  3a) Structural Assignment
  3b) Structure Confirmation
4) Quantitation
  4a) Relative Quant
  4b) Absolute Quant

Building a Case for Identification

- Chemical knowledge can be used to validate IDs
- Relationships can be determined without complete assignment of chemical structure

Usual Suspects for Elevated Scrutiny

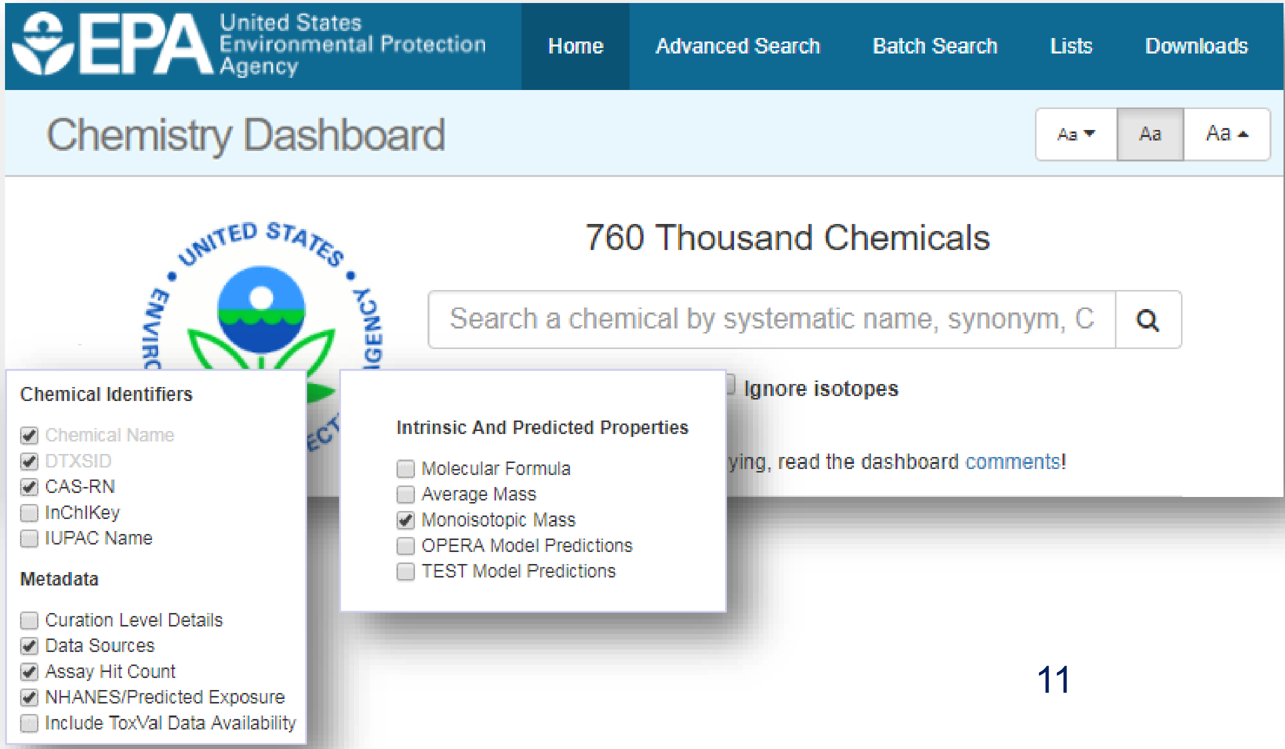
- Abundant peaks
- Contain halogens (F, Cl, Br)
- Negative mass defect
- Related to known chemicals or processes of interest

CompTox Chemicals Dashboard for Screening

- Search masses and formulas against chemical database
- Can suggest chemical class if not exact structure

- Confirmation of structure requires MS/MS or NMR follow-up

- Tox metadata can prioritize investigations



https://comptox.epa.gov/

McEachran et al *Analytical and Bioanalytical Chemistry* **2017,** *409* (7), 1729-1735.

CompTox Chemistry Dashboard Output

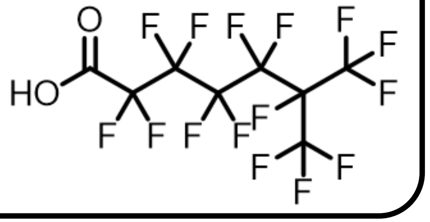
$C_8HF_{15}O_2$

Predicted molecular feature, neutral formula

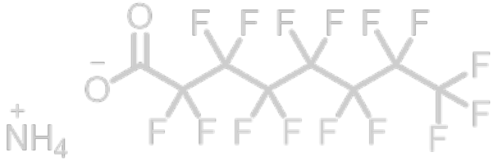
Two structures to one formula

PFOA, $C_8HF_{15}O_2$
Monoisotopic mass: 413.9737
DTXSID8031865

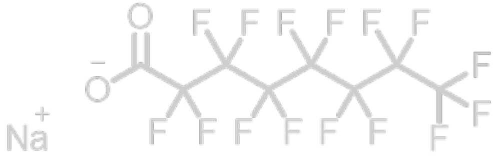
PFOA (isomer), $C_8HF_{15}O_2$
Monoisotopic mass: 413.9737
DTXSID50562865



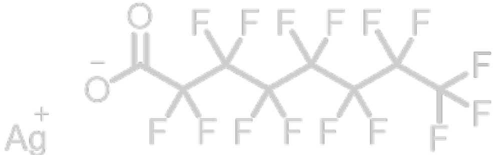
PFOA-NH_4^+, $C_8H_4F_{15}NO_2$
Monoisotopic mass: 431.0003
DTXSID8037708



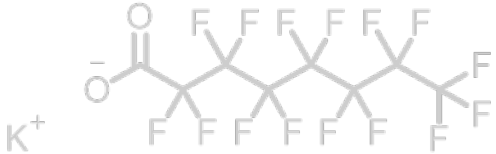
PFOA-Na^+, $C_8F_{15}NaO_2$
Monoisotopic mass: 435.9557
DTXSID40880025



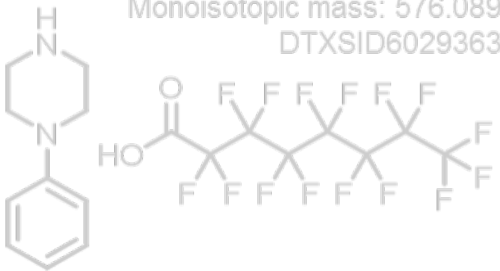
PFOA-Ag^+, $C_8AgF_{15}NO_2$
Monoisotopic mass: 519.8710
DTXSID00880127



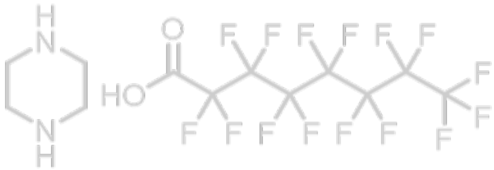
PFOA-K^+, $C_8F_{15}KO_2$
Monoisotopic mass: 451.9296
DTXSID00880026



PFOA-Ph-piperazine, $C_{18}H_{15}F_{15}N_2O_2$
Monoisotopic mass: 576.0894
DTXSID60293633



PFOA-piperazine, $C_{12}H_{11}F_{15}N_2O_2$
Monoisotopic mass: 500.0581
DTXSID50712909



PFOA-pyridine, $C_{13}H_6F_{15}NO_2$
Monoisotopic mass: 493.0159
DTXSID70562266

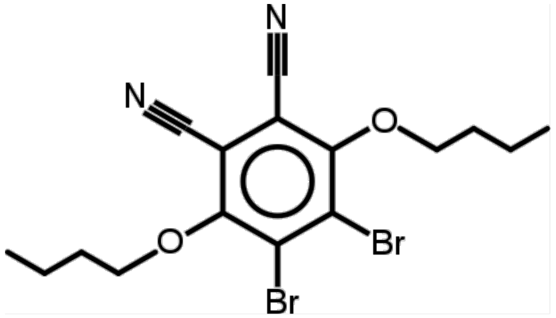
CompTox Chemistry Dashboard Output

427.97295

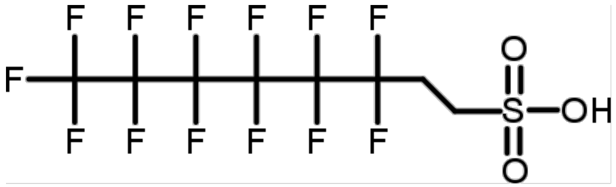
Mass with poor formula generation

Three formulas, Three structures

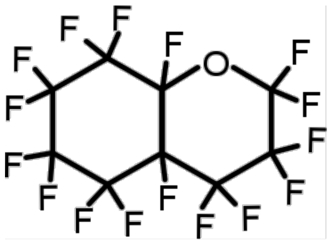
Confirmation relies on further experiments or standards



4,5-Dibromo-3,6-dibutoxybenzene-1,2-dicarbonitrile
$C_{16}H_{18}Br_2N_2O_2$ - Monoisotopic Mass: 427.973504
DTXSID70579319



6:2 Fluorotelomer sulfonic acid
$C_8H_5F_{13}O_3S$ - Monoisotopic Mass: 427.975181
DTXSID6067331



Hexadecafluorooctahydro-2H-1-benzopyran
$C_9F_{16}O$ - Monoisotopic Mass: 427.969365
DTXSID20823157

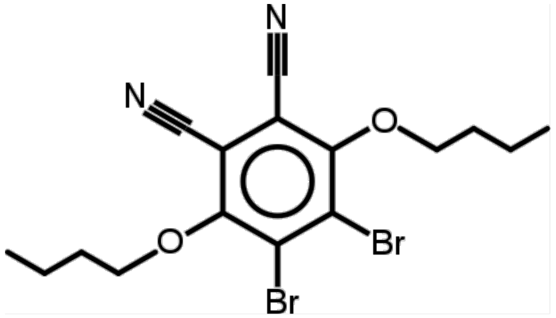
CompTox Chemistry Dashboard Output

427.97295

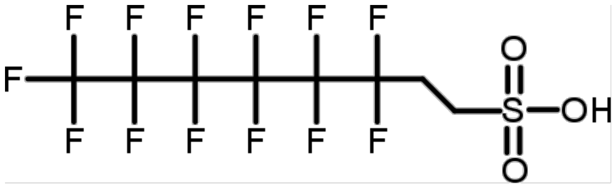
Mass with poor formula generation

Three formulas, Three structures

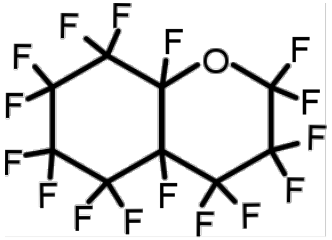
Confirmation relies on further experiments or standards



4,5-Dibromo-3,6-dibutoxybenzene-1,2-dicarbonitrile
$C_{16}H_{18}Br_2N_2O_2$ - Monoisotopic Mass: 427.973504
DTXSID70579319



6:2 Fluorotelomer sulfonic acid
$C_8H_5F_{13}O_3S$ - Monoisotopic Mass: 427.975181
DTXSID6067331

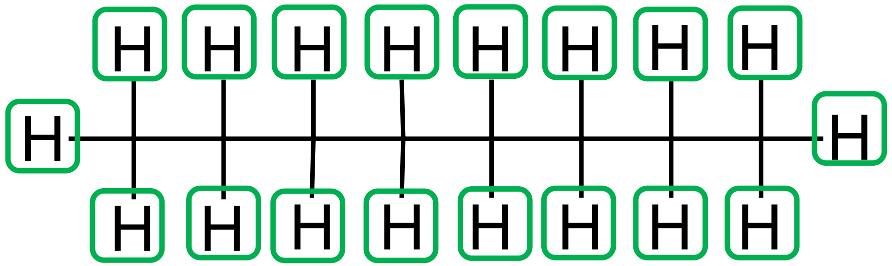


Hexadecafluorooctahydro-2H-1-benzopyran
$C_9F_{16}O$ - Monoisotopic Mass: 427.969365
DTXSID20823157

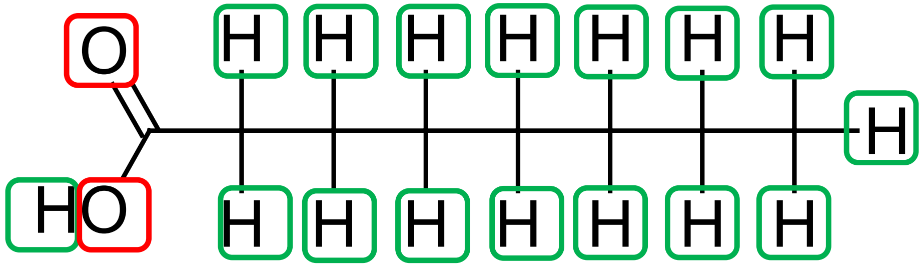
???

Unknown Compound
$C_8H_2O_4F_{14}$ - Monoisotopic Mass: 427.97295

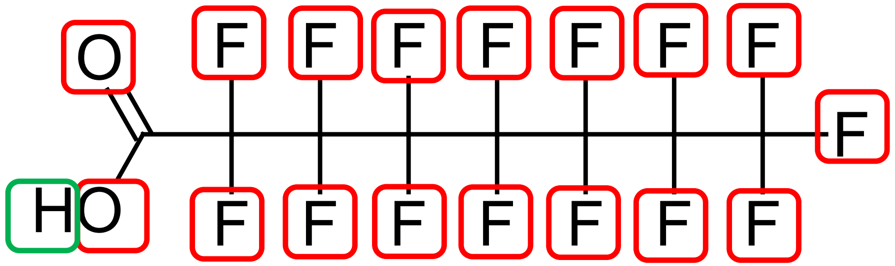
Mass Defect Signature



Octane
MI mass 114.**1409**

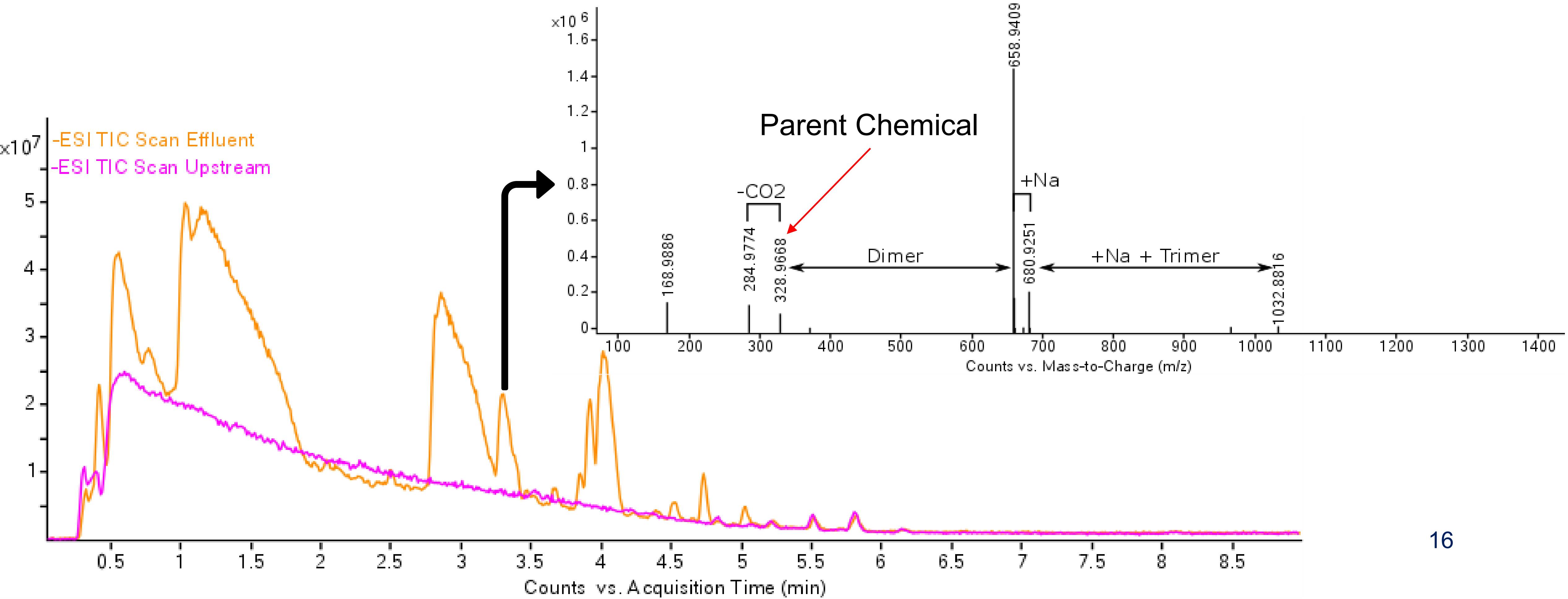


Octanoic Acid
MI mass 144.**1150**

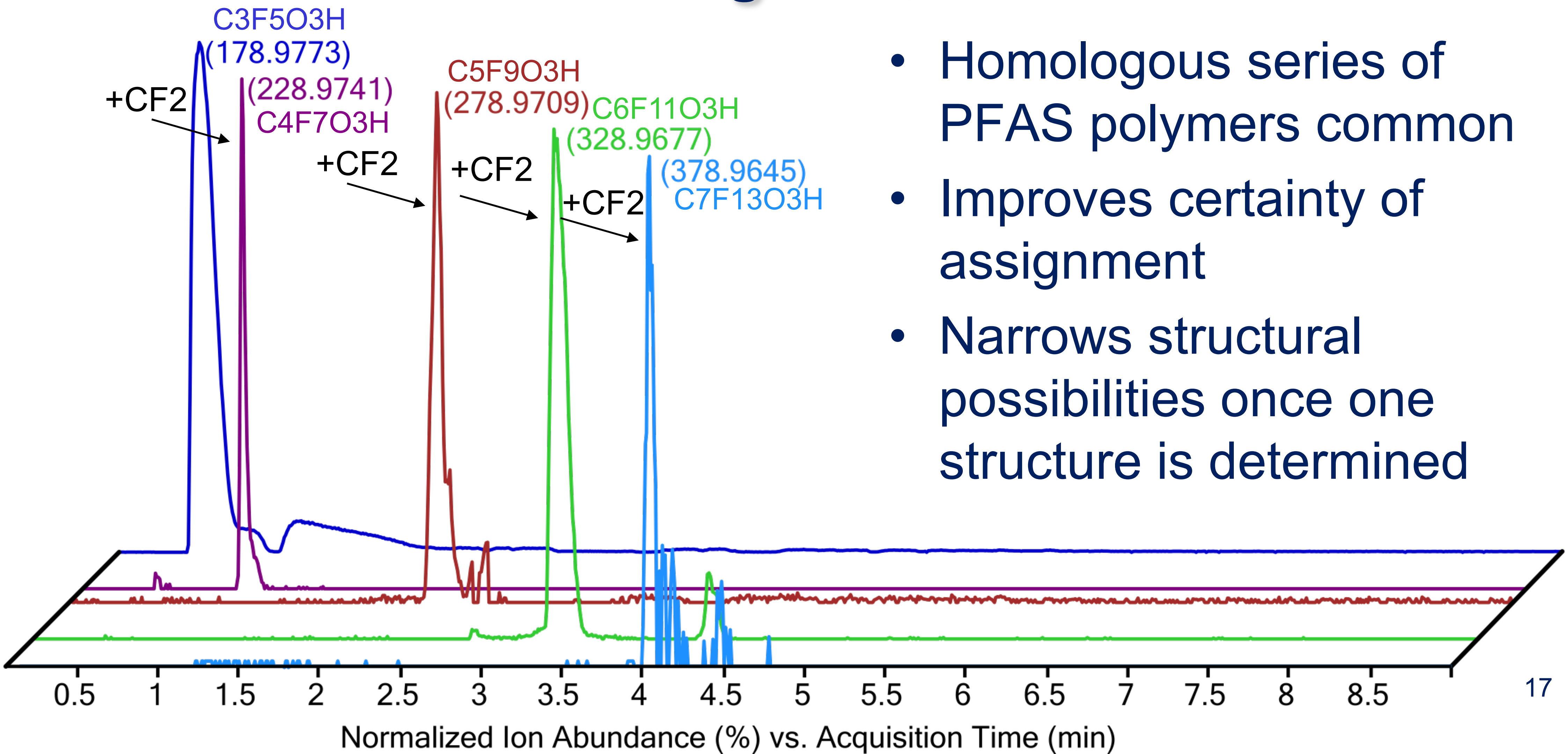


Perfluorooctanoic Acid
MI mass 413.**9737**

Chromatographic and MS Data

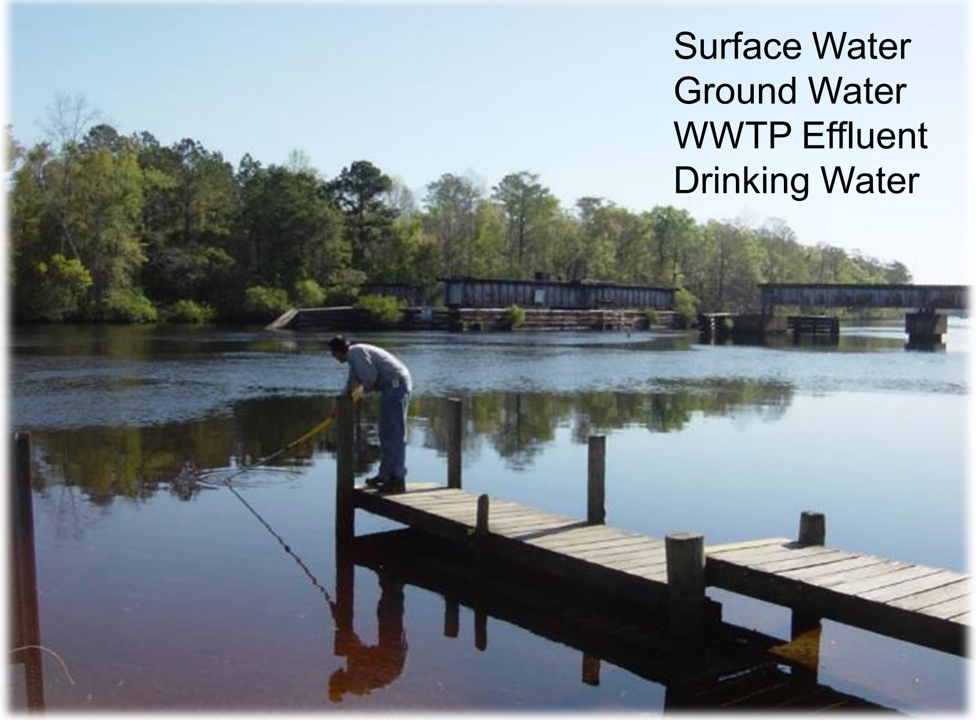


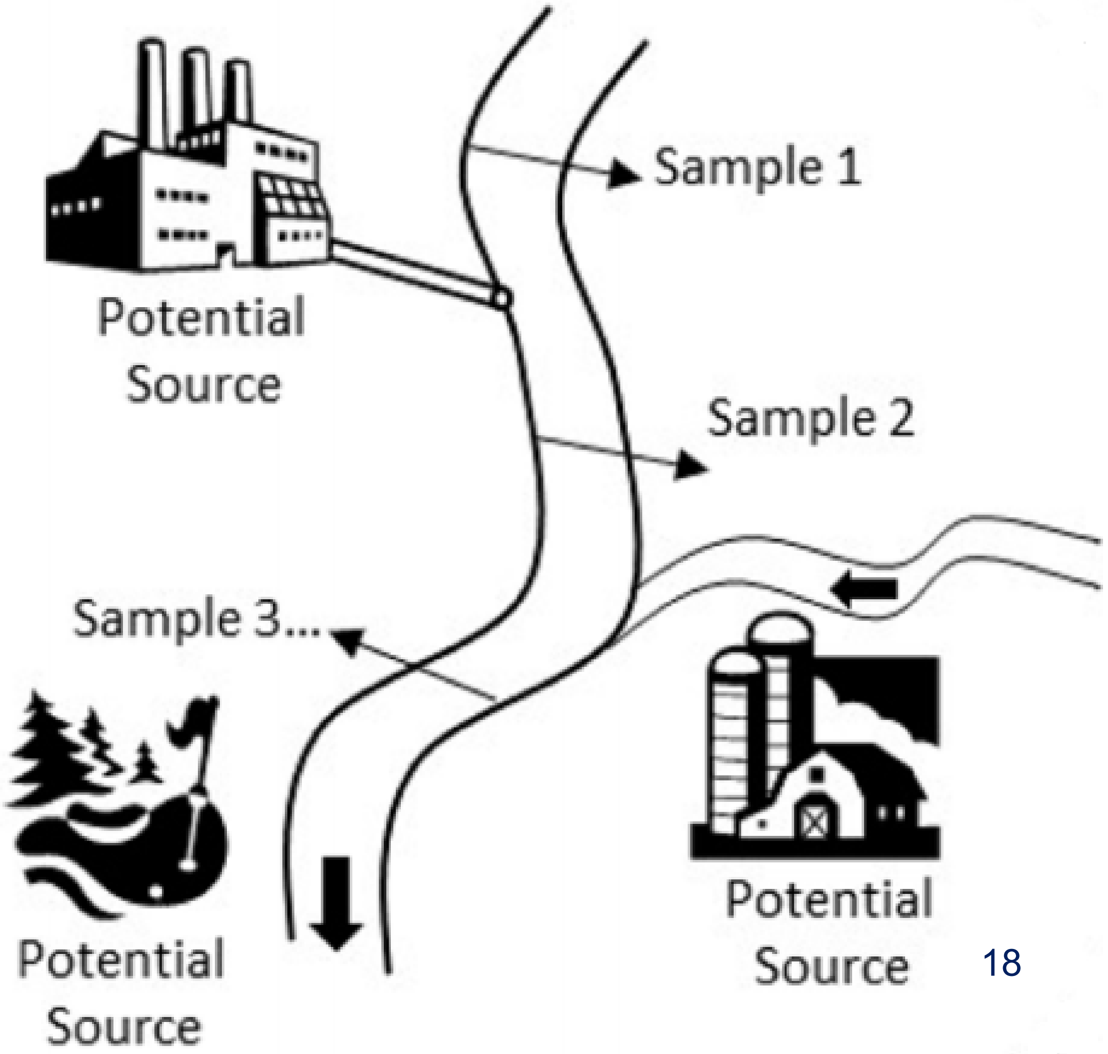
Homologous Series



- Homologous series of PFAS polymers common
- Improves certainty of assignment
- Narrows structural possibilities once one structure is determined

Source Examination by NTA





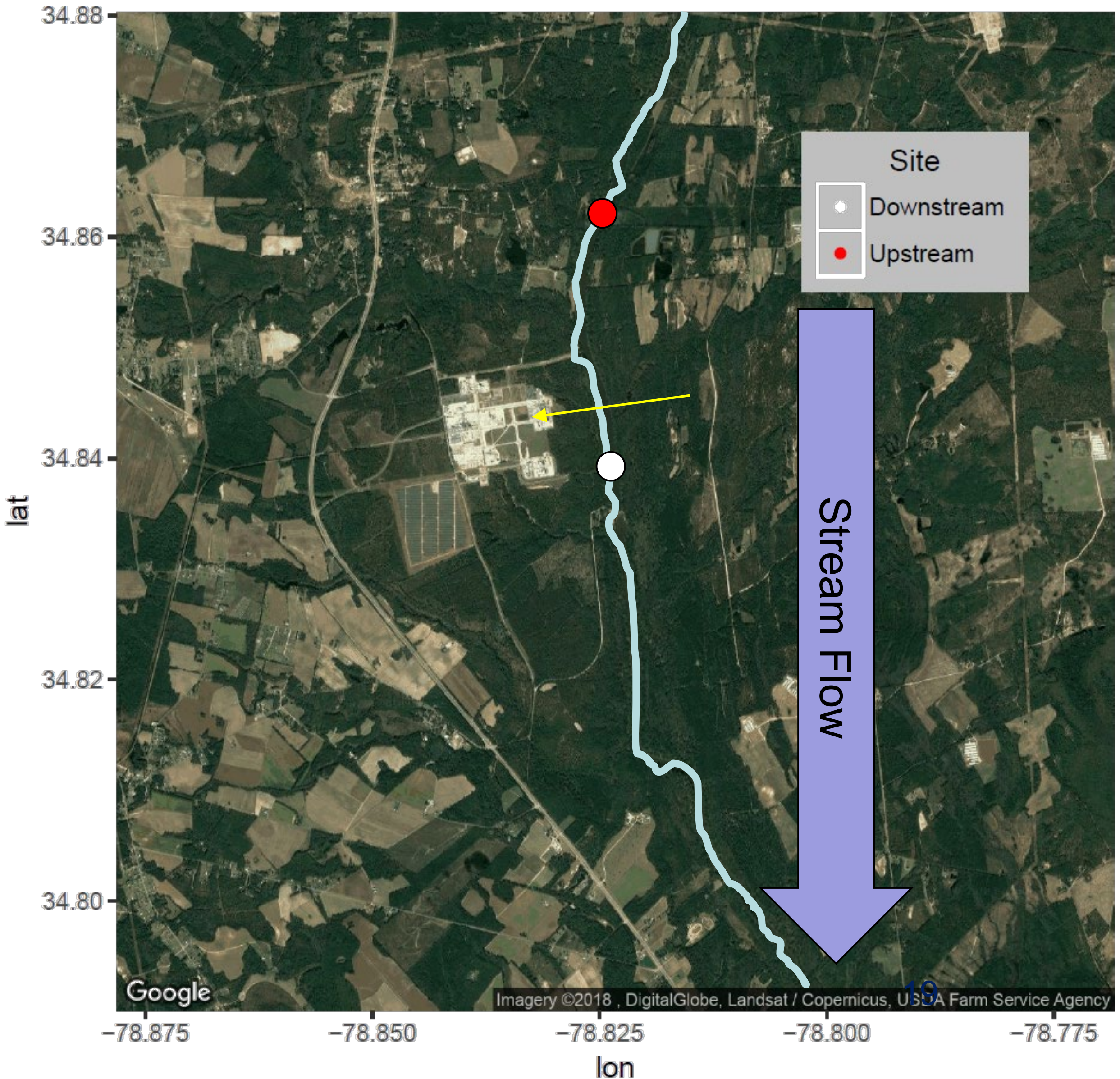
Sampling from geographically or temporally displaced locations allows triangulation of sourcing

Fluorochemical Plant

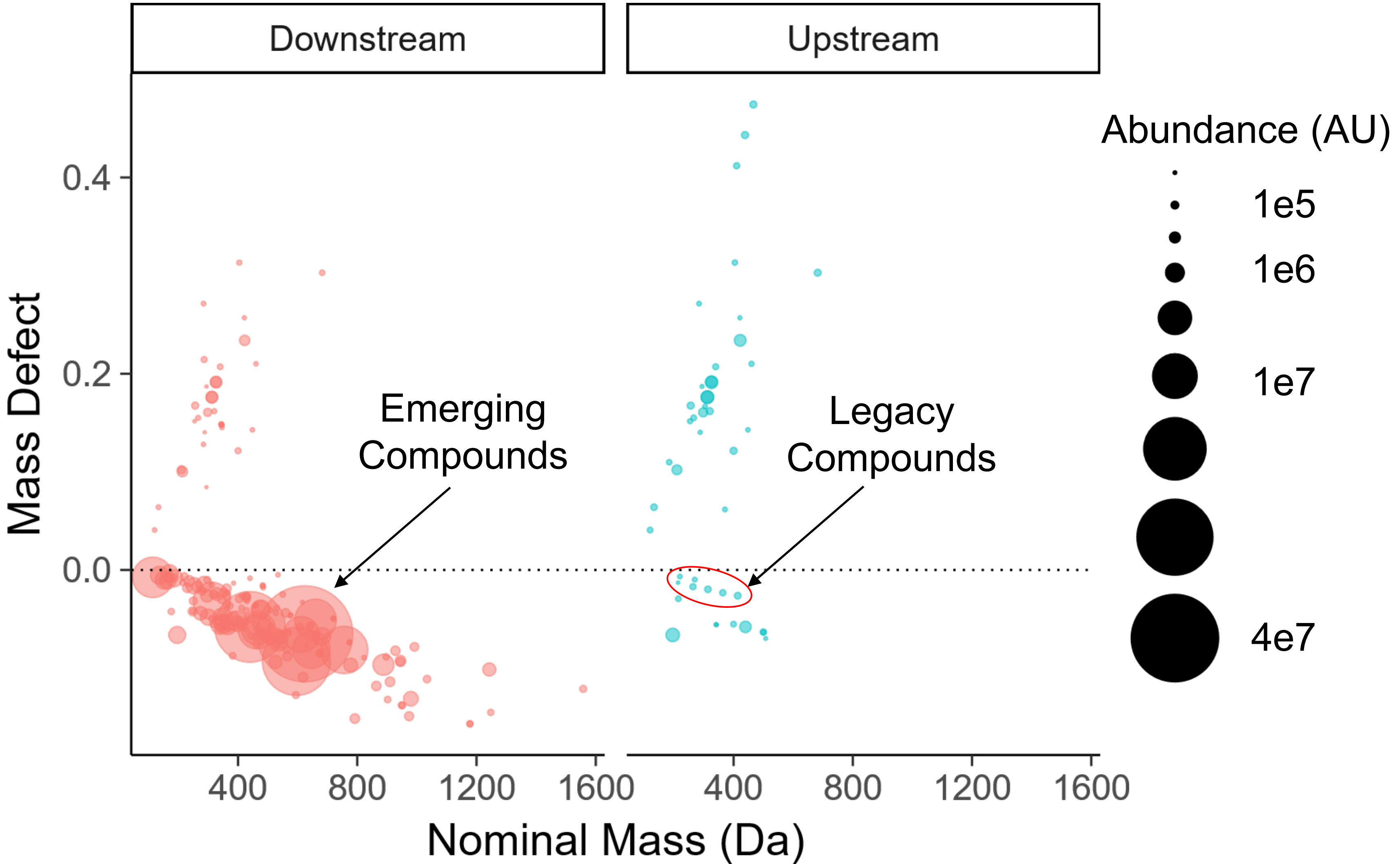
Multiple sampling events up and downstream from production facility. Earliest sampling 2011. Most recent 2018.

Targeted Analytes (2012)

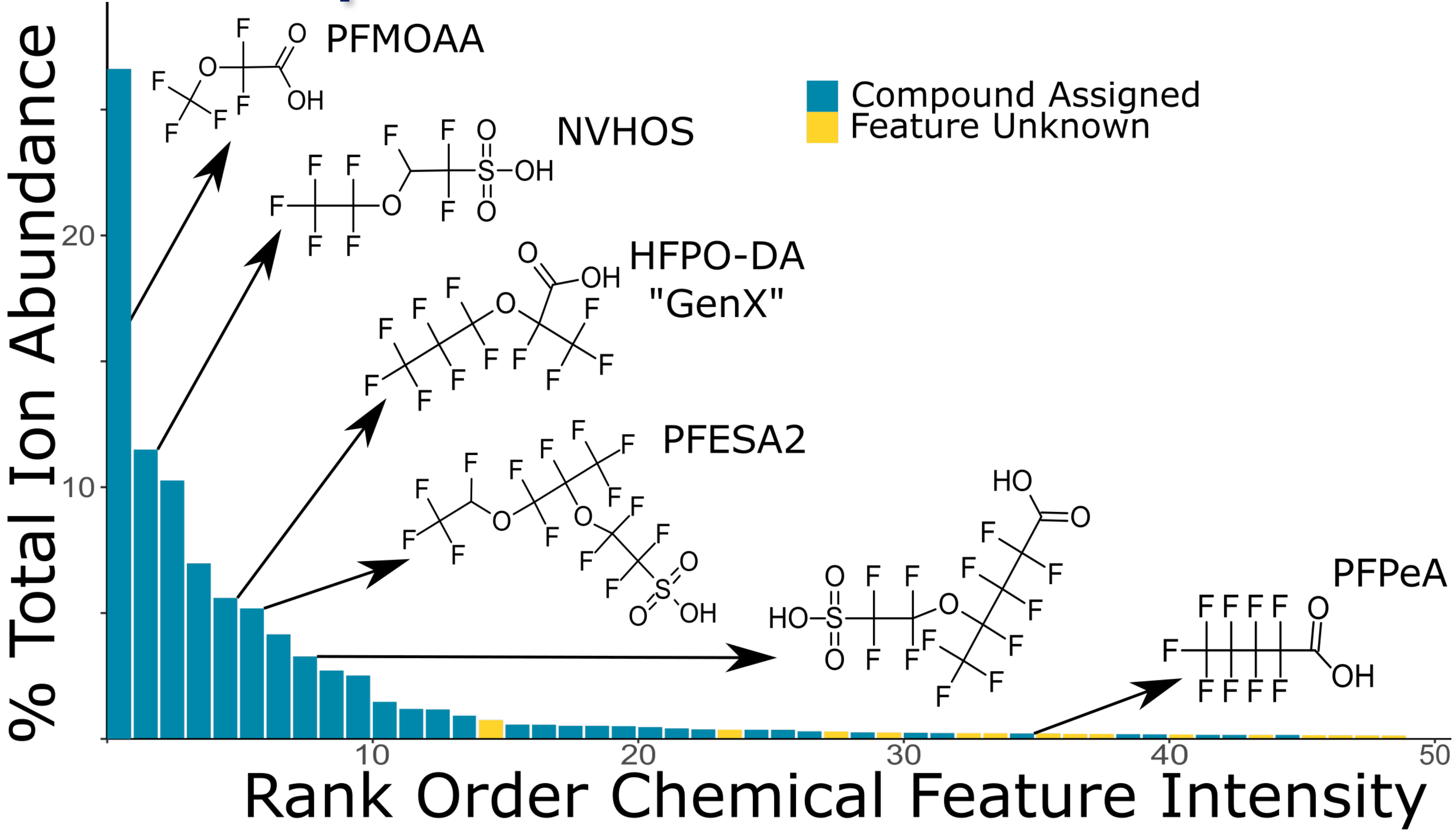
Analyte	Upstream (ng/L)	Downstream (ng/L)
C4	6	3761
C5	17	43590*
PFBS	4	3
C6	18	434
C7	14	3873
PFHxS	9	10
C8	33	71



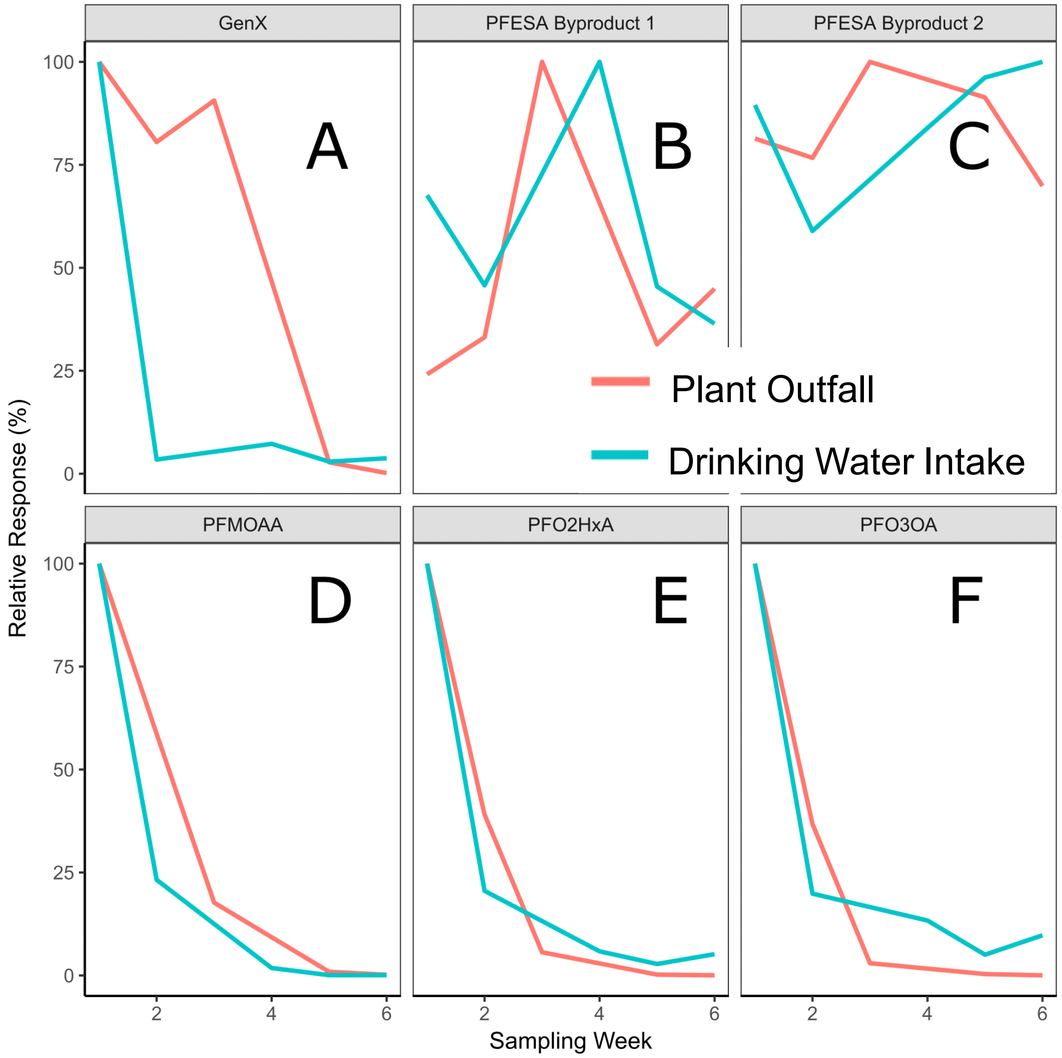
Feature Finding: Unique & Highly Different Features



Initial Comparative Abundance of Chemicals

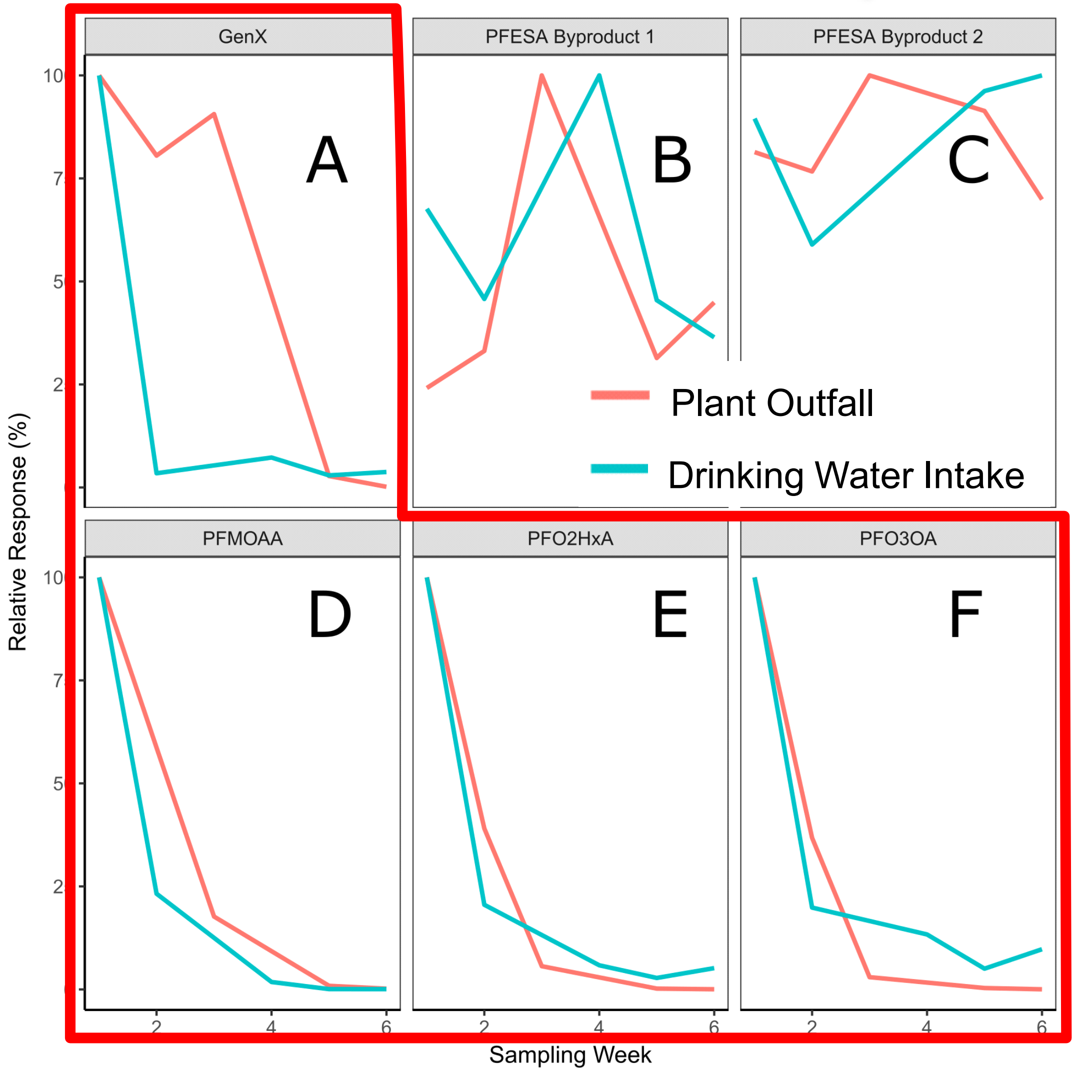


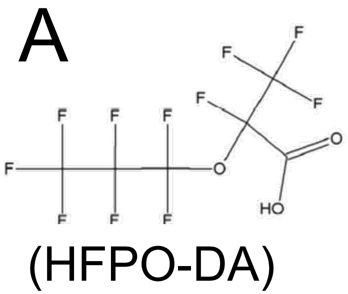
Relative Quantitation Time Trends



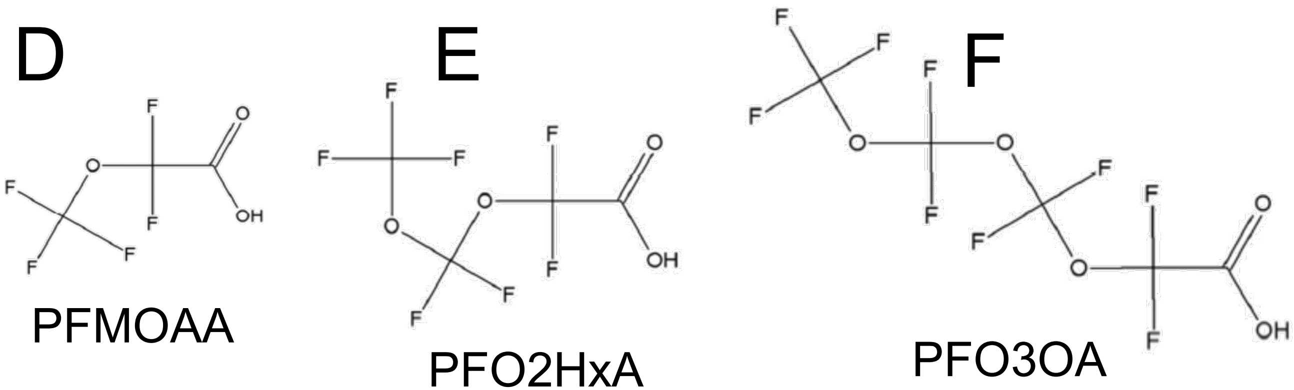
Consecutive sampling following sequestration of a polyvinylether production waste stream

Relative Quantitation Time Trends

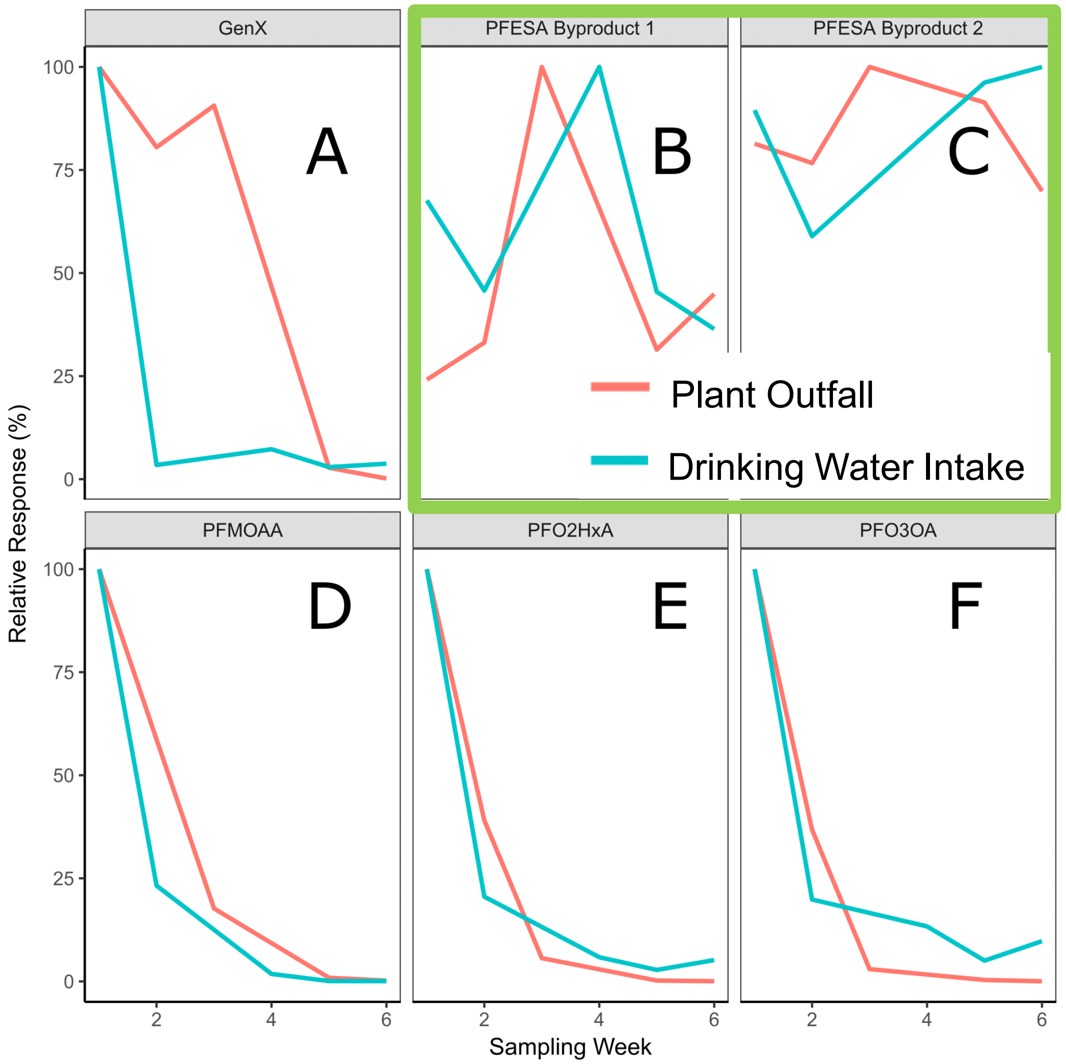




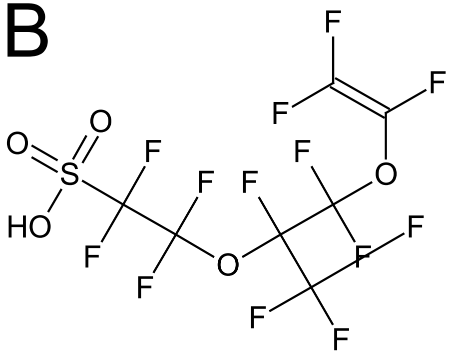
Six weeks following outfall shutoff
Relative abundance decreases over time



Relative Quantitation Time Trends

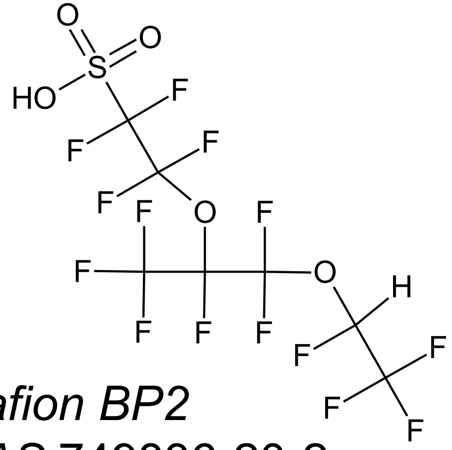


B



Nafion BP1
CAS 29311-67-9

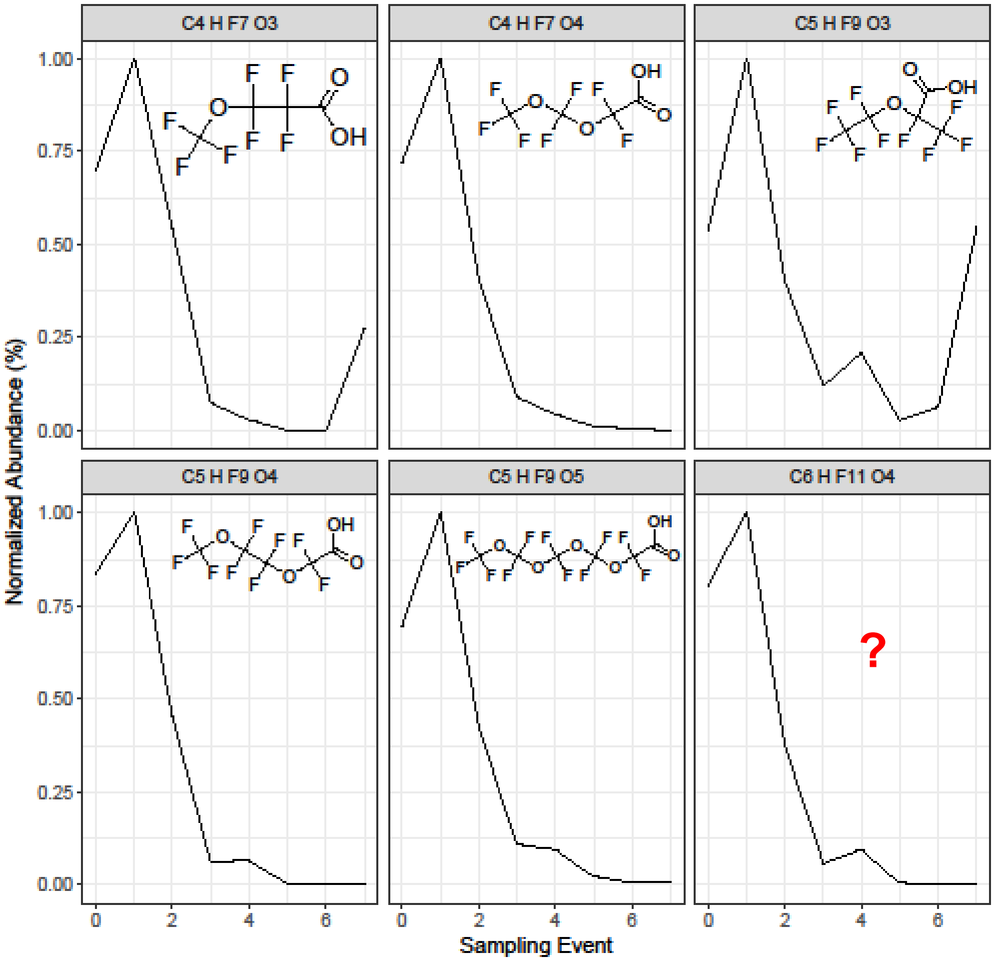
C

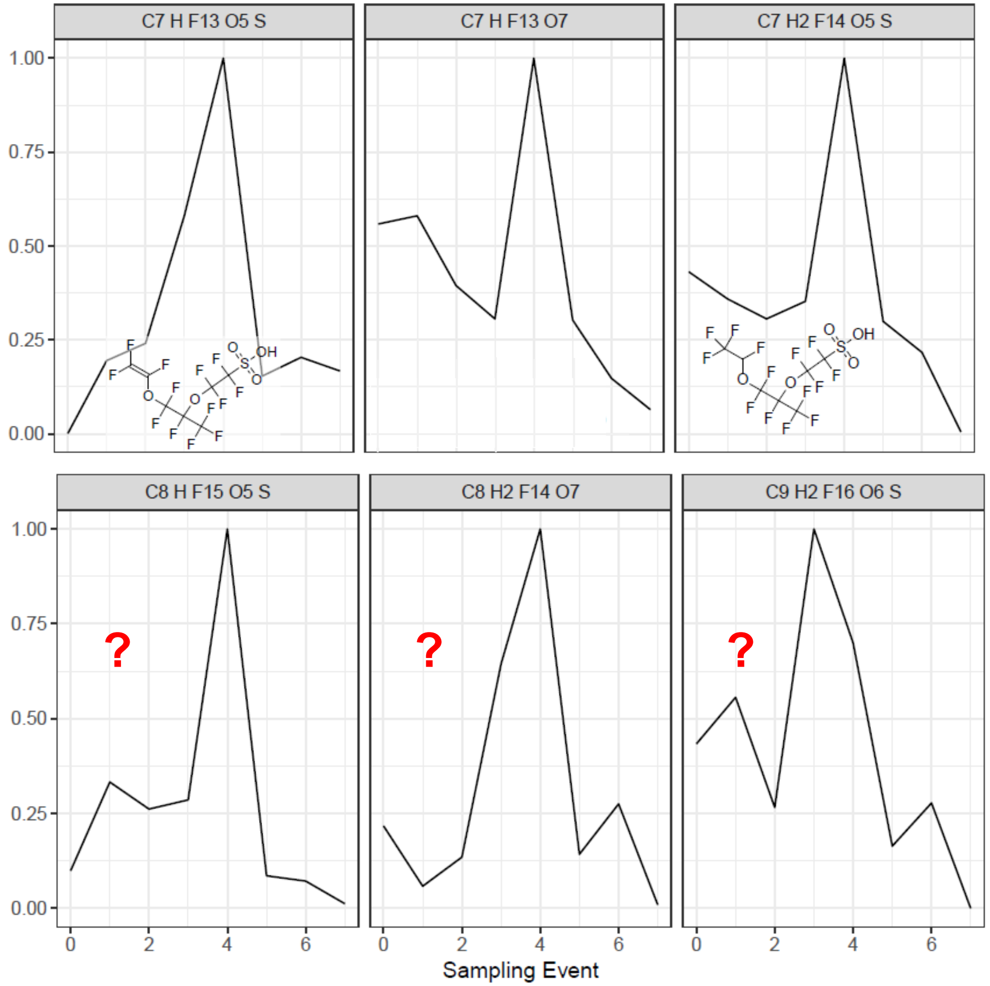


Nafion BP2
CAS 749836-20-2

Six weeks following outfall shutoff
Abundance fluctuates but does not decrease

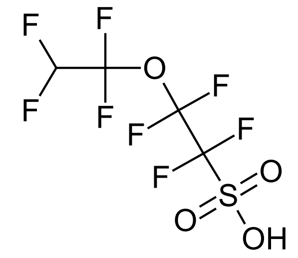
Finding Other Unknowns by Correlation





Retrospective Analysis

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	✗	✗	✗
	1-26-12	✓	✗	✗	✓	✓	✗	✗	✗
2012	2-1-12	✓	✗	✗	✓	✓	✗	✓	✗
	2-9-12	✓	✓	✓	✓	✓	✓	✗	✗
	5-4-12	✓	✗	✗	✓	✗	✗	✗	✗
	5-4-12	✓	✗	✗	[illegible]	[illegible]	✗	✗	✗
2014	11-24-14	✓	✗	✗	[illegible]	[illegible]	✗	✗	✗
2015	5-12-15	✓	✓	✓	[illegible]	[illegible]	✓	✓	✓
	5-12-15	✓	✓	✓	[illegible]	[illegible]	✓	✓	✓
	8-6-15	✓	✓	✓	[illegible]	[illegible]	✓	✓	✓
2017	5-12-17	✓	✗	✓	[illegible]	[illegible]	✓	✓	✓
	6-20-17	✓	✓	✓	[illegible]	[illegible]	✗	✓	✓
	6-27-17	✓	✓	✓	[illegible]	[illegible]	✗	✗	✗
	7-4-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-11-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-18-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-25-17	✓	✓	✓	✓	✓	✗	✗	✗
	8-3-17	✓	✓	✓	✓	✓	✗	✗	✗



Formula: $C_4H_2F_8O_4S$
[M-H]-: 296.9473 Da

NVHOS

Retrospective Analysis

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	✗	✗	✗
	1-26-12	✓	✗	✗	✓	✓	✗	✗	✗
2012	2-1-12	✓	✗	✗	✓	✓			
	2-9-12	✓	✓	✓	✓	✓			
	5-4-12	✓	✗	✗	✓	✗			
	5-4-12	✓	✗	✗	✗	✓			
2014	11-24-14	✓	✗	✗	✓	✗			
2015	5-12-15	✓	✓	✓	✓	✓			
	5-12-15	✓	✓	✓	✗	✓			
	8-6-15	✓	✓	✓	✗	✓			
2017	5-12-17	✓	✗	✓	✗	✓			
	6-20-17	✓	✓	✓	✓	✓			
	6-27-17	✓	✓	✓	✓	✓			
	7-4-17	✓	✓	✓	✓	✓			
	7-11-17	✓	✓	✓	✓	✓			
	7-18-17	✓	✓	✓	✓	✓			
	7-25-17	✓	✓	✓	✓	✓	✗	✗	✗
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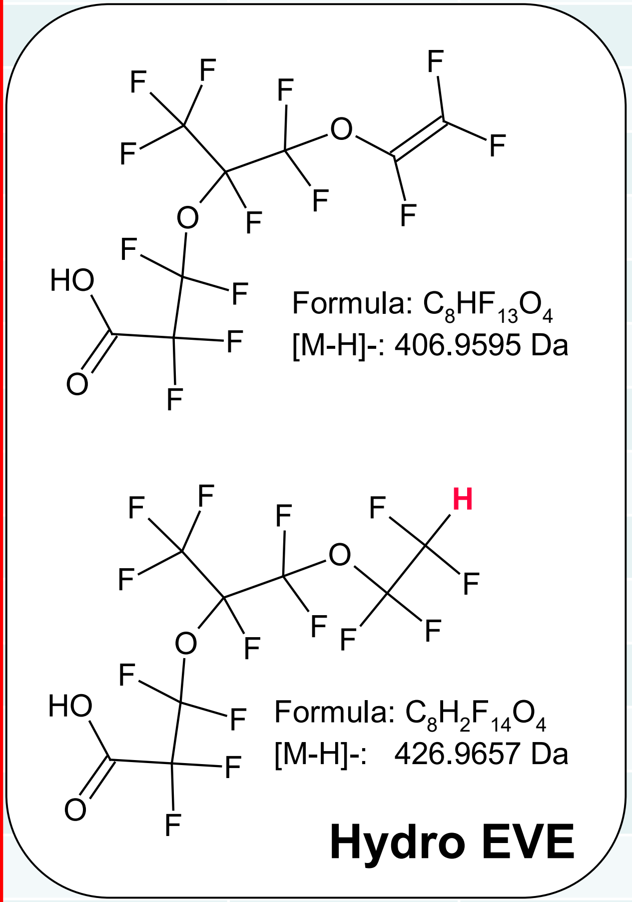

Retrospective Analysis

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	✗	✗	✗
	1-26-12	✓	✗	✗	✓	✓	✗	✗	✗
2012	2-1-12	✓	✗	[illegible]	[illegible]	[illegible]	✗	✓	✗
	2-9-12	✓	✓	[illegible]	[illegible]	[illegible]	✓	✗	✗
	5-4-12	✓	✗	[illegible]	[illegible]	[illegible]	✗	✗	✗
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2014	11-24-14	✓	✗	[illegible]	[illegible]	[illegible]	✗	✗	✗
2015	5-12-15	✓	✓	[illegible]	[illegible]	[illegible]	✓	✓	✓
	5-12-15	✓	✓	[illegible]	[illegible]	[illegible]	✓	✓	✓
	8-6-15	✓	✓	[illegible]	[illegible]	[illegible]	✓	✓	✓
2017	5-12-17	✓	✗	[illegible]	[illegible]	[illegible]	✓	✓	✓
	6-20-17	✓	✓	✓	✓	✓	✗	✓	✓
	6-27-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-4-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-11-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-18-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-25-17	✓	✓	✓	✓	✓	✗	✗	✗
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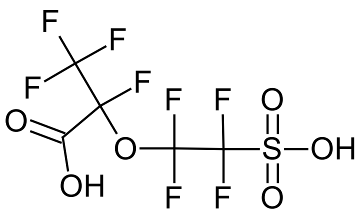

Formula: $C_5H_2F_8O_6S$
[M-H]-: 340.9372 Da

Acknowledgements:

- EPA
  - Mark Strynar
  - Andy Lindstrom
  - Seth Newton
  - John Washington
  - Nidal Azzam
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  - Antony Williams
  - Jon Sobus
  - Andrew McEachran
  - Johnsie Lang
  - Larry McMillan
- NC State
  - Detlef Knappe
  - Zack Hopkins
- UNC Charlotte
  - Mei Sun
- NC DEQ
  - Chris Johnson
  - Linda Culpepper
- Public Utilities
  - Michael Richardson and Ben Kearns (CFPUA)
  - Adam Pickett (Town of Pittsboro)
  - Chris Smith (Fayetteville Public Works Commission)

Questions?

Contact Information

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PFAS and Other Emerging Contaminants Conference

Raleigh, NC

Atmospheric deposition as a source of contamination at PFAS-impacted Sites

Presented by:

Stephen Zemba, Ph.D., P.E.

Sanborn Head and Associates, Inc.

and

Christopher D. Zevitas, Sc.D.

U.S. Department of Transportation

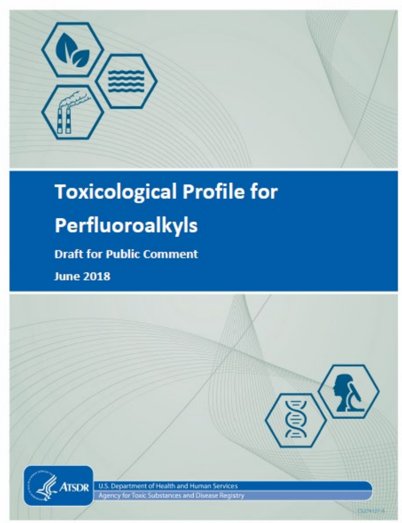
Volpe National Transportation Systems Center

April 23, 2019

PFAS Health Effects

- PFAS readily absorbed via inhalation or oral exposure and not metabolized in humans or laboratory animals
- Most epidemiological studies focus on PFOA and PFOS
- Provisional Minimum Risk Levels (MRLs) derived for PFOA, PFOS, PFHxS, and PFNA via oral exposure
- Inhalation data limited and considered inadequate for deriving MRLs

ATSDR
AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY



Source: ATSDR 2018

Observed Human Health Effects:

- ❑ Cancers (kidney, testicular)
- ❑ Pregnancy-induced hypertension/pre-eclampsia
- ❑ Liver damage
- ❑ Increases in serum lipids
- ❑ Thyroid disease
- ❑ Decreased antibody response to vaccines
- ❑ Asthma
- ❑ Decreased fertility
- ❑ Lower birth weight
- ❑ Osteoarthritis

PFAS Occurrence - Outdoor Air

- Elevated concentrations observed or expected in urban areas nearest to major emission sources:
  - Industrial facilities producing or using PFAS
  - Areas where Class B firefighting foams used
  - Landfills and wastewater treatment plants
  - Biosolids production and application
- PFOA and PFOS in air typically fall within a range of about 1-20 pg/m^3 (although concentrations as high as 900,000 pg/m^3 observed near large manufacturers)
- Concentrations of volatile PFAS such as FTOHs can be in the hundreds of pg/m^3 in outdoor air

Sources: Ge et al. 2017; Bossi et al. 2016; Lai et al. 2016; Liu et al. 2015; Wang et al. 2015; Ahrens et al. 2011; Cai et al 2012; Goosey and Harrad 2012; Shoeib et al. 2011; Dreyer et al. 2010; Shoeib et al. 2010; Dreyer et al. 2009; Suja et al. 2009; Loewen et al. 2008; Barton et al. 2007; Jahnke et al. 2007; Kim and Kannan 2007; Piekarz et al. 2007; Barton et al. 2006; Shoeib et al. 2004; Stock et al. 2004.

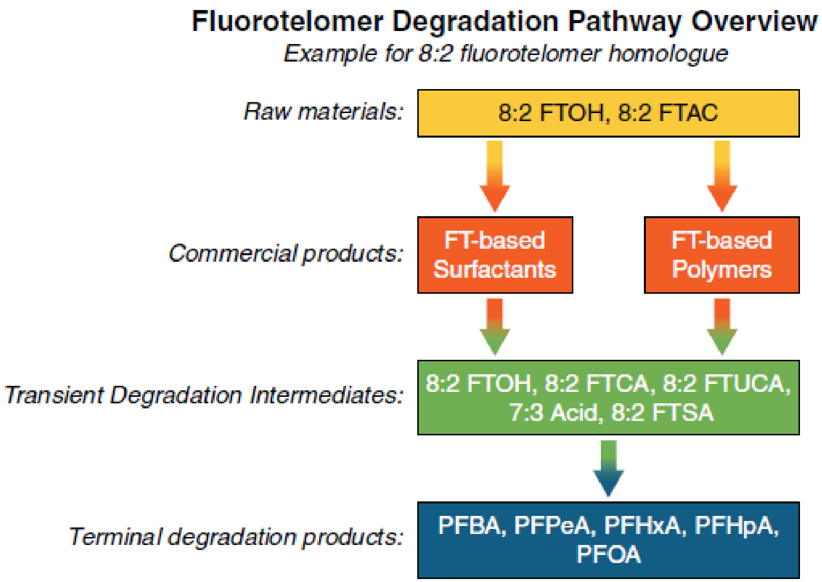
PFAS Species in Outdoor Air

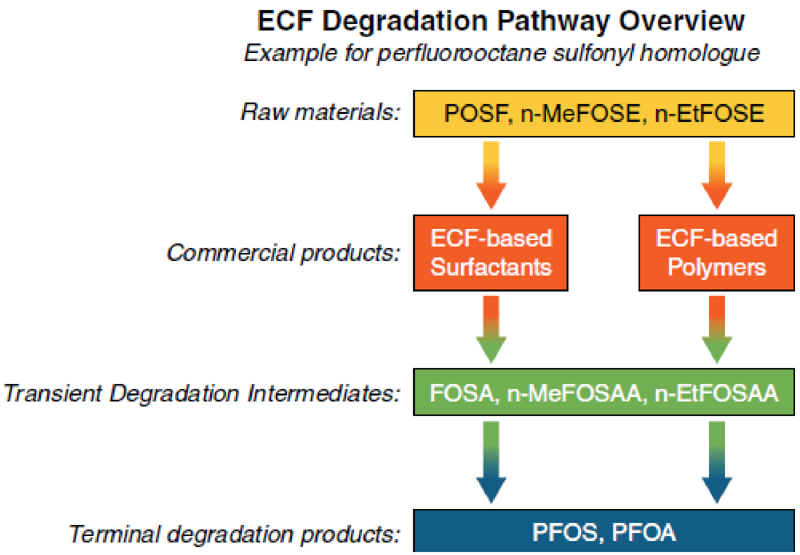
- Wide range of PFAS observed in ambient air, examples include:
  - Perfluoroalkyl acids (PFAAs)
  - Perfluoroalkane sulfonamides (FASAs)
  - Fluorotelomer alcohols (FTOHs)
  - Fluorotelomer carboxylic acids (FTCAs)
  - Perfluoroalkane sulfamido ethanols (FASEs)
- Certain classes of PFAS are volatile or semivolatile and can travel long distances
- Some termed “precursors” can degrade into “terminal degradation products” (PFOA, PFOS, and other PFAAs)

Classification	Examples	Uses
PFAAs	PFOA PFOS PFBA PFHxS PFPeA PFHxA PFHpA PFNA	Surfactants
FASAs	EtFOSA MeFOSA	Intermediate environmental transformation products
FTOHs	6:2 FTOH 8:2 FTOH 10:2 FTOH	Raw material for surfactant and surface protection
FTCAs	8:2 FTCA	Intermediate environmental transformation product
FASEs	EtFOSE MeFOSE	Raw material for surfactant and surface protection

Sources: ITRC 2018; Ge et al. 2017; Bossi et al. 2016; Lai et al. 2016; Liu et al. 2015; Wang et al. 2015; Ahrens et al. 2011; Buck et al. 2011; Cai et al 2012; Goosey and Harrad 2012; Shoeib et al. 2011; Dreyer et al. 2010; Shoeib et al. 2010; Dreyer et al. 2009; Suja et al. 2009; Loewen et al. 2008; Barton et al. 2007; Jahnke et al. 2007; Kim and Kannan 2007; Piekarz et al. 2007; Barton et al. 2006; Shoeib et al. 2004; Stock et al. 2004.

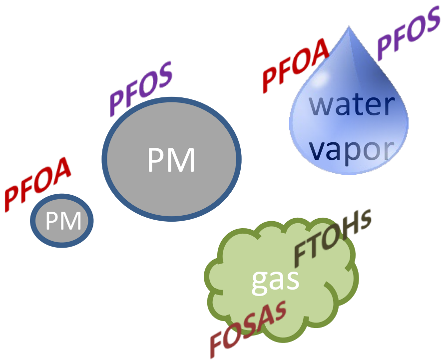
Precursor Degradation Pathways





Sources: ITRC 2018; Buck et al. 2011

Distribution of PFAS in Air



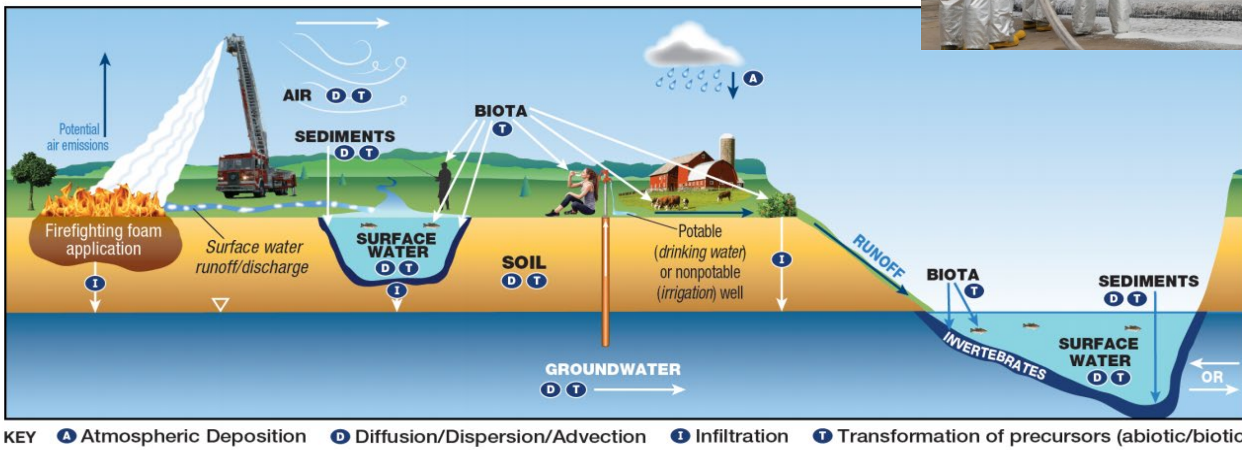
- PFAS occur in gas and particle phases or other aerosols suspended in air (e.g., water vapor)
- Neutral PFAS such as FTOHs often the most dominant PFAS in the gas phase in urban areas, over open ocean, and in remote regions
- Ionic PFAS such as PFOA and PFOS (with low vapor pressure, high solubility) tend to be dominant species in airborne particulate matter
- PFOA associated with smaller, ultrafine particles, while PFOS associated with larger, coarser fractions
- PFAS also found in rainwater and marine aerosols (sea spray)

Sources: Ge et al. 2017; Bossi et al. 2016; Lai et al. 2016; Wang et al. 2015; Ahrens et al. 2012; Dreyer et al. 2009

Conceptual Site Models

Considering air emissions when conducting a site investigation

FIRE TRAINING



INDUSTRIAL

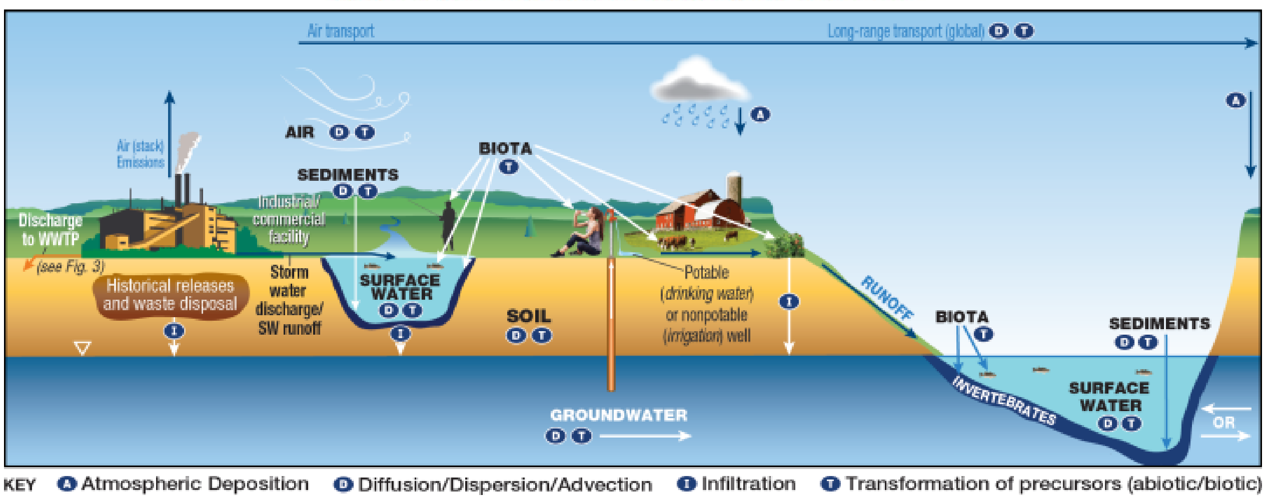


Figure 2. Conceptual site model for industrial sites.

Sources: MADEP 2018; ITRC 2018 (L. Trozzolo)

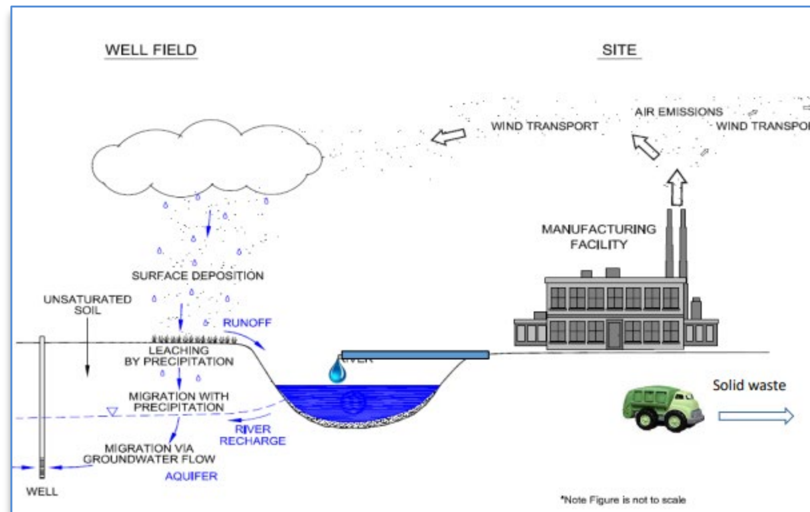
Where to Look for PFAS (MADEP Guidance):

- PFAS manufacturers
- Landfills
- Former and current DoD sites
- Airport hangars, rail yards, petrochemical sites
- Firefighting, training, and equipment areas
- Crash sites (air, rail, motor vehicle)
- Metal coating and plating

Fate and Transport of PFAS in Air

SHORT-RANGE ATMOSPHERIC TRANSPORT

- PFAS commonly found in precipitation (rain and snow)
- Wet and dry deposition major removal mechanisms from atmosphere, on a timescale of a few days
- Short-range atmospheric transport can result in contamination to terrestrial and aquatic systems near emission sources with multi-media impacts
- Evidence of releases observed miles from source where hydrologic transport unlikely

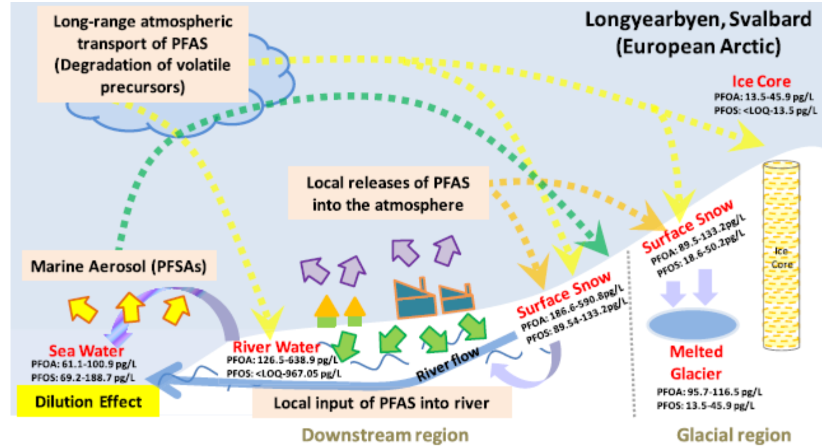


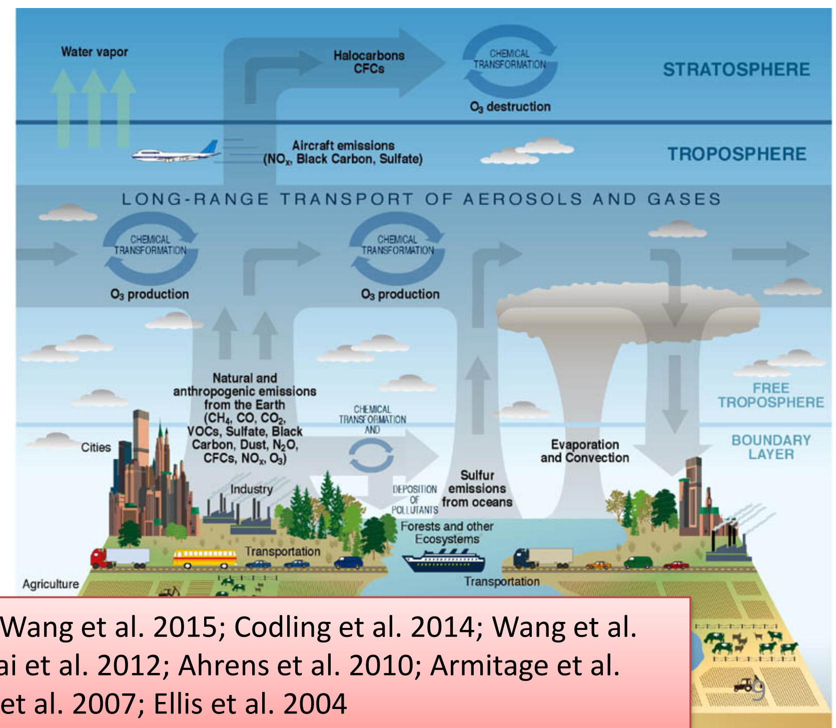
Sources: Liu et al. 2017; NHDES 2017; Chen et al. 2016; NYDOH 2016; Lin et a. 2014; Post 2013; Taniyasu et al. 2013; Zhao et al. 2013; Post 2012; Dryer et al. 2010; Kwok et al. 2010; Frisbee et al. 2009; Barton et al. 2007; Davis et al. 2007; Kim and Kannan 2007; Hurley et al. 2004

Fate and Transport of PFAS in Air

LONG-RANGE ATMOSPHERIC TRANSPORT (LRT)

- LRT responsible for wide distribution of PFAS across earth as evidenced by occurrence in biota, surface snow, ice cores, seawater, and other media as far as the Arctic and Antarctic
- Distribution to remote regions believed to occur from:
  - LRT and subsequent degradation of precursors
  - Transport via ocean currents and release into air as marine aerosols
- Processes and effects similar to atmospheric transport of other recalcitrant compounds





Sources: Bossi et al. 2016; Kirchgeorg et al. 2016; Rankin et al. 2016; Wang et al. 2015; Codling et al. 2014; Wang et al. 2014; Kirchgeorg et al. 2013; Kwok et al. 2013; Benskin et al. 2012; Cai et al. 2012; Ahrens et al. 2010; Armitage et al. 2009; Dasilva et al. 2009; Dryer et al. 2009; Young et al. 2007; Wania et al. 2007; Ellis et al. 2004

PFAS Occurrence - Indoor Air

- PFAS can also be present in indoor air
- Indoor concentrations can be higher than outdoors due to the presence of indoor sources
- Most exposures may occur indoors where we spend ~ 90% of our time
- PFAS in indoor air reported in the range of about 1-440 pg/m^3 for PFOA and PFOS
- Volatile PFAS such as FTOHs have been observed on the order of 10,000-50,000 pg/m^3 in schools, homes, and offices and in excess of 300,000 pg/m^3 in commercial buildings

Indoor PFAS Sources:

- **Stain resistant coatings used on carpets and upholstery**
- **Water resistant clothing**
- **Grease-resistant paper**
- **Food packaging**
- **Nonstick cookware**
- **Cleaning products**
- **Personal care products**
- **Cosmetics**
- **Paints, varnishes, and sealants**

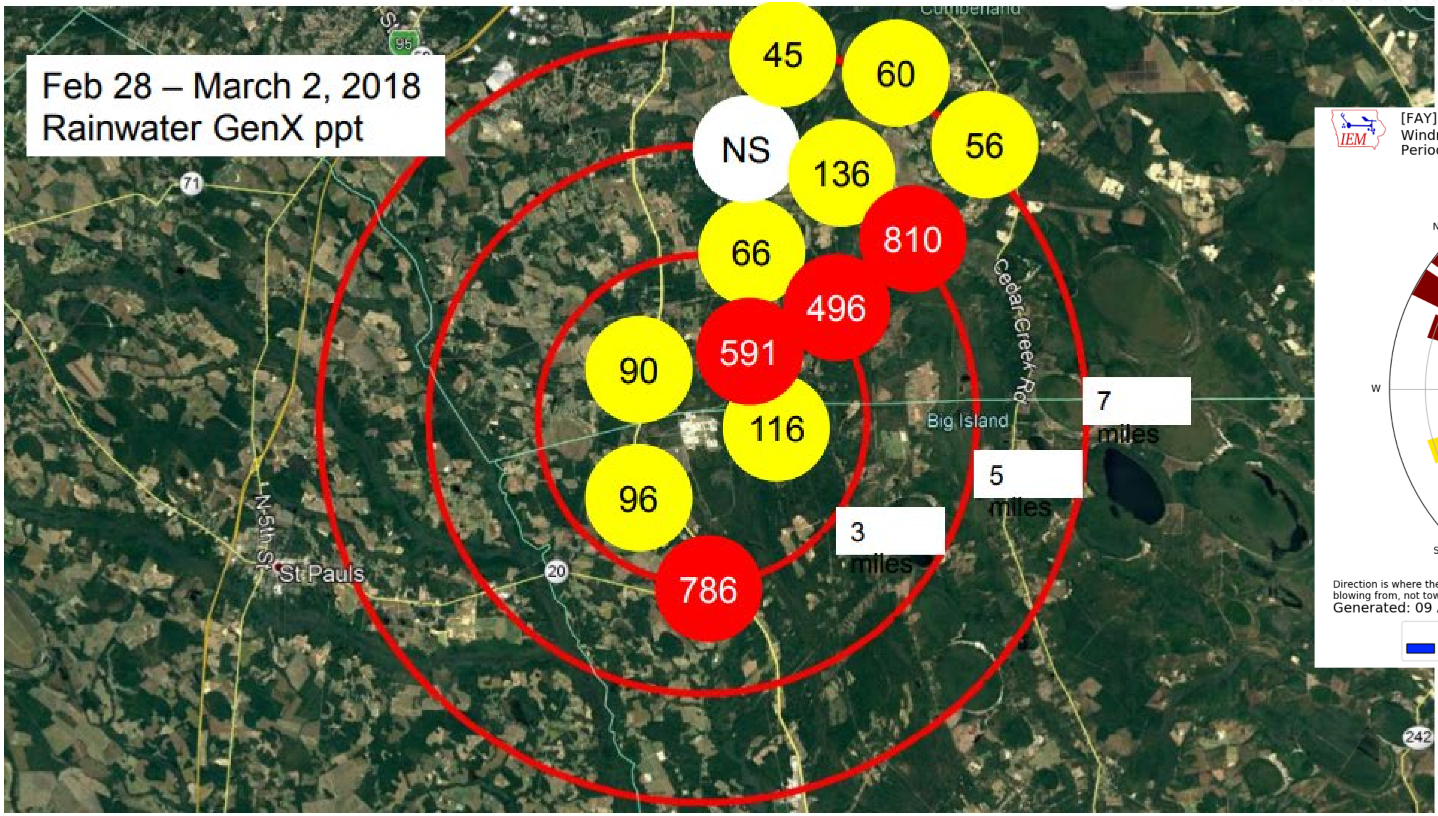
Sources: ATSDR 2016; Fromme et al. 2015; Liu et al. 2015; Liu et al. 2014; Fraser et al. 2012; Goosey and Harrad 2012; Shoeib et al. 2011; Fromme et al. 2010; Kaiser et al. 2010; Langer et al. 2010; Gewurtz et al. 2009; Guo et al. 2009; Strynar and Lindstrom 2008; Shoeib et al. 2004

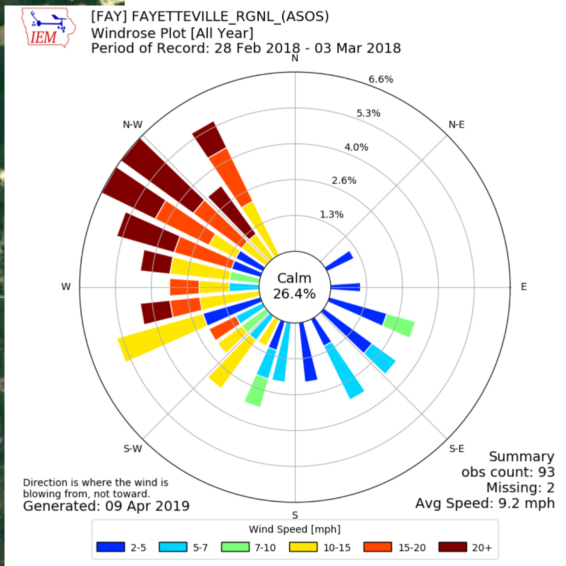
Atmospheric Deposition of PFAS

NCDEQ & NCDHHS Report on GenX

"Measured air emissions of the GenX from some processes at the Chemours/DuPont plant are higher than previously understood or reported. GenX has also been measured in rainwater as far as 20 miles downwind of the facility, indicating atmospheric transport and deposition of this compound."

Evidence of GenX Deposition

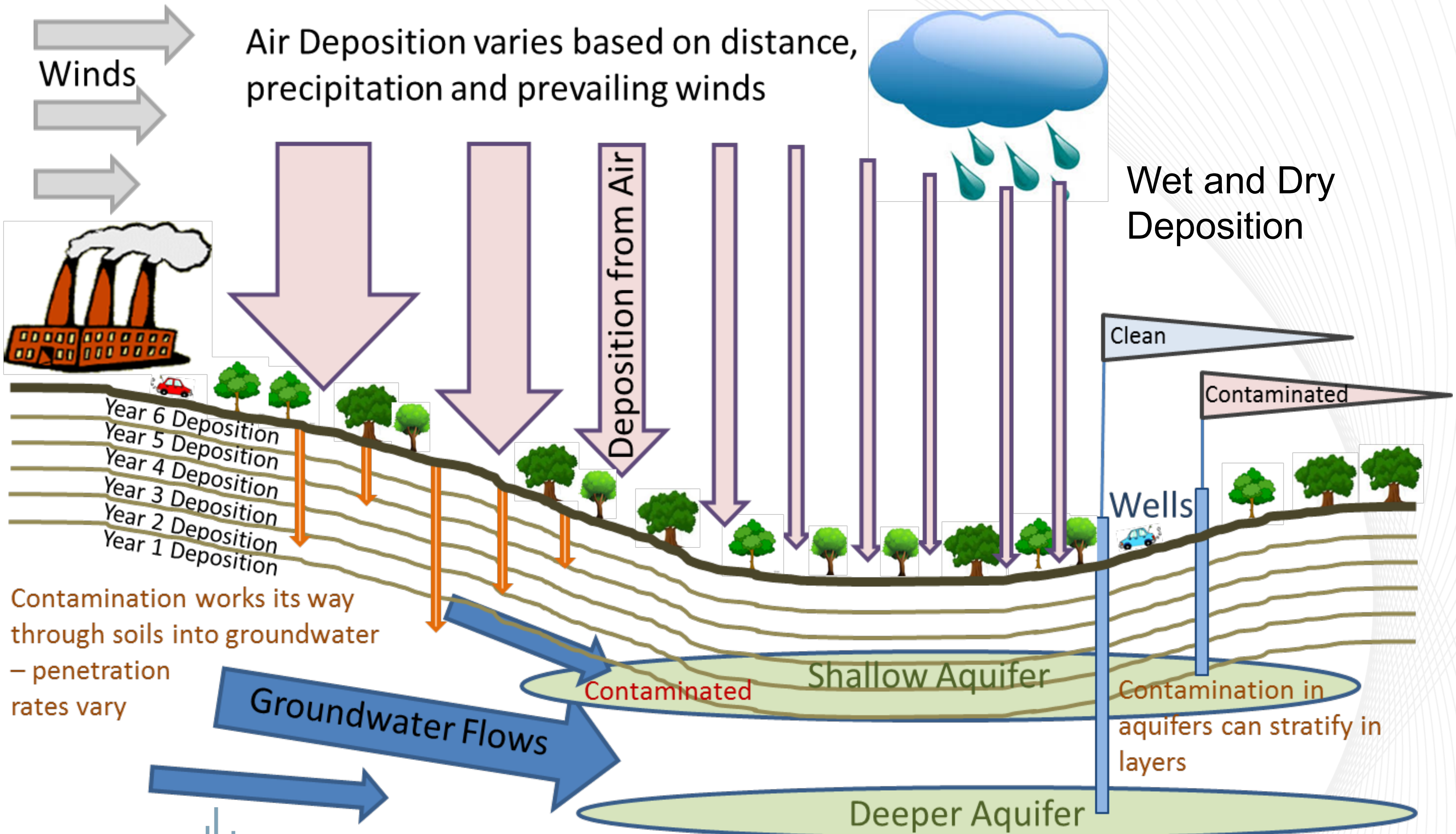




NORTH CAROLINA DEQ Department of Environmental Quality

SANBORN HEAD

Atmospheric Deposition of Contaminants

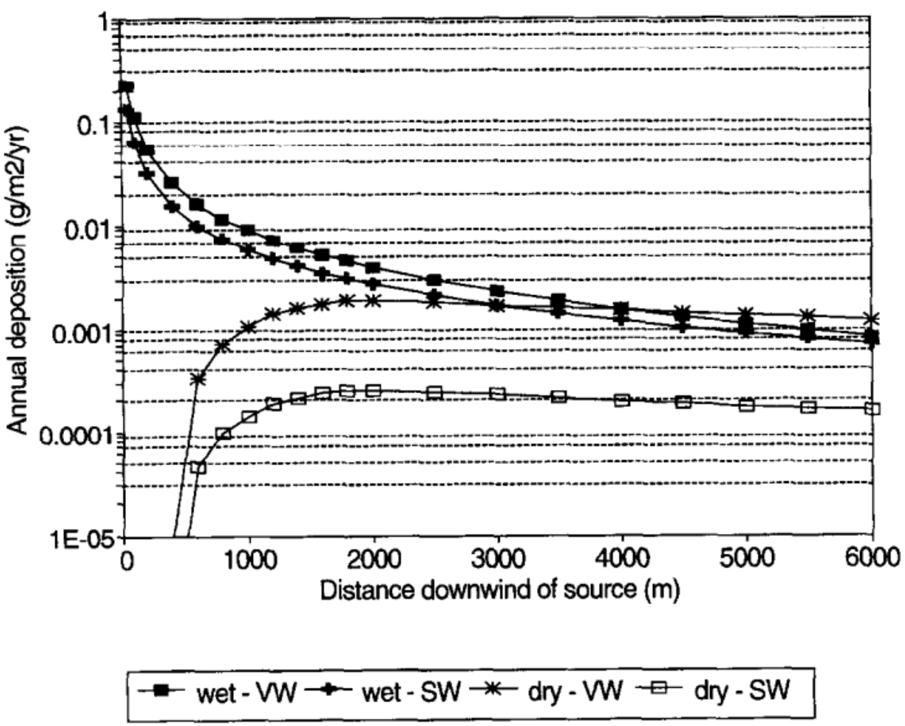


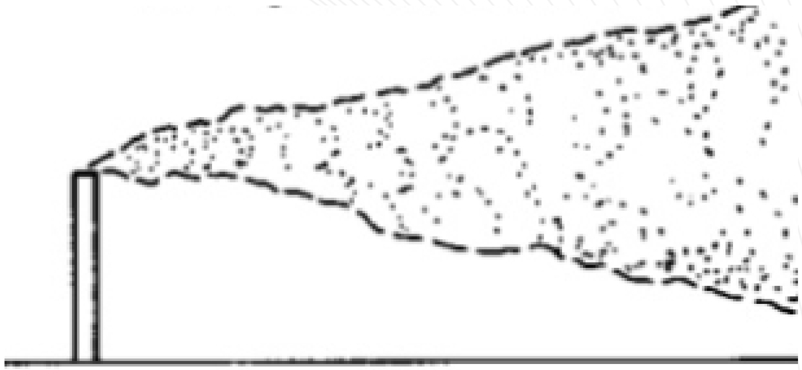
SANBORN HEAD

Courtesy of NH Department of Environmental Services

Deposition Factors/Considerations

S.G. Zemba et al. / Journal of Hazardous Materials 47 (1996) 229–275

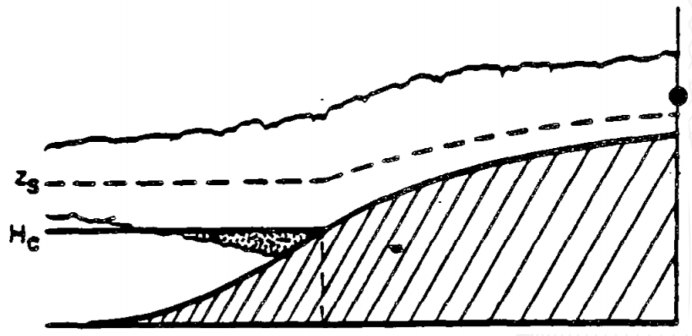




- Dry *v.* Wet
- Dry “Donut Hole”

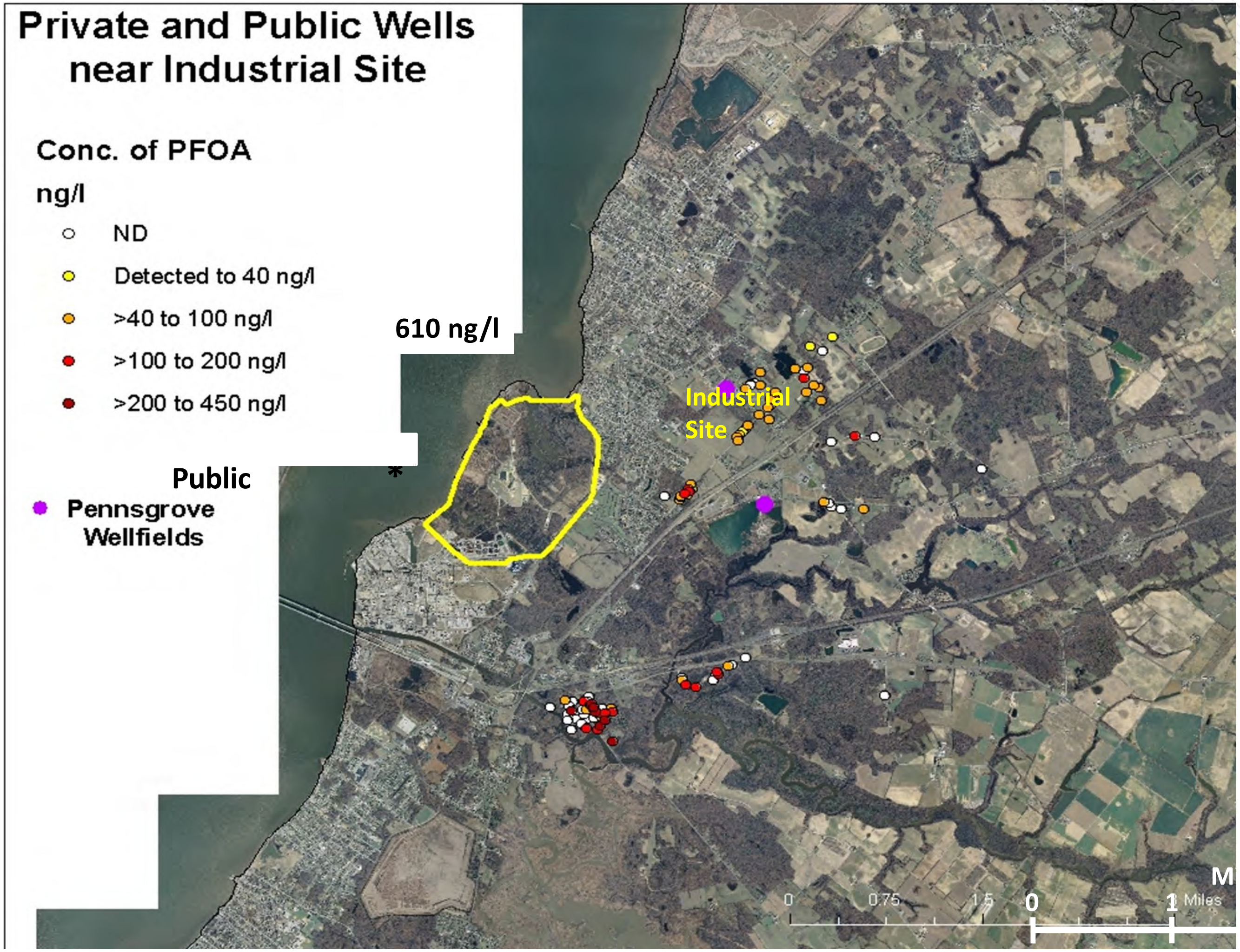
Plume

Impaction



SANBORN | HEAD

PFAS Airborne Transport Found Near NJ Facility

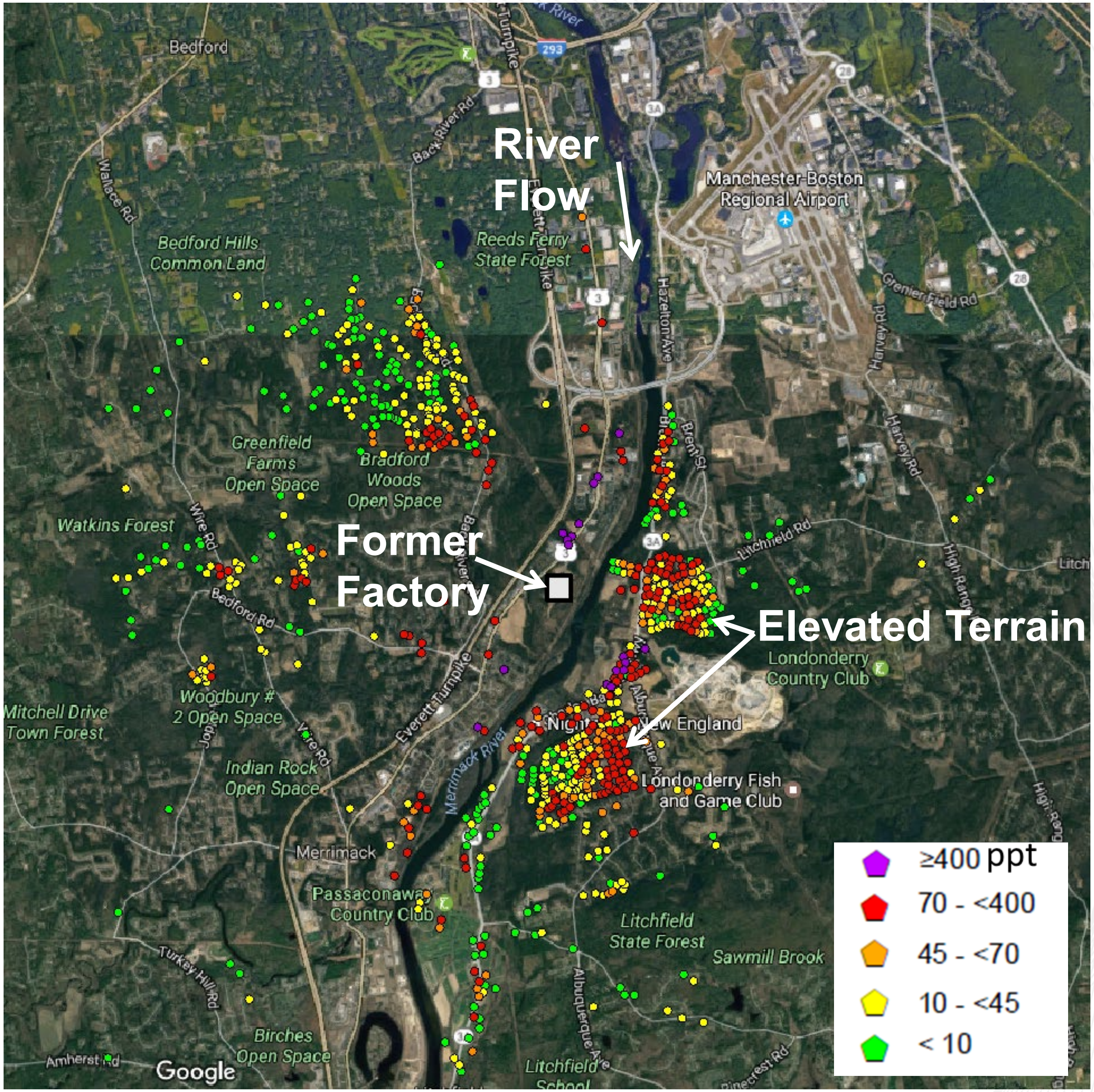


*Detected in public water supply wells at up to 280 ng/L.

SANBORN | HEAD

Courtesy of Gloria B. Post, NJDEP, June 5, 2013

PFAS – Private Well Samples in NH

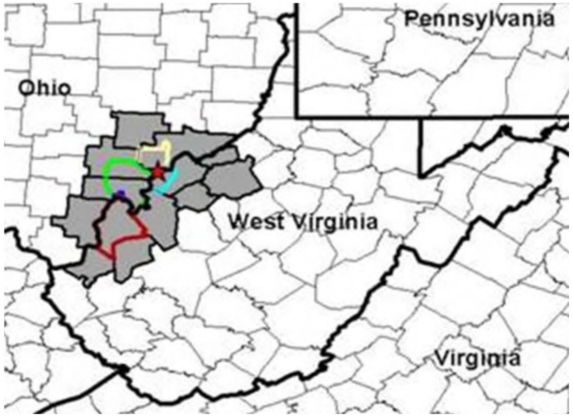


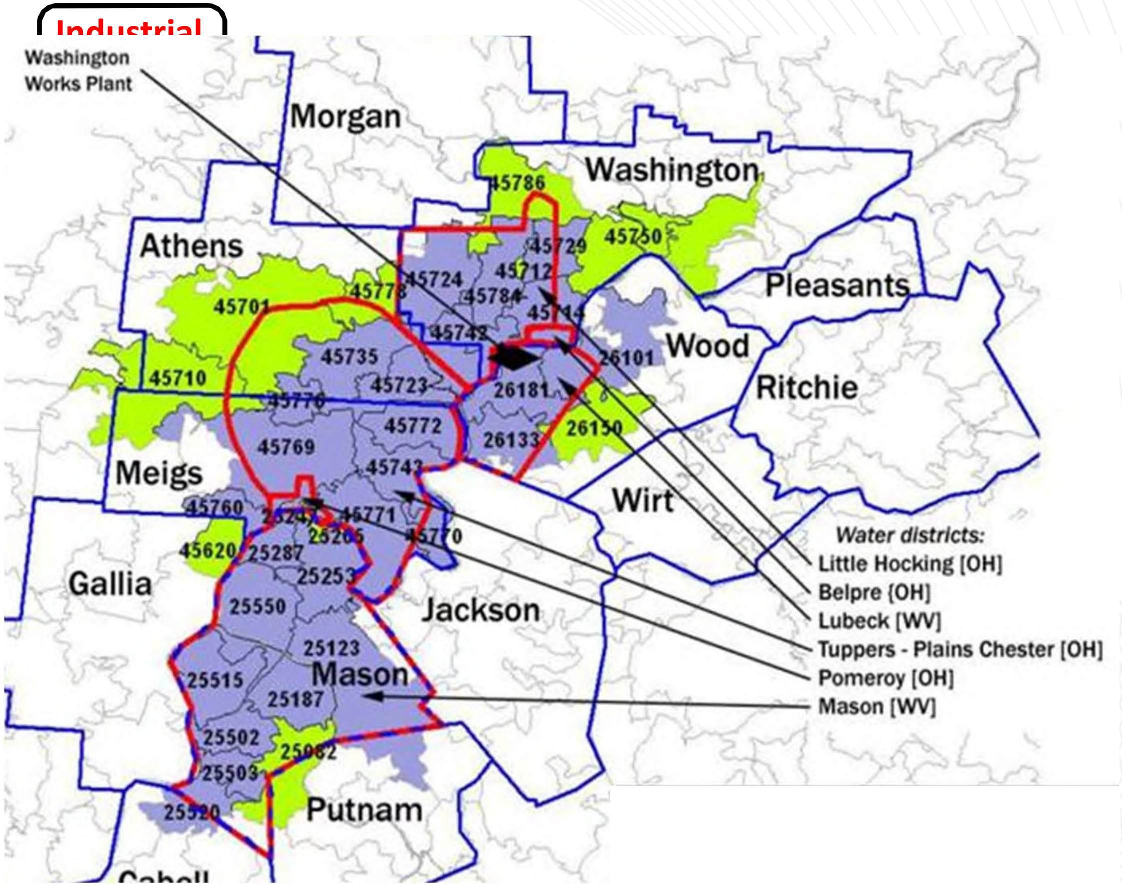
Courtesy of NH Department of Environmental Services

SANBORN HEAD

PFAS Investigation Near Manufacturing Plant

Drinking water wells up to ~20 miles from industrial source were contaminated with PFOA through air deposition (WV & Ohio).





Source: S. Frisbee, West Virginia Univ. School of Medicine. 2008.

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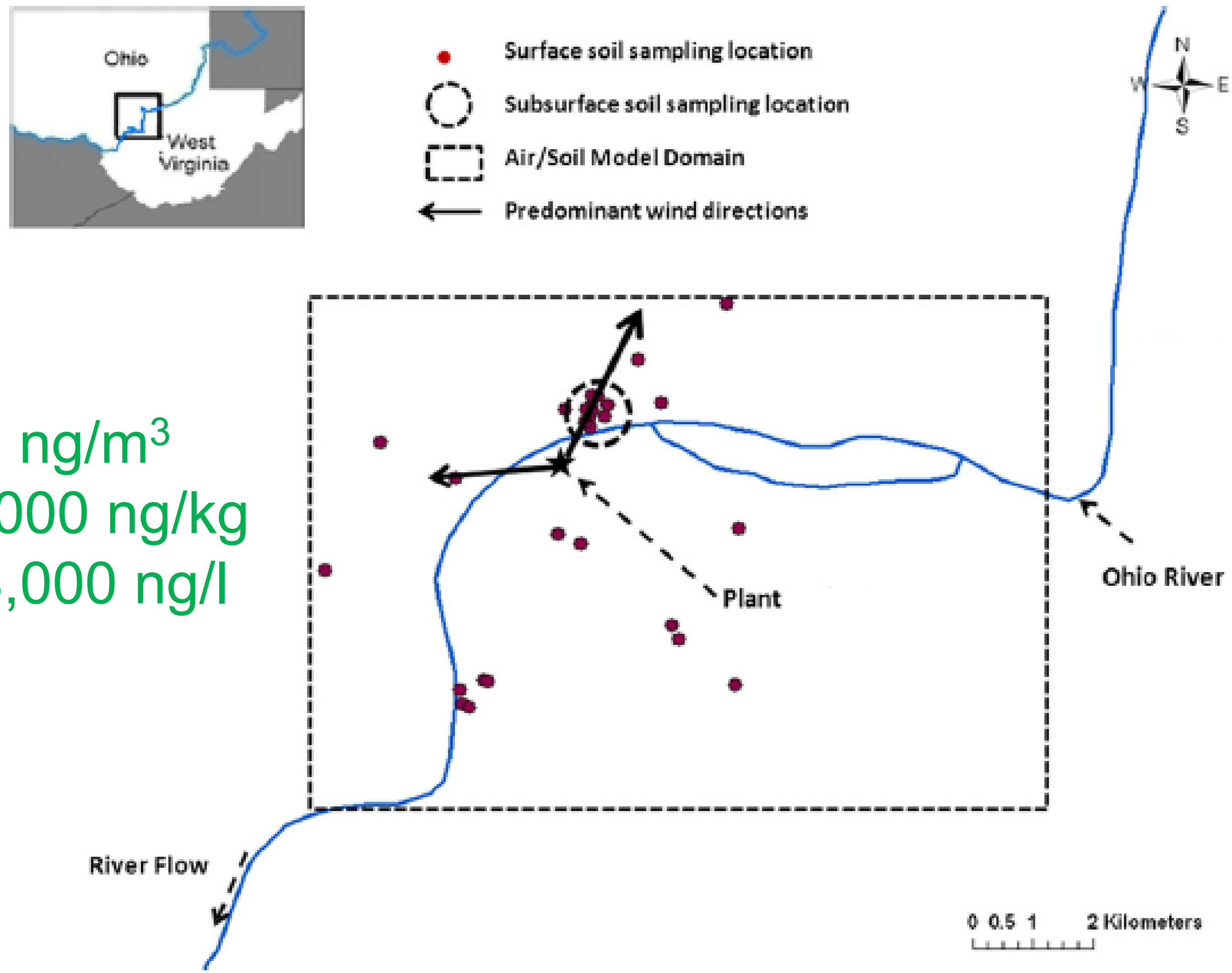
Courtesy of Gloria B. Post, NJDEP, June 5, 2013

PFAS Modeling Study Example

H.-M. Shin *et al.* (2012), Atmospheric Environment 51 (2012) 67-74



Air: 200 ng/m^3
Soil: 11,000 ng/kg
Water: 4,000 ng/l

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PFAS Modeling Study Example

H.-M. Shin *et al.* (2012), Atmospheric Environment 51 (2012) 67-74

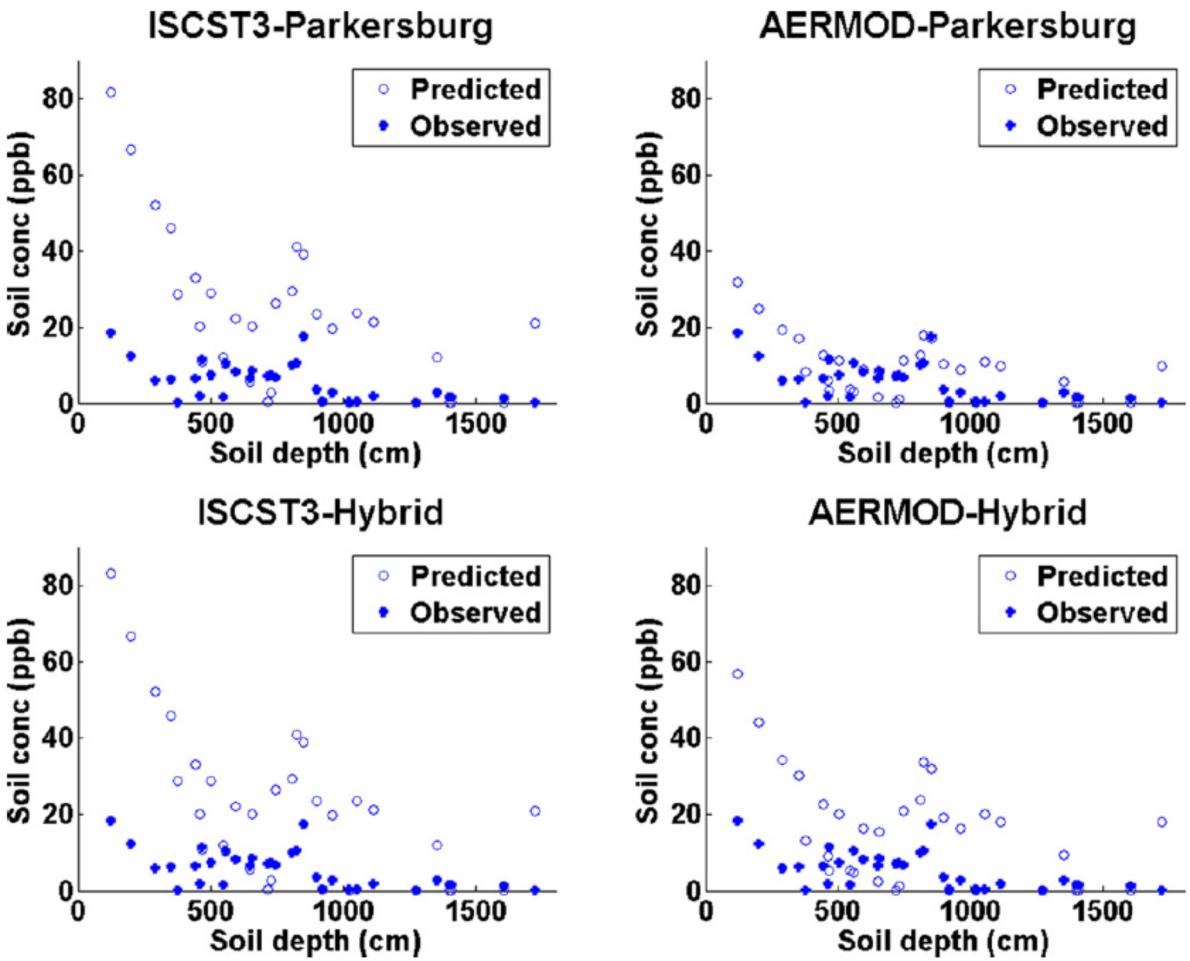
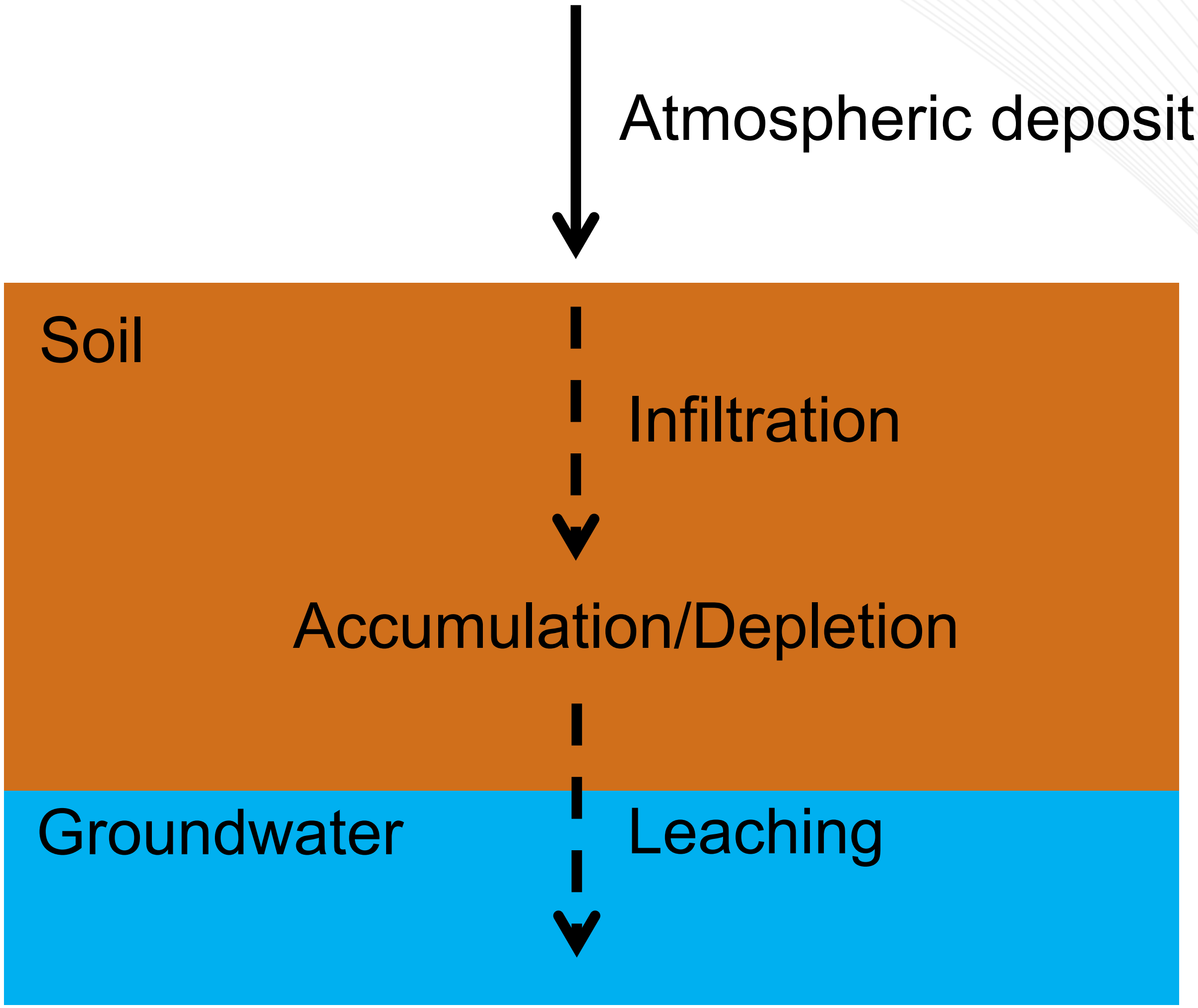


Fig. 4. Scatter plots of cross-sectional subsurface soil concentration prediction profiles by soil depths (cm). Averaged predicted and observed concentrations across sampling locations are shown as filled and blank dots, respectively.

Comments on Modeling

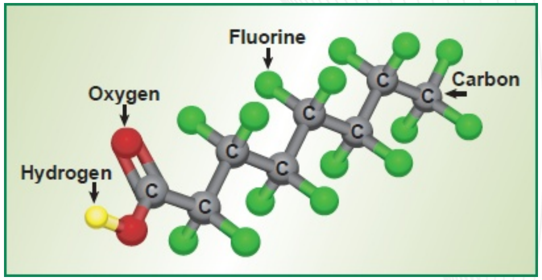
- Basic inputs (*e.g.*, emission rates, particle size distribution, *etc.*) may be unknown or uncertain
- AERMOD deposition models are not fully validated and Method 1/2 options may give varying results
- Coupled air-soil-groundwater models may be difficult to uniquely calibrate
- Hybrid approaches that combine modeling and measurements may be prudent
- Air dispersion/deposition modeling may be useful in predicting expected patterns of PFAS deposition in the vicinity of an air emission source

Soil: The Critical PFAS Reservoir



How Much PFAS in Air is Needed to Contaminate Groundwater?

- Assume:
  - PFAS deposits and mixes with precipitation
  - Deposition velocity 1 cm/s
  - 1 m annual precipitation depth
- Find by mass balance:
  - 3.2 ng/m^3 in air produces 1,000 ng/l in water
- Perspective:
  - 70 – 170 ng/m^3 detected in air near Dupont in WV



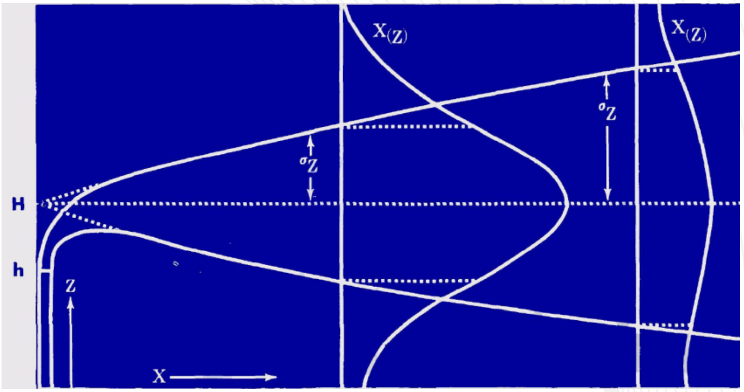
PFAS Emissions

- Chromium plating facilities
  - Concentration 4.9 µg/m^3 in vented exhaust corresponds to 1 lb/yr PFOS (1)
  - Lake Calhoun, MN mass balance: 36 lb/yr (2)
- Dupont plant in Washington, WV (3)
  - > 10,000 lb/yr from 1978 through 2002
  - Peaked at 34,000 lb/yr (1999)

(1) NAVFAC TR-2243-ENV, March 2004
(2) https://www.minneapolisparks.org/_asset/0jd11p/water_resources_report_2015.pdf (1.8 × 10^7 m^3 and 4.2 yr residence)
https://www.pca.state.mn.us/sites/default/files/c-pfc1-02.pdf (average 108 ppt)
(3) Paustenbach et al (2007), *J Toxicol Environ Health* **1**:28-57

What PFAS Emission Rate Produces Observed Air Levels?

- Ballpark Assumptions:
  - PFAS in air at 10 ng/m^3
  - Emission height ~ 30 m
  - Class D/E stability
  - Wind speed ~5 m/s
  - Transport distance ~1,000 to 1,500 m



- Guesstimate:
  - Impact Cu/Q of 5.0×10^{-5} m^{-2} (Turner's Workbook)
  - Implied emission Q = 0.008 lb/hr = 70 lb/yr

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Is Soil a Reservoir for PFAS?

- Estimate 0.014 g/m^2 PFOA/PFOS in soil based on:
  - 10 ng/g of PFOA/PFOS in soil
  - Contaminated depth of 3 ft
  - Soil bulk density of 1,500 kg/m^3
- Annual deposition rate of 0.003 g/m^2-yr based on previous example:
  - Based of 10 ng/m^3 PFOA/PFOS in air
  - Deposition velocity of 1 cm/s

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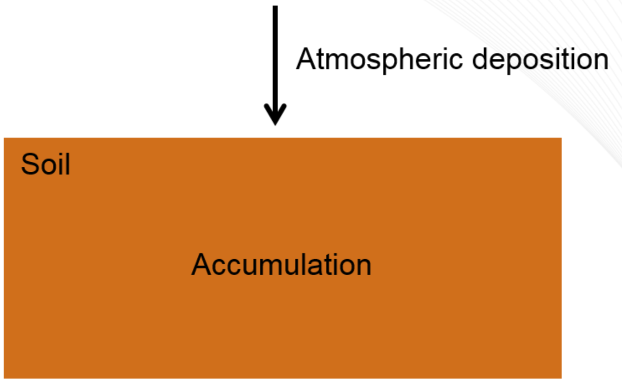
PFAS Background in Soil?

- Ballpark Assumptions:
  - PFAS in air at 10 pg/m^3 = 0.01 ng/m^3
  - Deposition velocity = 1 cm/s
  - Soil depth = 1 ft
  - Deposition time = 30 yrs
  - No loss or removal from soil
  - Soil bulk density = 1500 kg/m^3
- Find
  - Soil concentration = 0.2 ng/g



Special Thanks!

ITRC PFAS Team: Fate and Transport Sub-team

Photo Gallery

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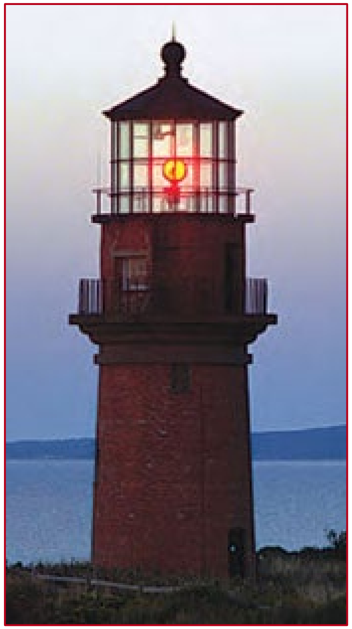


Treatment Options for PFAS Impacted Matrices

Jeffrey McDonough, P.E.
Arcadis North American PFAS co-Lead

Photo Source: ABS Materials 2018

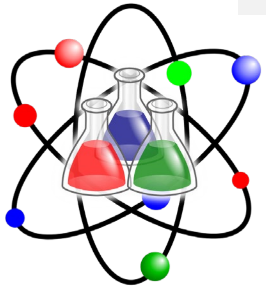
Photo Source: Evocra 2017

Pressure Points

ARCADIS Design & Consultancy for natural and built assets

Visibility	Uncertainty	Vulnerability
• Regulatory drivers are actively changing • Reputational risk linked to public sensitivity	• Evolving science and toxicology • Minimal practical approaches • Interim response outpaces science	• Evaluation and prioritization • Risk of re-openers • “Future proofing”

>



Emerging contaminants create unique challenges

Sizing Up the PFAS Challenge

- Wide Range Molecular Weight
- Thermally resistant
- Oleophobic/ Hydrophobic
- >5,000 compounds
- Strongly Electronegative
- Polar/ Soluble
- Surfactant characteristics
- Biologically recalcitrant
- Properties *f*(chain length)
- Parts per trillion criteria
- Negligible relevant volatility
- Critical Micelle Concentrations
- Ubiquitous

PFAS Water Treatment Quick Take-Aways

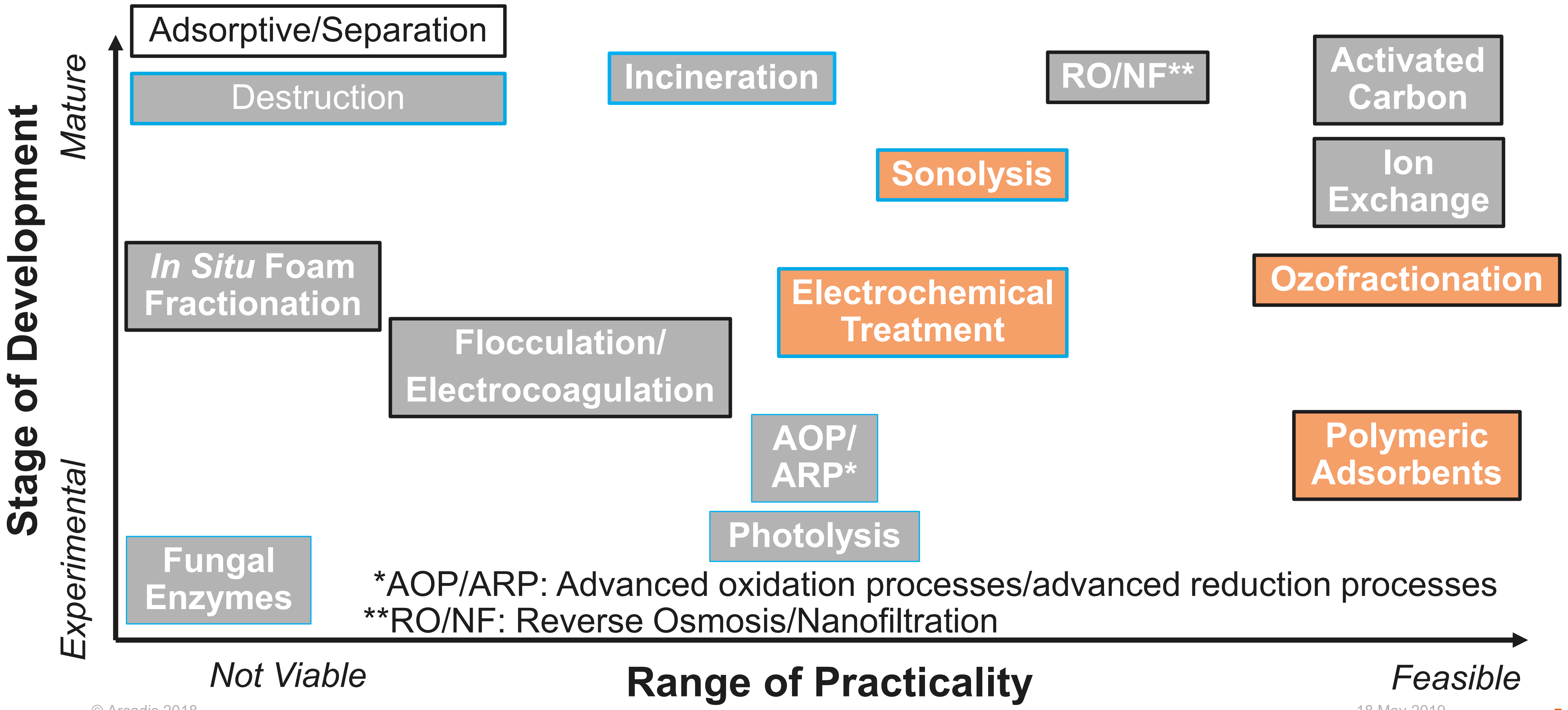
- PFASs defy remediation engineering convention (no bio**degradation**, nearly impractical chemical oxidation, minimal phase change removal, energy-intensive destruction)

- Current state of the practice is a **combination** of treatment technologies

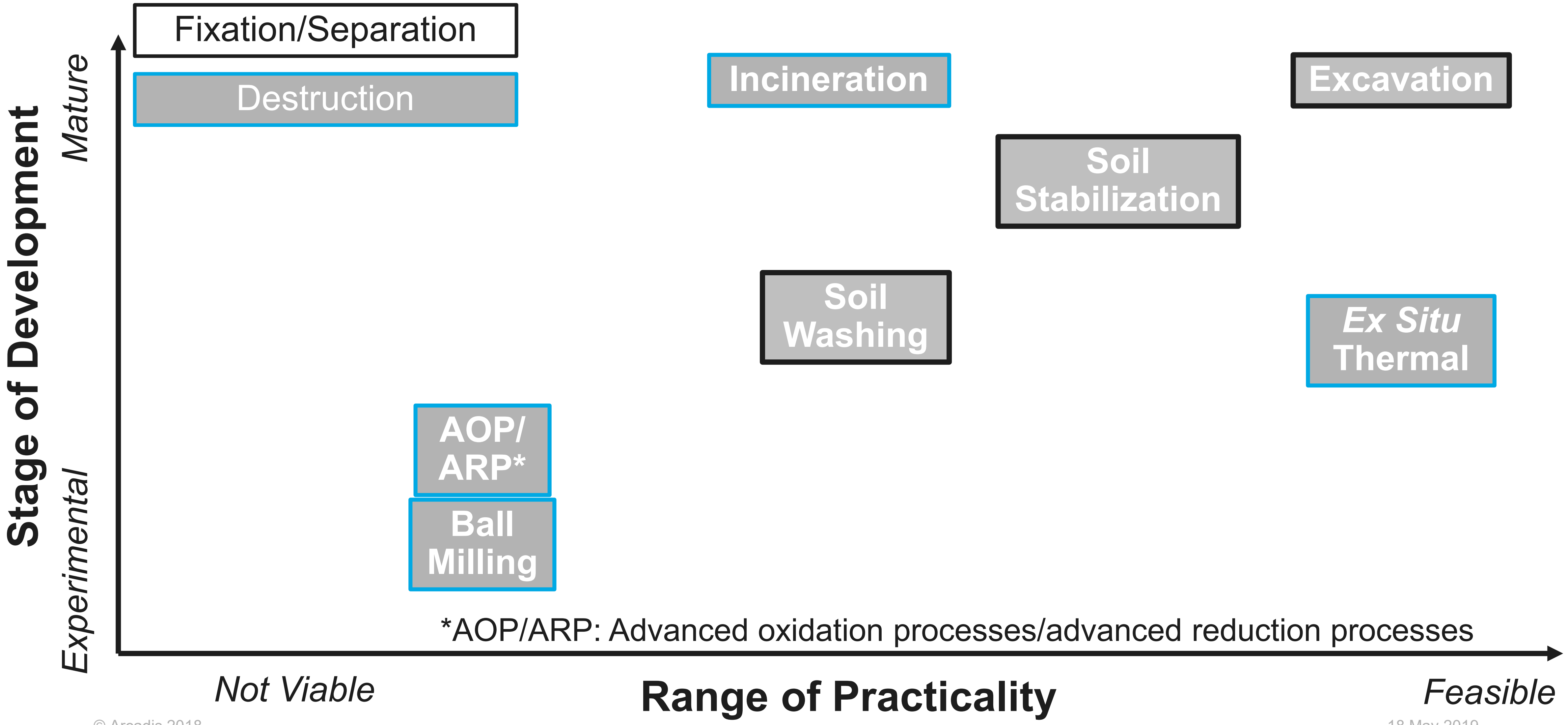
- Ultimate goal is to **concentrate PFAS** for energy-intensive destruction

ADSORPTION	SEPARATION / CONCENTRATION	DESTRUCTION

PFAS Treatment Technologies for Water



PFAS Treatment Technologies for Soil/Sediment



Conventional Technologies for PFASs

Activated carbon (AC)

Photo Source: Evoqua 2017

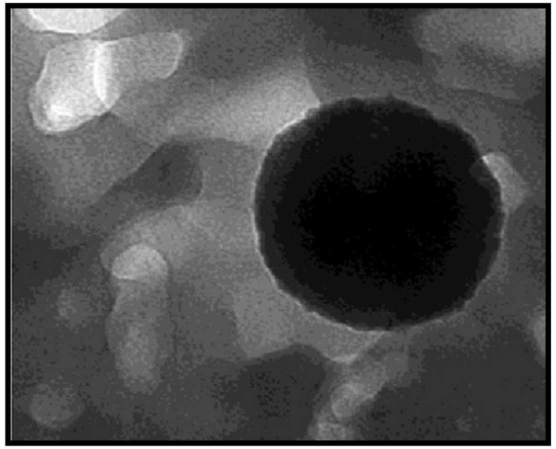


Photo Source: Zaggia et al. 2016

Anion/Ion Exchange Resins

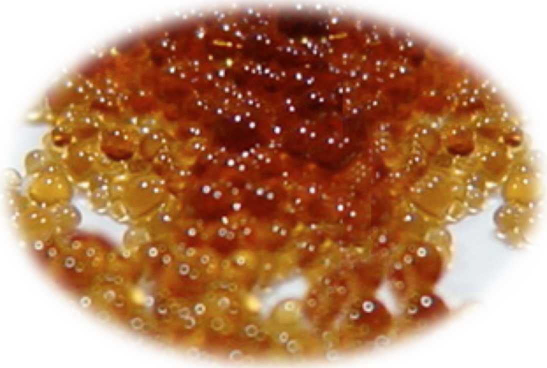
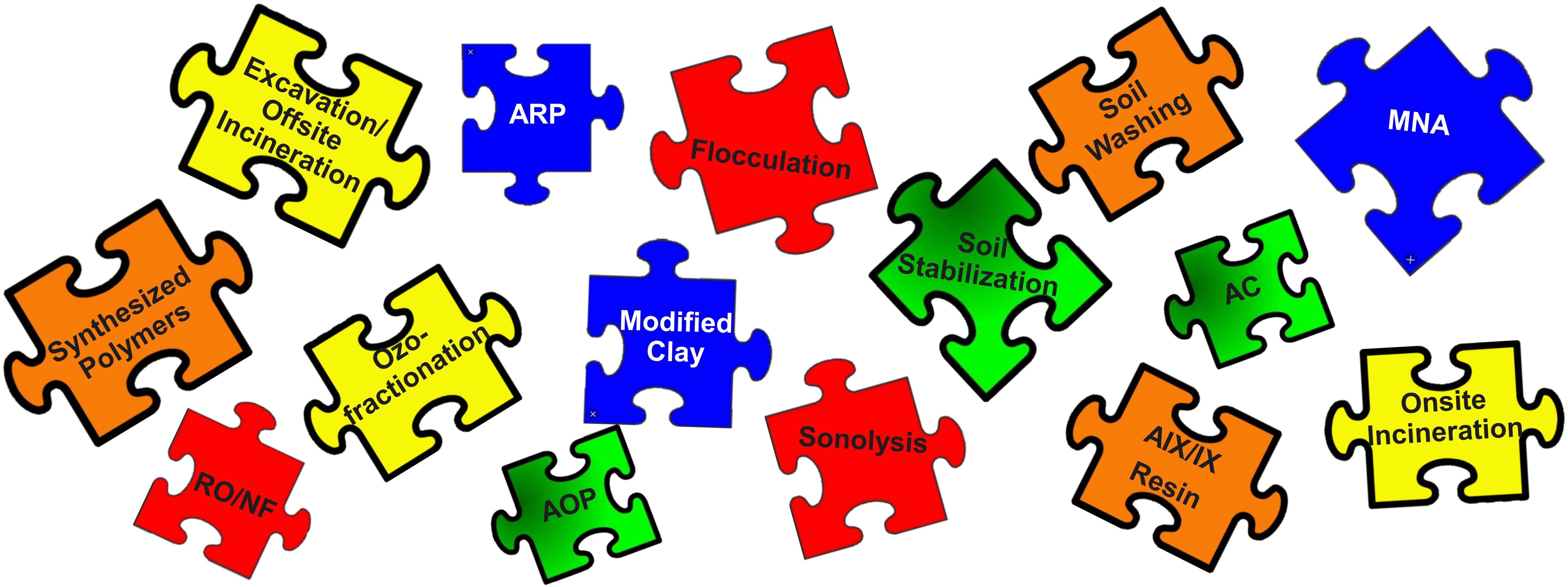


Photo Source: Evoqua 2017

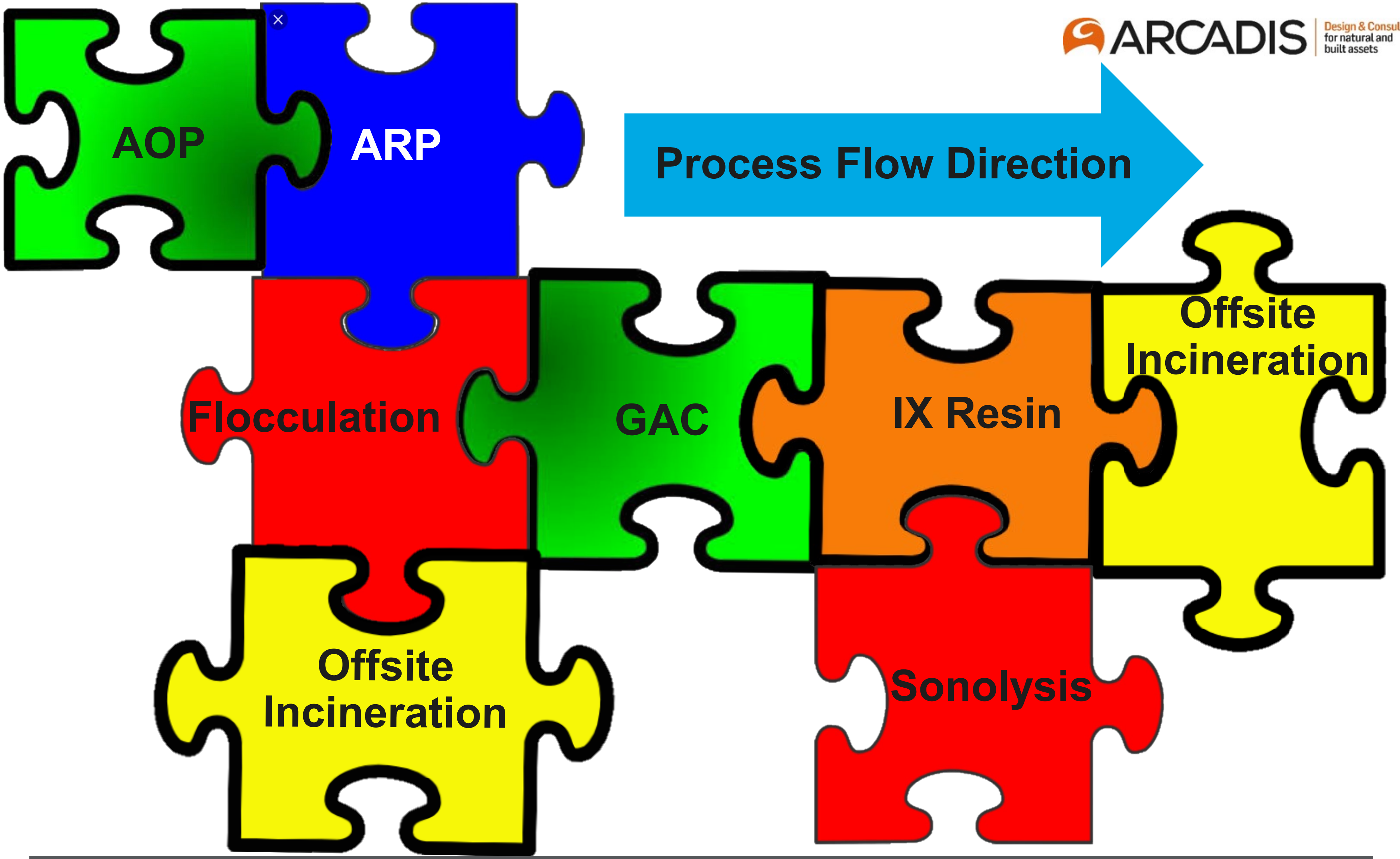
Reverse Osmosis/Nanofiltration

Photo Source: Peter Storch 2018

Thinking Through a Treatment Strategy…

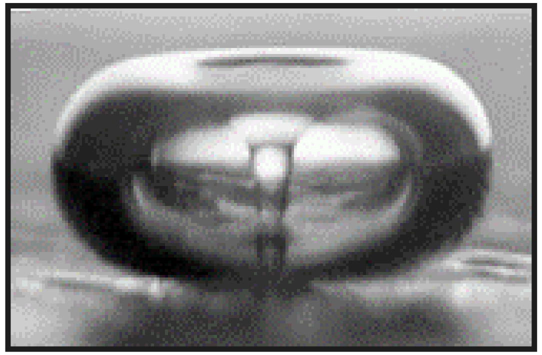


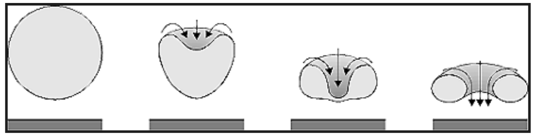
No "silver bullet" for PFAS remediation; treatment train is current state of the practice



No “silver bullet” for PFAS remediation; treatment train is current state of the practice

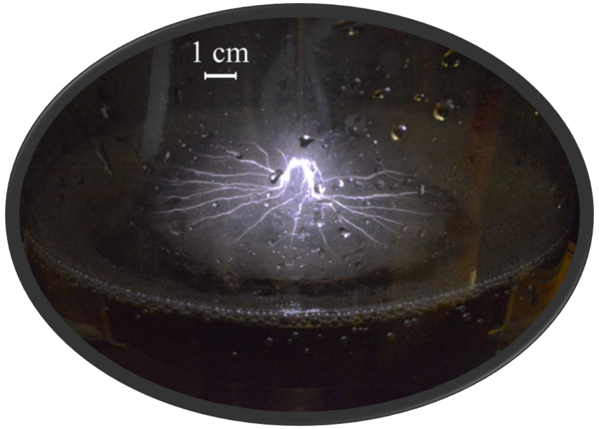
Developing Technologies for PFASs



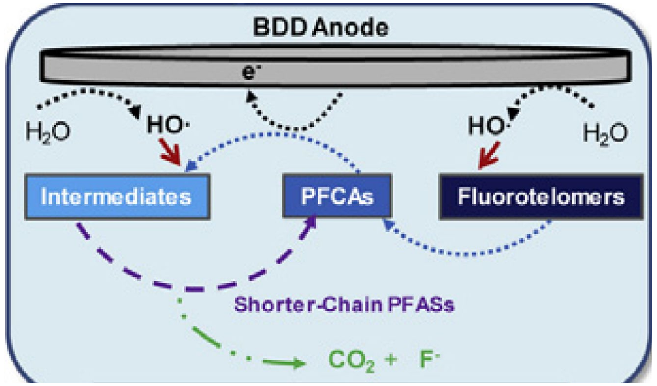


Sonolysis *Photo Source: Temple University 2017*

Mesoporous Organosilica
Source: Edmiston 2018



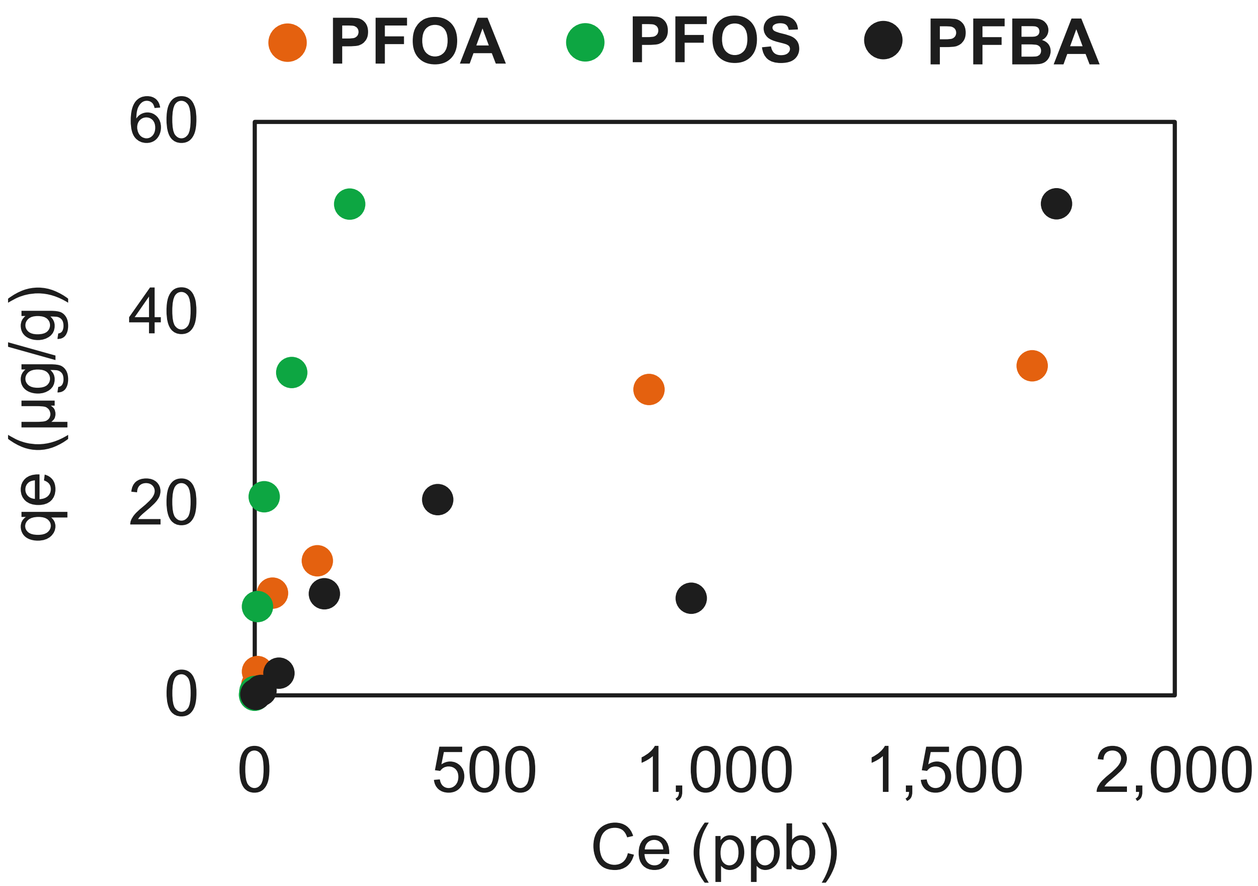
Plasma
Source: Stratton et al 2017



Electrochemical Treatment
Source: Gomez-Ruiz et al 2017

Photo Source: Evocra 2017

Mesoporous Organosilica (MPOS)



Adsorption isotherms; MPOS coated sand (30 min)

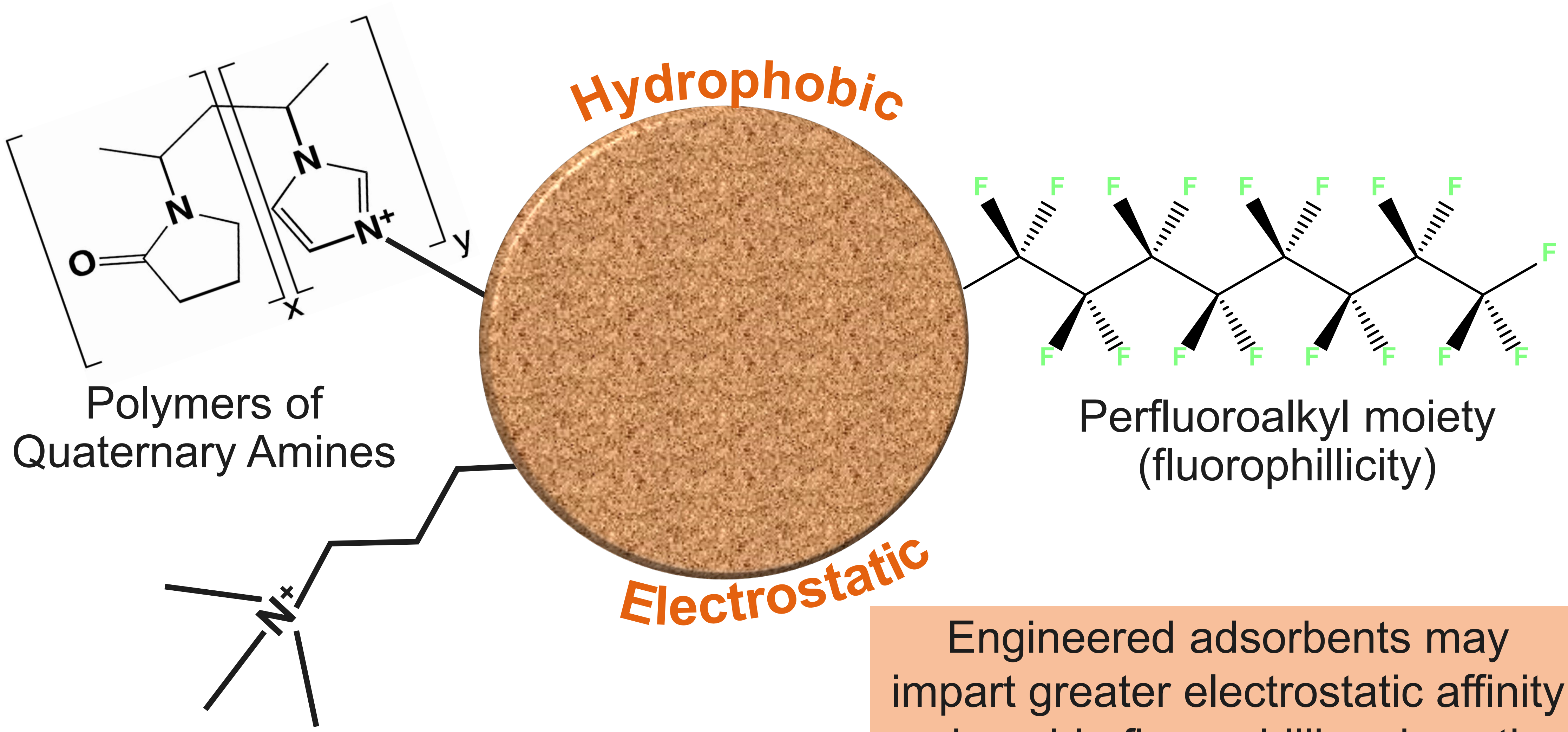
- Crosslinked alkoxysilanes forming an adaptable matrix; affinity for organics
- Synthesized polymers could use fluorinated chains to enhanced adsorption

Fine Sand

Organosilica Coated Sand

Source: Edmiston 2017

Polymeric Adsorbents



Polymers of Quaternary Amines

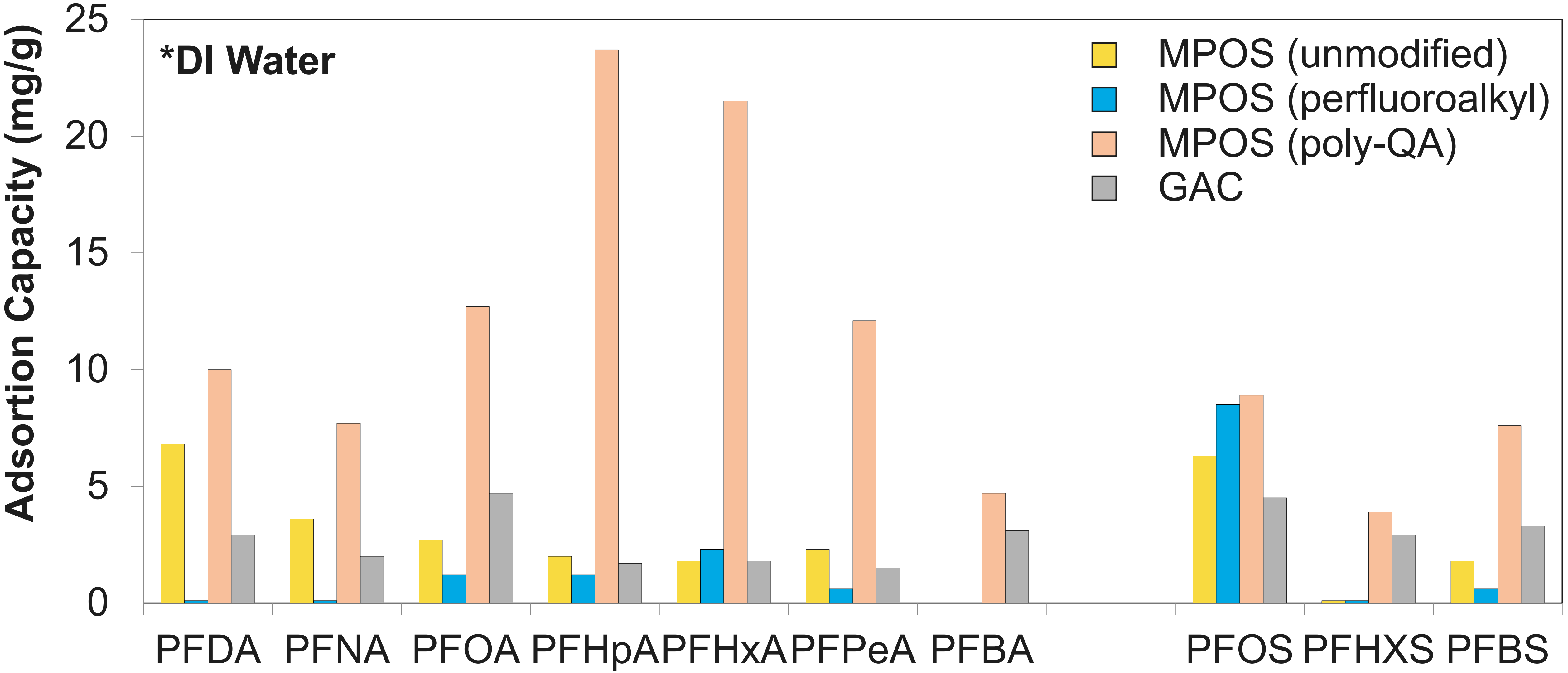
Perfluoroalkyl moiety (fluorophillicity)

Quaternary Amines

Engineered adsorbents may impart greater electrostatic affinity and enable fluorophillic adsorption

Source: Edmiston 2019

Comparative Adsorption Capacity (C_e = 200 ppb)



Source: Edmiston 2019

Ozofractionation (OZF) – Concept

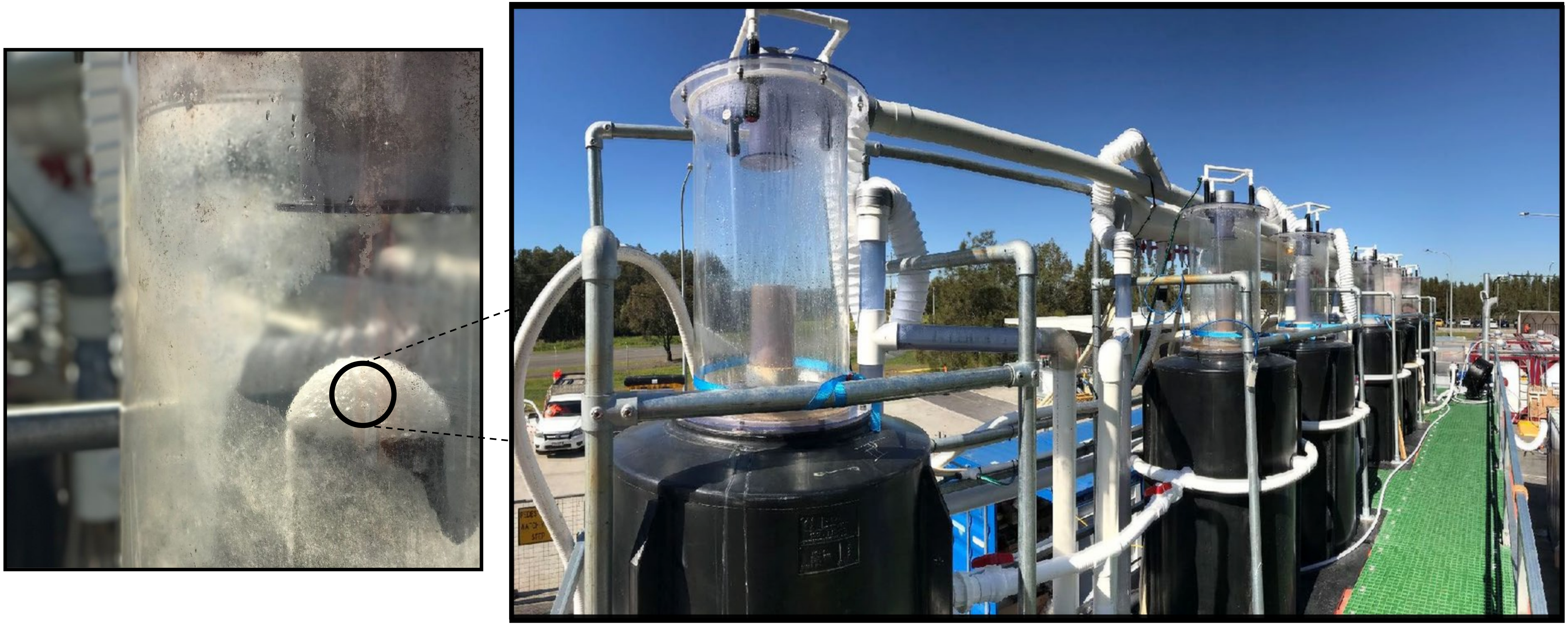
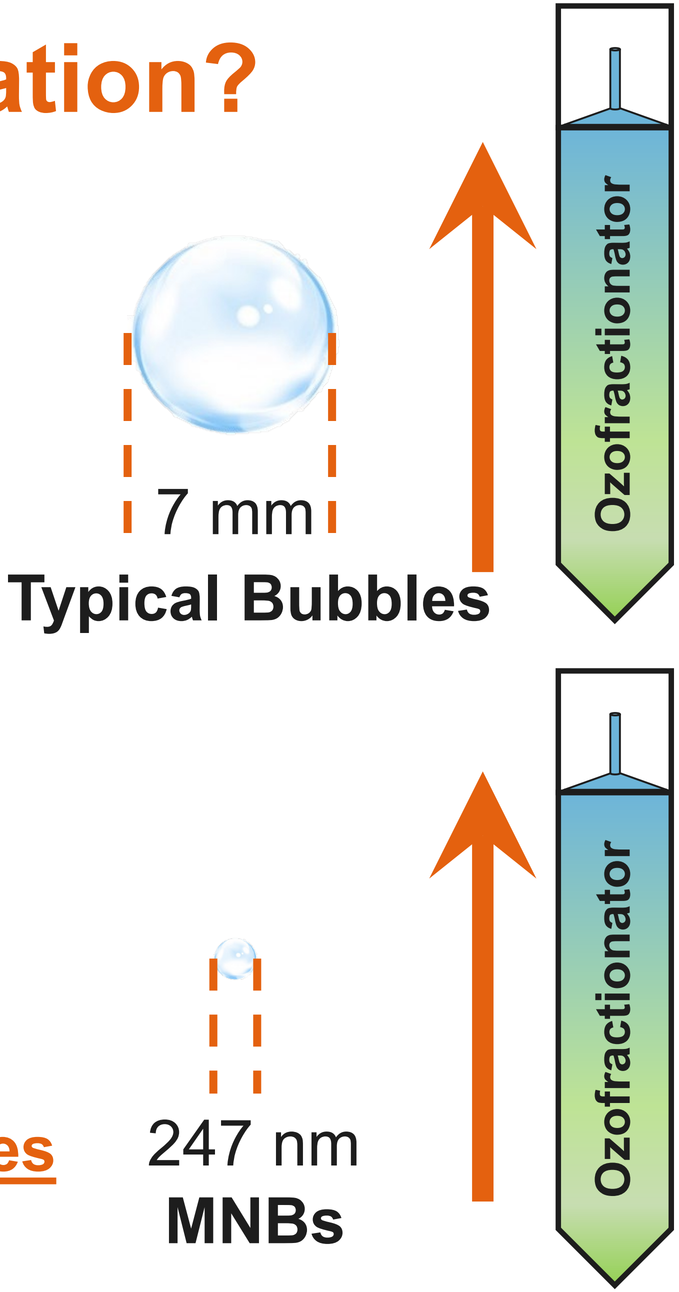


Photo Source: Evocra 2017

Why "Ozo"fractionation?

ARCADIS Design & Consultancy for natural and built assets

- Fractionation efficiency likely associated with available bubble surface area
- Ozone used in the literature to create micro-nano-bubbles (MNBs) ranging from 10s nm to 10s µm
- MNBs increase bubble quantity and **available surface area**
- Ozone MNBs may have a high zeta potential which mitigates bubble coalescence and **improves stability**



2.1×10^{6} bubbles/100 gal

3.2×10^{2} m^2/100 gal

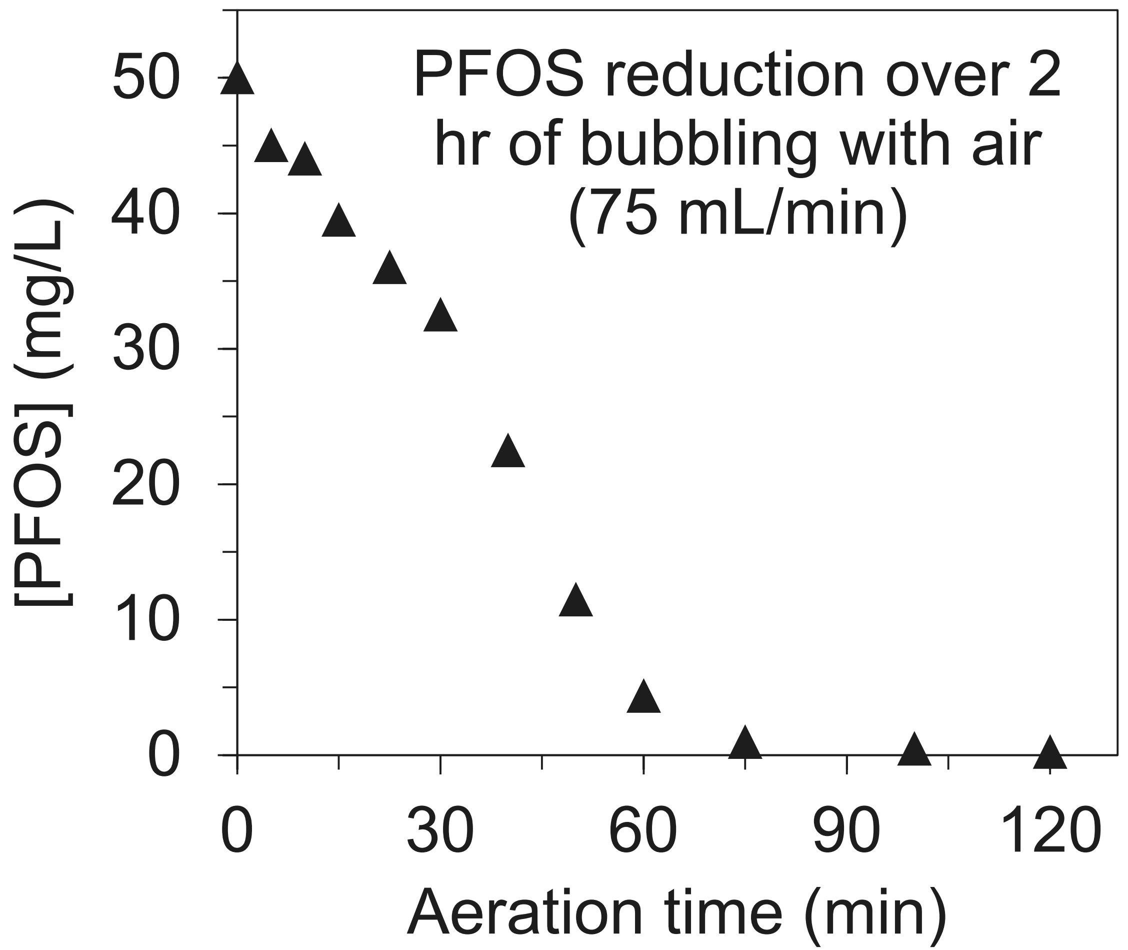
>28,000,000% surface area increase, less incidence of coalescence; more stability

4.8×10^{22} bubbles/100 gal

9.2×10^{7} m^2/100 gal

After Hu and Xia 2018

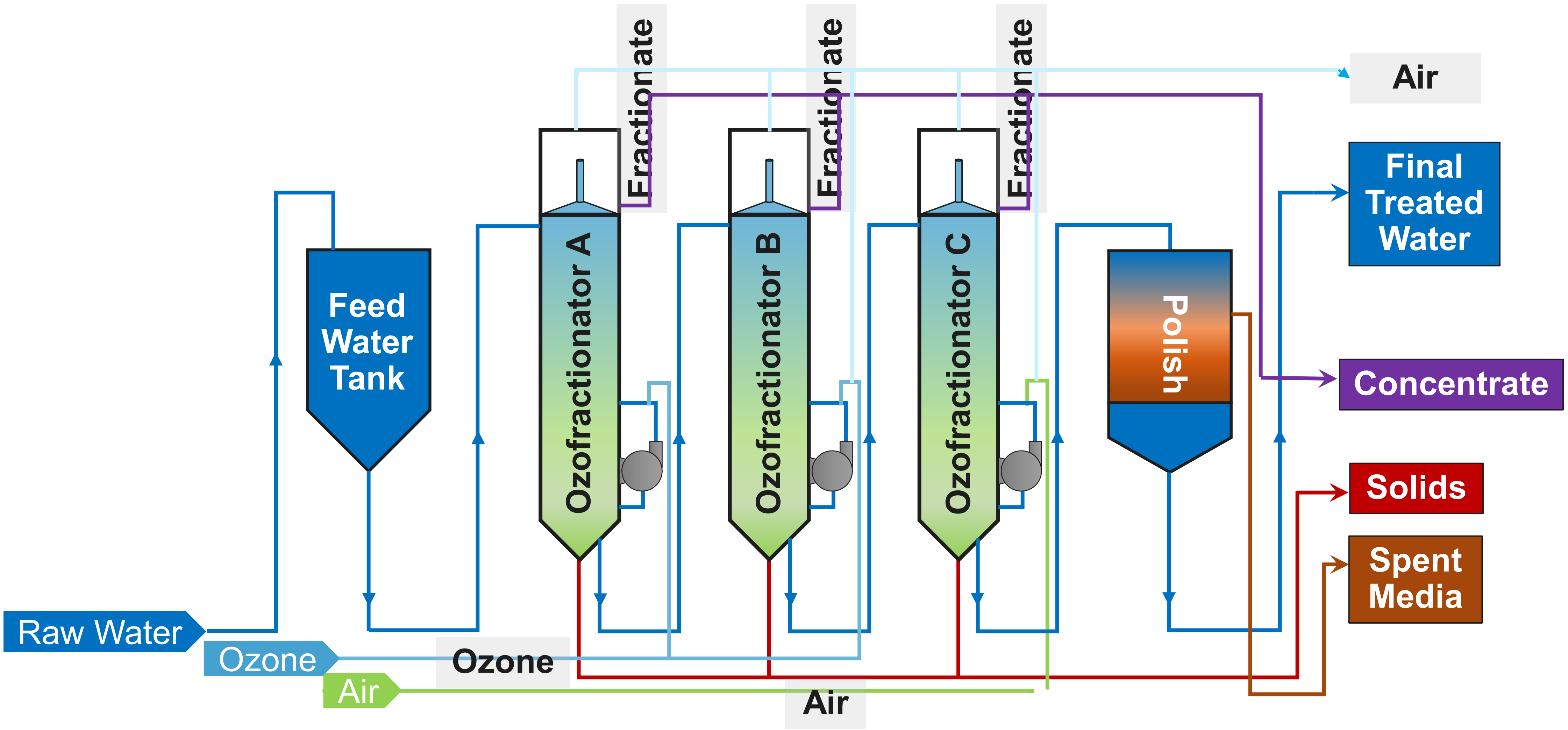
Will Other Gases Be Effective?



Adapted from Meng et al 2018

- Ongoing topic of research, with some indications that other gases can be **effective**
- Questions regarding **efficiency** to achieve parts per trillion regulatory criteria within reasonable residence times
- Pre-treatment concerns for co-contaminants?
- Mitigated potential for precursor transformation to short chain PFAAs?

OZF – Concept (cont.)



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OZF – Case Study

Sewage, trade waste, brackish creek water, chemical flush fluids, stormwater

- ~4 million gallons of water
- Total [PFAS] ~ 5,000 μg/L; targeted discharge [PFAS] = 0.25 μg/L
- Laboratory analysis includes total oxidizable precursor (TOP) assay per country-specific regulations

Treatment train operation selected

- Ozofractionation with engineered polish
- Polish necessary for low discharge limit
- Foam concentrate to be thermally destroyed offsite

Photo Source: Evocra 2017

OZF – Case Study (cont.)

Ozofractionation highly effective at removing PFOS, PFOA, and C6 PFAA precursors.

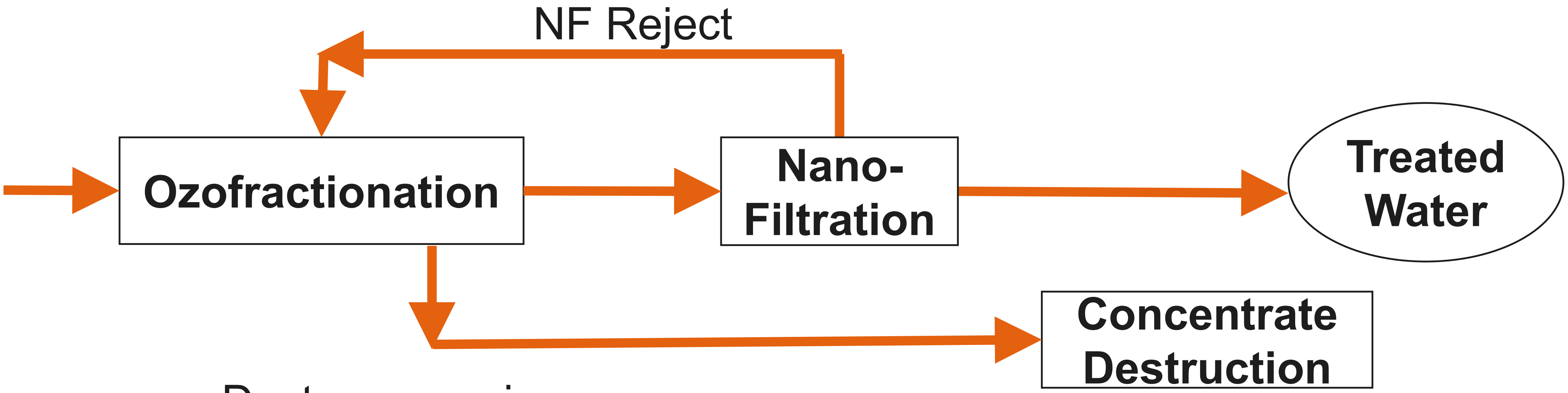
Ozofractionation converted some C6 precursors to PFHxA, PFPeA – net production of these compounds

Polishing adsorption stage was effective at removing PFHxA and, to a lesser extent, PFPeA; PFBA was not detectable in these samples

Identification	Influent (µg/L)	Ozofraction % Removal	Polish % Removal (Adsorbent)	Treated Water (µg/L)	Total % Removal
PFOS	2.61	98.2%	81.3%	0.009	99.7%
PFOA	1.37	97.4%	94.4%	0.002	99.9%
6:2 FtS	87.4	95.6%	89.2%	0.416	99.5%
PFPeA	2.08	-66.3%	83.4%	0.575	72.4%
PFHxA	6.91	-66.4%	99.7%	0.034	99.5%
Sum PFAS	103	78.8%	95.1%	1.07	99.0%
Total PFAS, TOPA	**3,950**	**99.6%**	**89.6%**	**1.76**	**99.96%**

Ozofractionation and engineered polish achieve 99.96% PFAS removal, post TOP

OZF – Case Study (cont.)



- Destroy organics
- Remove PFASs incl. short chains
- Remove and manage solids
- Manage odour

- Remove remaining PFASs <0.25 µg/L

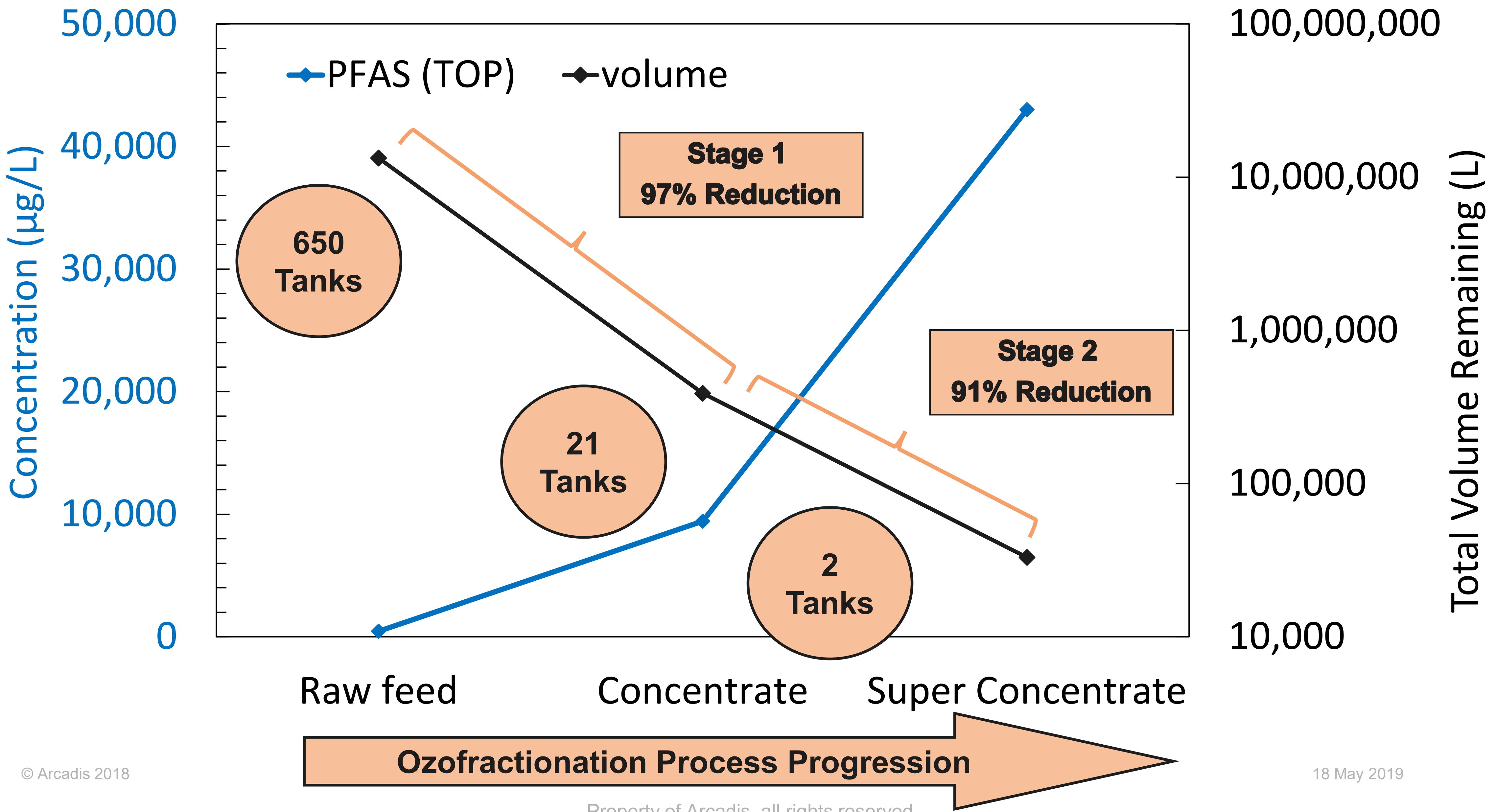
- Onsite Destruction
- Offsite Thermal Destruction

OZF – Case Study (cont.)

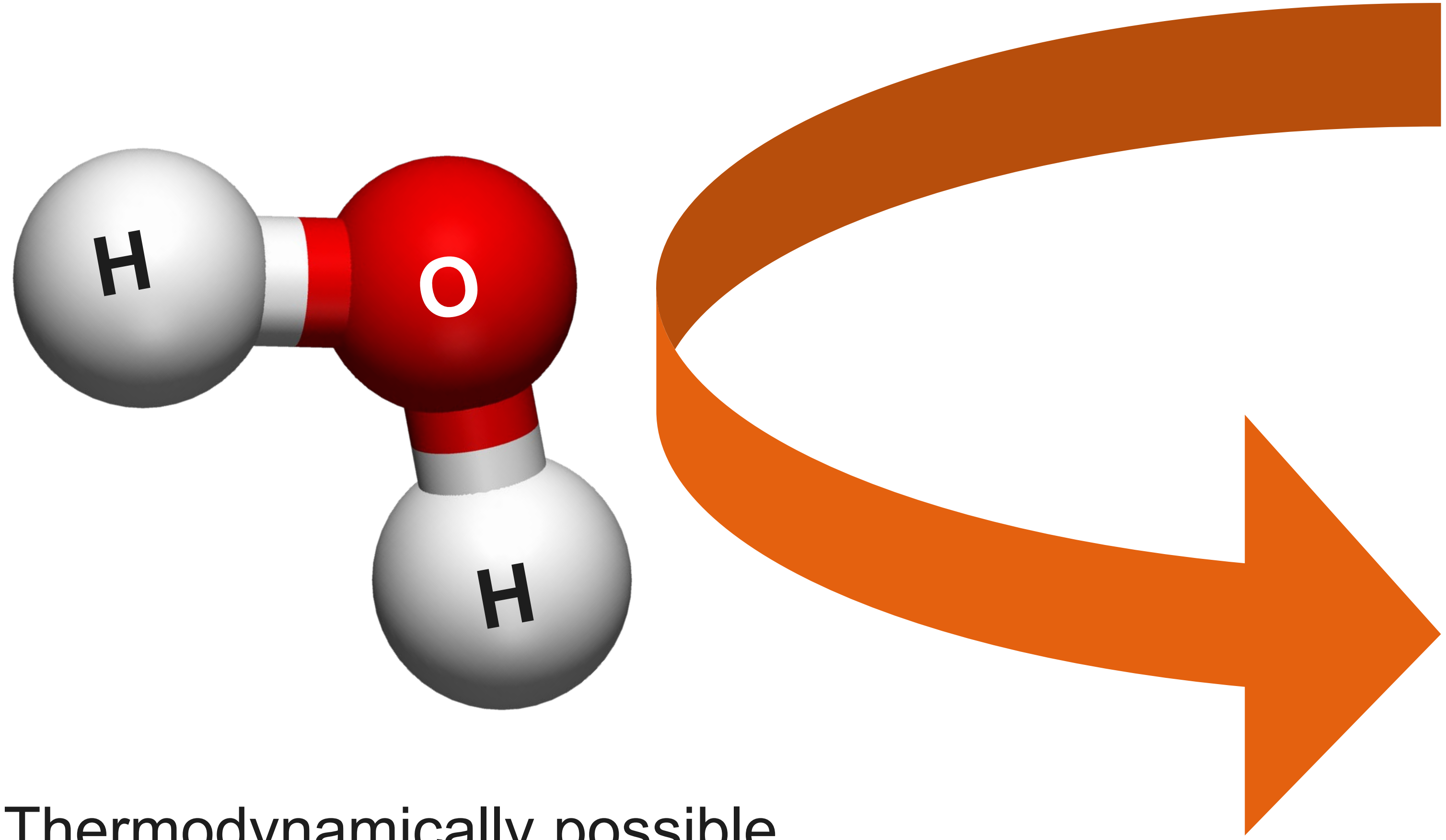
Identification	Influent (µg/L)	Ozofraction % Removal	Polish % Removal (Nanofiltration)	Treated Water (µg/L)	Total % Removal
PFOS+PFHxS	0.5	98.13%	--	<0.002	99.63%
PFOA	0.3	97.07%	--	<0.002	99.41%
6:2 FtS	18.4	99.14%	96.84%	<0.005	99.97%
PFPeA	1.1	82.46%	99.00%	<0.002	99.82%
PFHxA	1.1	96.19%	95.00%	<0.002	99.81%
Sum PFAS	7.5	96.87%	99.15%	<0.002	99.97%
Total PFAS, TOP Assay	**28.8**	**98.58%**	**99.51%**	**<0.002**	**99.99%**

Ozofractionation and engineered polish achieve 99.99% Total PFAS removal; concentrated waste stream is 0.5% to 2% of the treated water volume

OZF – Case Study (cont.)



Advanced Reducing Processes – ARP



Sound waves

Electricity

Radiation

H•

Disproportionation into oxidizing and reducing radicals

OH•

e•

- Thermodynamically possible...
- Kinetically meaningful (scavengers)?

Electrochemical Degradation

Applicability:

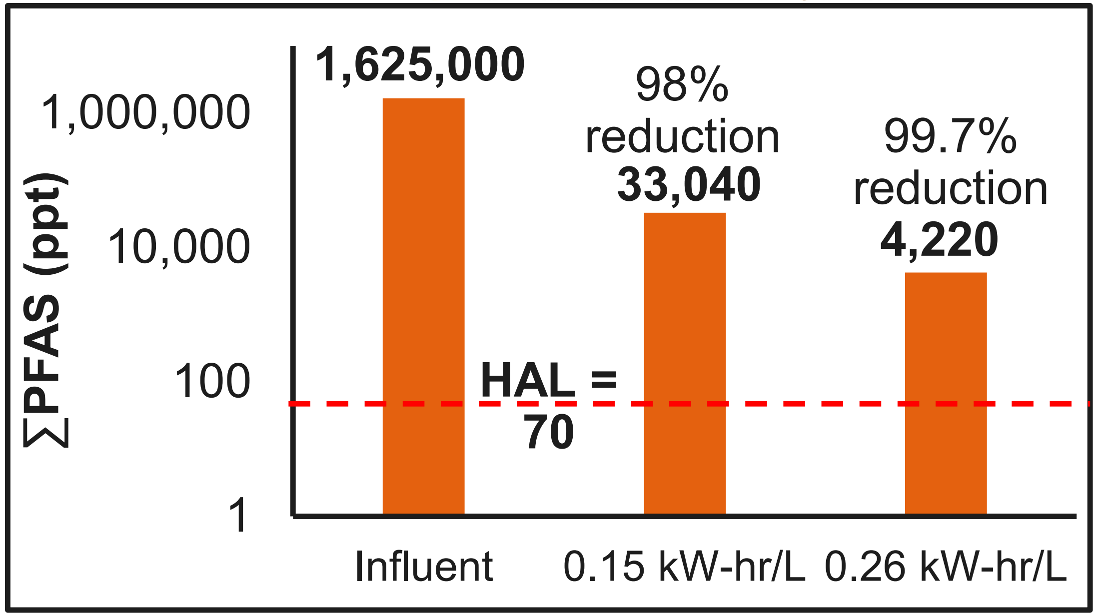
- Electrochemical cells can degrade PFAS through direct electron transfer at the surface of the anode.

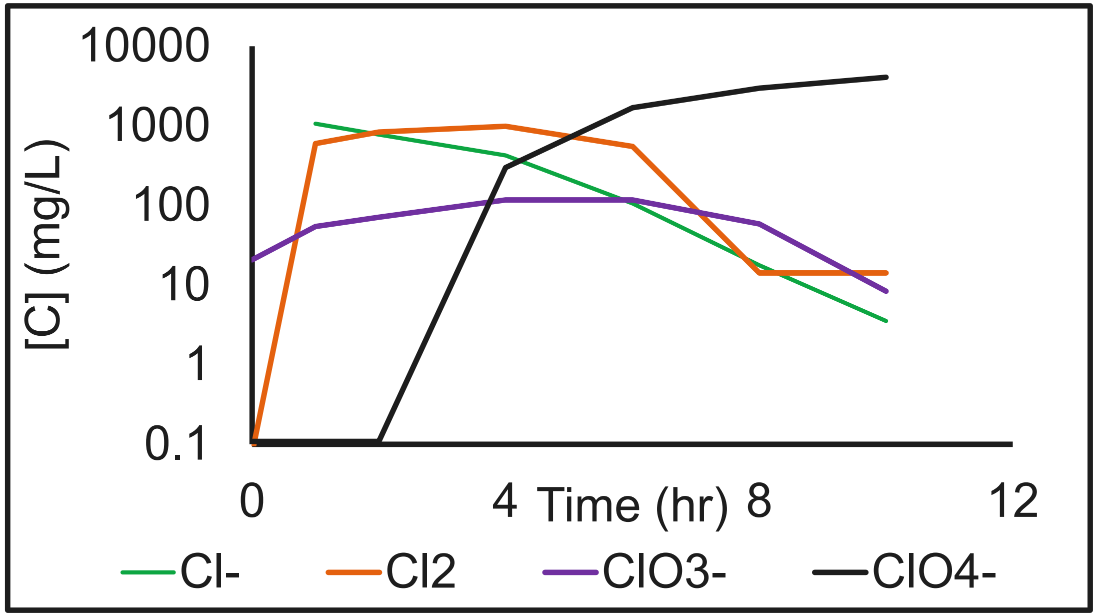
Benefits:

- Provides a feasible destruction mechanism for concentrated PFAS waste streams at low flow rate.
- PFAS degradation confirmed (fluorine mass balance); effective for both laboratory and real groundwater/wastewater.

Limitations:

- Energy Intensive
- Geochemical constituents may cause secondary concerns (i.e., chloride oxidized to perchlorate).
- Acidity around anode may facilitate PFOS sorption; needs further investigation. Confirmed effectiveness for sulfonates?
- Short chain PFAAs appear to be recalcitrant at low current density (<50 mA/cm^2).





Adapted from Gomez-Ruiz et al 2017

Sonolysis

Applicability:

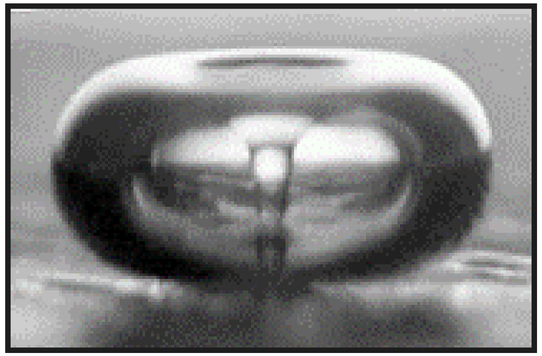
- Ultrasound applied to water results in successive rarefaction/compression of microbubbles ultimately yielding cavitation with extremely high temperatures on the surfaces of the bubbles resulting in pyrolysis of PFASs.

Benefits:

- Can reliably destroy concentrated PFAS waste streams with literature/laboratory supported fluoride mass balance.
- Opportunities to use green energy sources as technology develops (i.e., solar power).

Limitations:

- PFOA rate > PFOS rate. PFOS will require longer residence times and/or more energy.
- Requires specialized equipment and skilled implementation.
- High energy consumption and low flow rates.



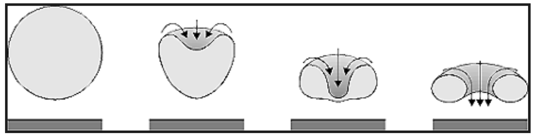


Photo Source: Temple University 2017

Sonolysis: The Effect of Pressure Wave Propagation

Sound energy applied to a liquid propagates as a pressure wave, creating microbubbles.

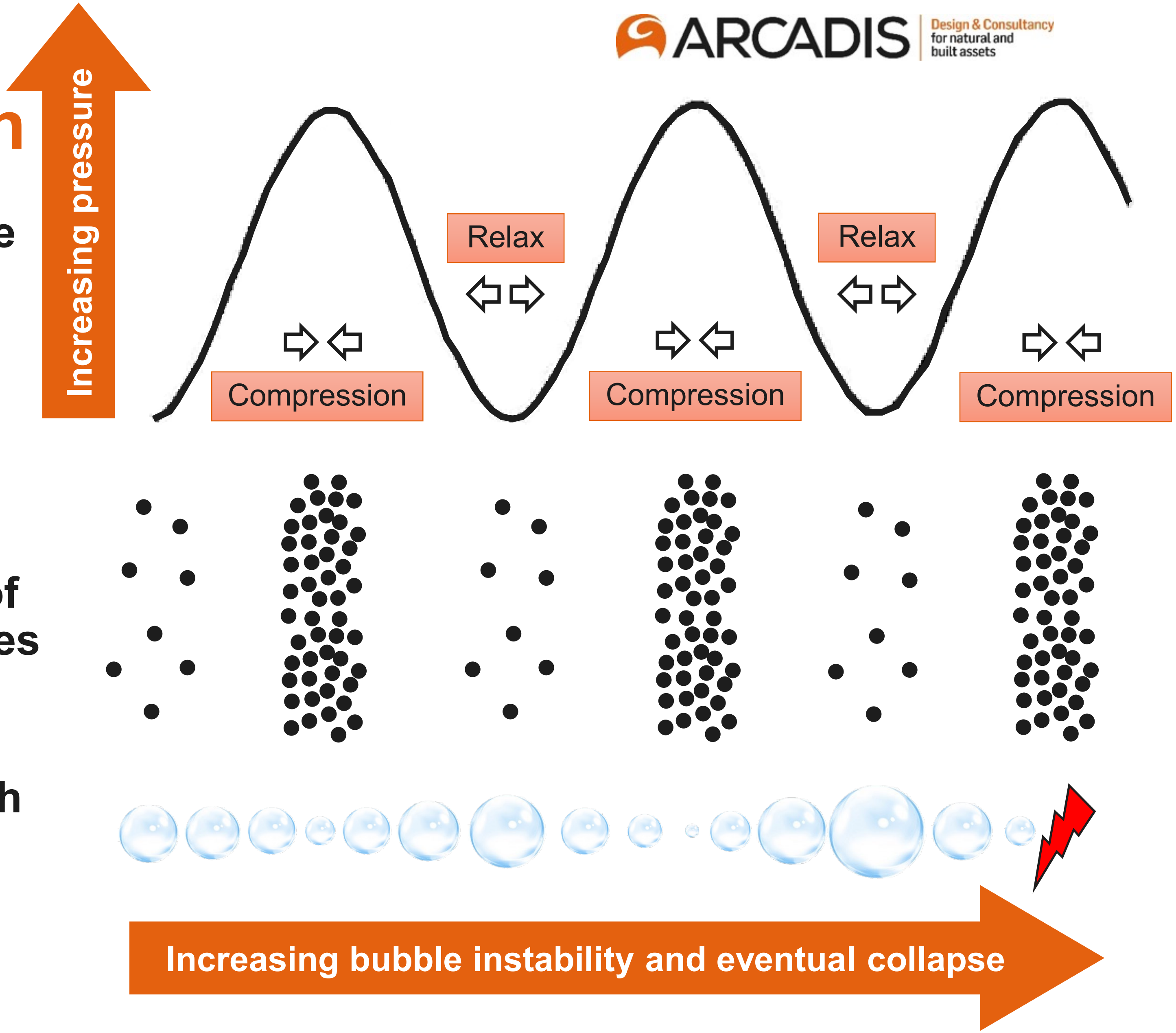
The pressure wave results in successive compression and rarefaction (elongation) of the microbubbles.

The microbubbles become unstable and eventually collapse, releasing energy in the form of heat (quasi-adiabatic) up to 5,000 K.

Pressure Wave

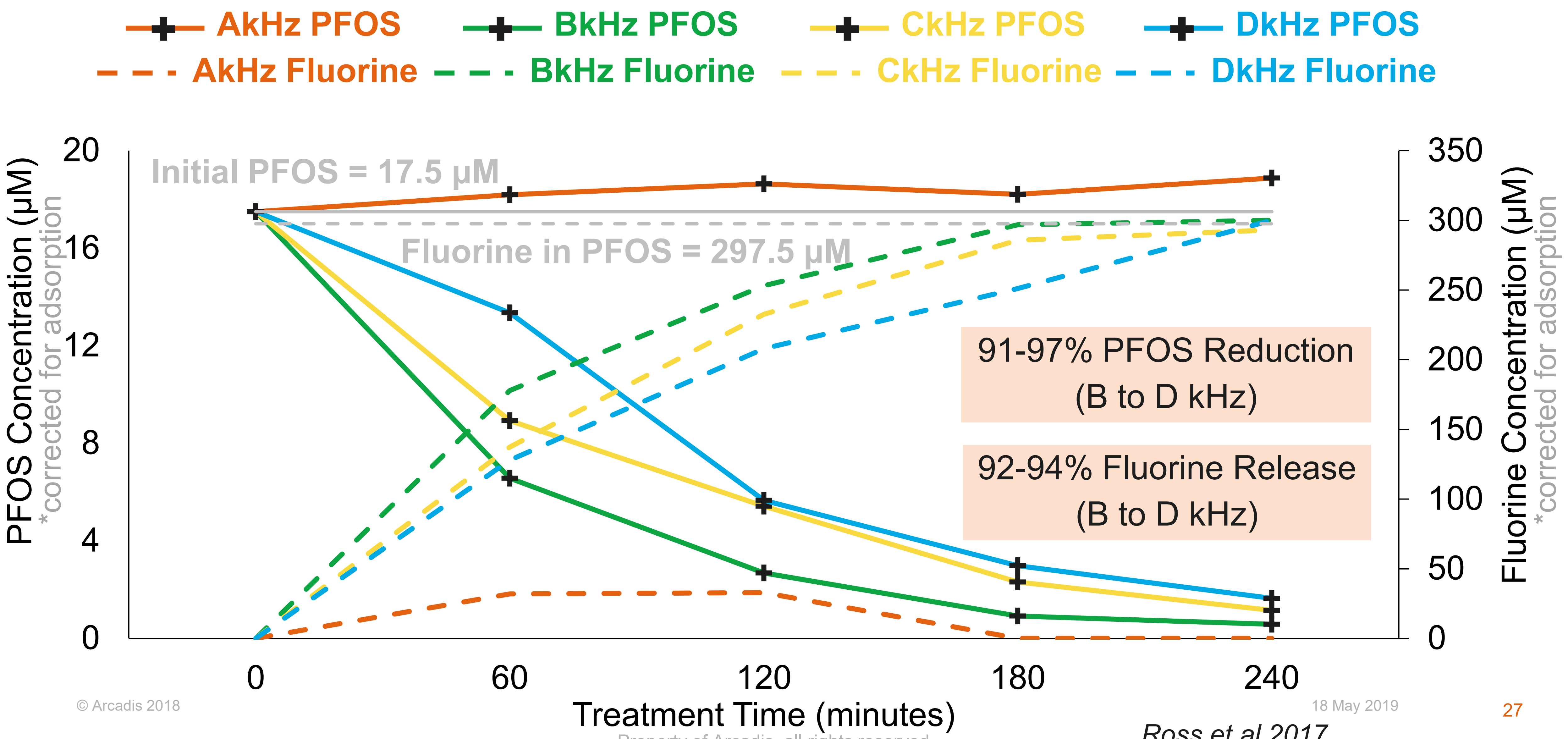
Distribution of liquid molecules

Bubble growth and collapse



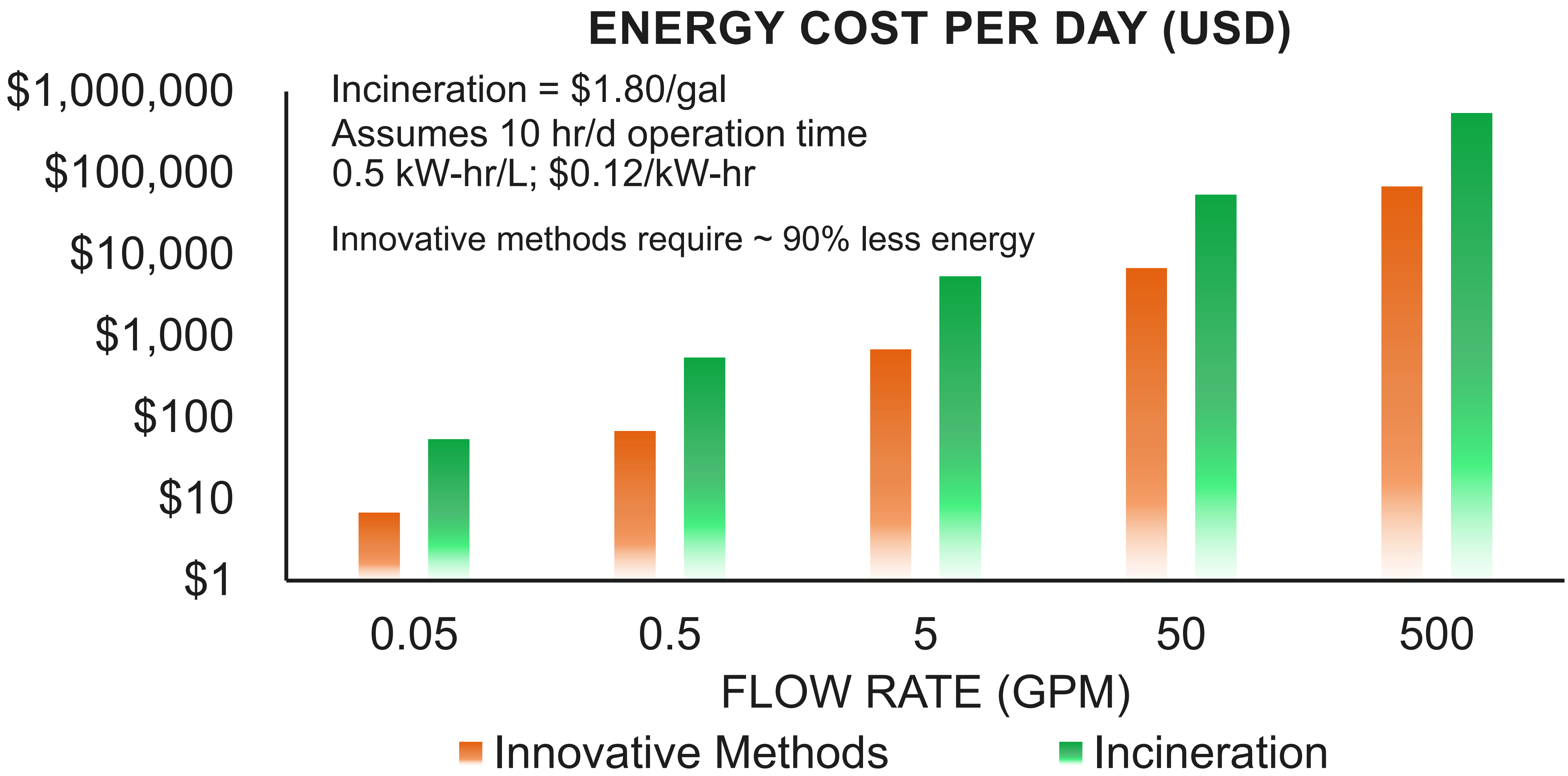
Adapted from Mason 2003

Sonolysis – Proof of Concept Testing



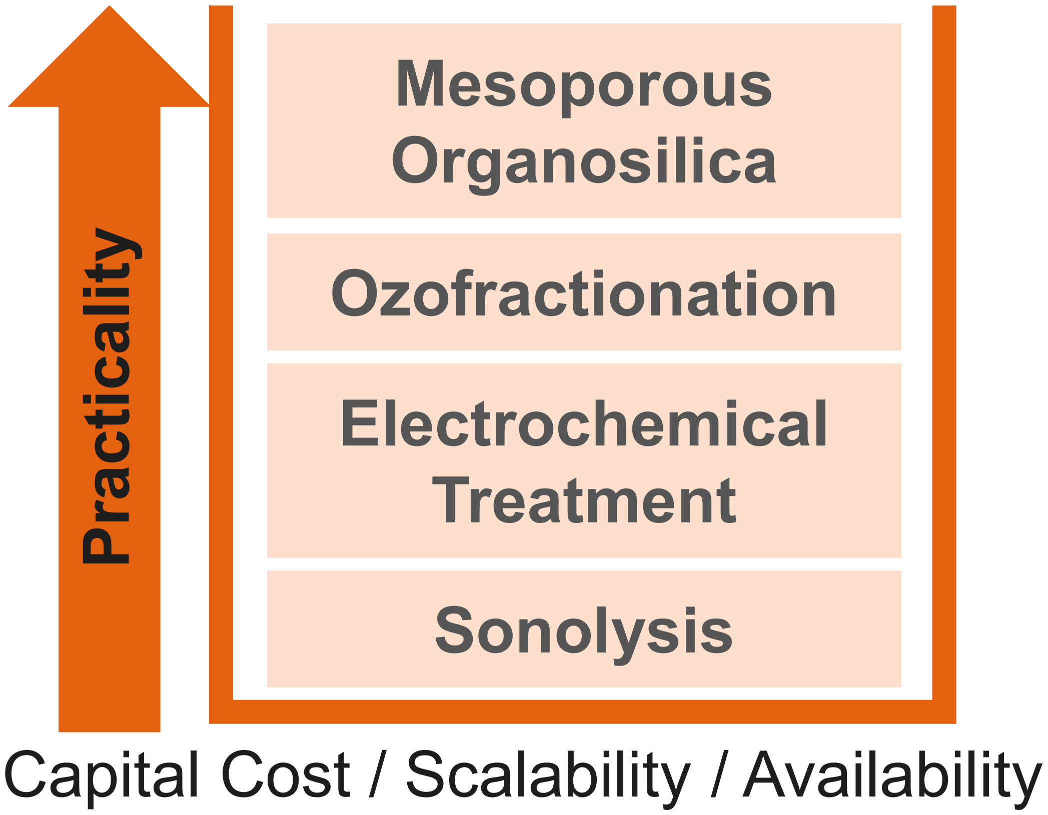
Ross et al 2017

PFAS Destruction Energy Considerations



ARP, Sonolysis, Electrochemical Treatment

Current Status of Developing Treatment



Summary

Recalcitrant PFAS chemistry and precursor loading are relevant in remediation consideration

Ex situ treatment trains are the current state of the practice for groundwater

Few practical destructive techniques exist, with some in development

"Quick fix" interim remedial actions come with a life-cycle price tag

Don't abandon institutional knowledge (myth busting, Remediation Hydraulics principles, etc.)!

Thank you!

Acknowledgements:

- Ian Ross, Arcadis
- Jeff Burdick, Arcadis
- Erika Houtz, Arcadis
- Paul Edmiston, College of Wooster
- Michael Dickson, Evocra
- Rominder Suri, Temple

TOP 10 TIPS FOR CHOOSING YOUR PFAS LABORATORY

Stephen Beek
Business Development Manager- New England

#10- Price

- Pricing can vary greatly from lab to lab
- Can vary greatly for $200 a sample- over $500 per sample
- Price can be dependent on many variables
  - Turn around Time(10 -30 Day TAT)
  - Method
  - Reporting Limits
  - Site History
  - Matrix
  - Compound List
  - Lab capacity
  - Deliverables

#9- Certifications

When choosing you need to make sure your laboratory has the proper certifications. NEVER ASSUME!

- DOD
- State Programs
- Special Programs within States
- Changing monthly if not weekly

#8- Data Packages

You want to verify your lab partner can provide these reports, with the scrutiny in which these projects are reviewed all of the data can matter:

- EDD's
- QC Data
- CLP Packages
- Tables Only not Recommended

#7- Correct Method

Method 537.1-Drinking Water 2018

ASTM Methods (D7979-17 & D7968-17A)

Isotope Dilution

Top Assay

QSM- 5.1 or Greater

SW-846

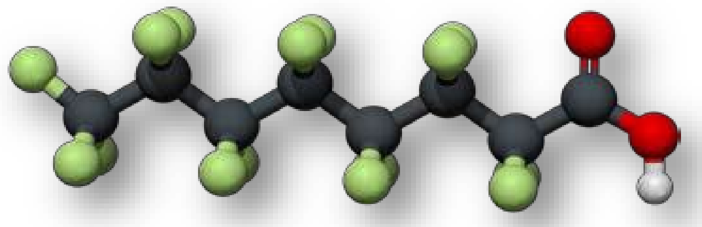
Method 8327 -Coming

Method 8328-Coming

PIGE

#6- Compound List

- There are thousands of PFAS compounds in the environment
- Commercial labs have standards for 40 or so compounds
- Most regulatory agencies are looking at even less



So Things to Consider:

  - What list to run?
  - How many compounds do you want to see?
  - What’s the goal of your sampling event?

#5-Reporting Limits

Extremely low limits here!

- On aqueous samples looking at Parts per Trillion
- Sludge/Soil Parts per Billion
- EPA Guidance
- State Guidance
- Consider the Risk Assessment

#4-Consulting Services

When your looking to speak to your lab partner:

- Are they available?
- Are they helpful?
- What access do you have to Lab Managers, Supervisors, Directors?
- Matrix Questions?

#3-Experience

Question to Ask Your Laboratory:

- How long has your lab been providing this type of analysis?
- Besides Certification how familiar are you with this method?
- What type of instrument?
- Does the lab participate in educational events or work groups?
- Does the lab have a working relationship with state regulatory bodies?

#2-Customer Service

Is your lab able to assist with the many FAQ's that come on these projects

- Proper Media
- Field Blanks
- Trip Blanks
- Duplicates
- MSD/MSRD
- Chain of Custody
- Project Set-Up in LIMS

#1-Data Quality

PFAS sites are getting a lot of scrutiny!

For many of you, your next project will be your first one

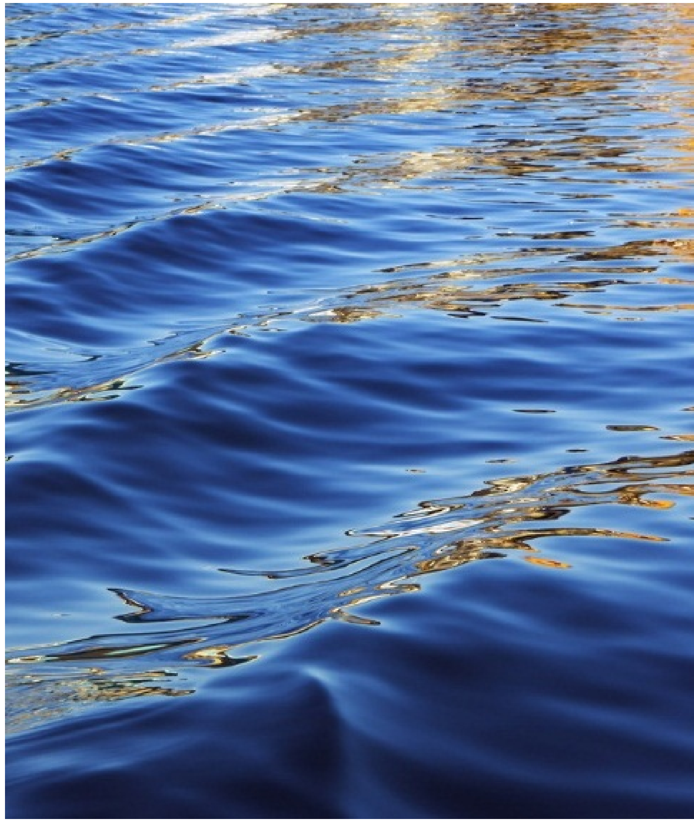
Make sure your lab partner is following the SOPs

This market is changing every month, week, and day.

Is your lab continuing to invest and keep up?

Thank You!

Stephen Beek
Con-Test Analytical Laboratory
Stephen.beek@contestlabs.com
(413) 519-9497



An overview of what we know about PFAS toxicology

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East Carolina University
Greenville, NC
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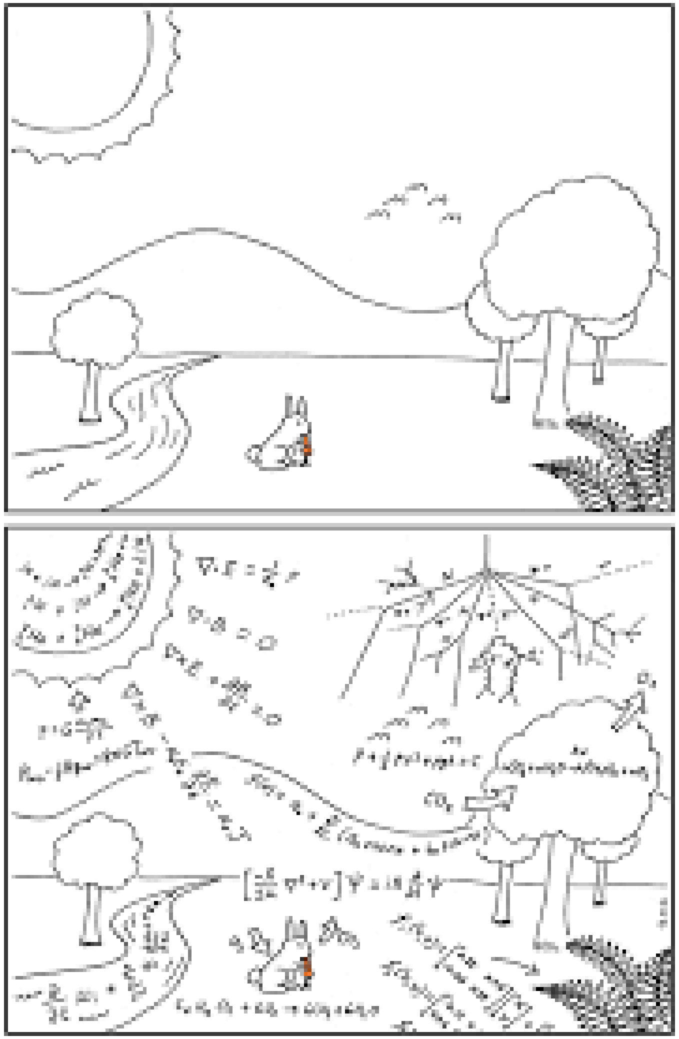
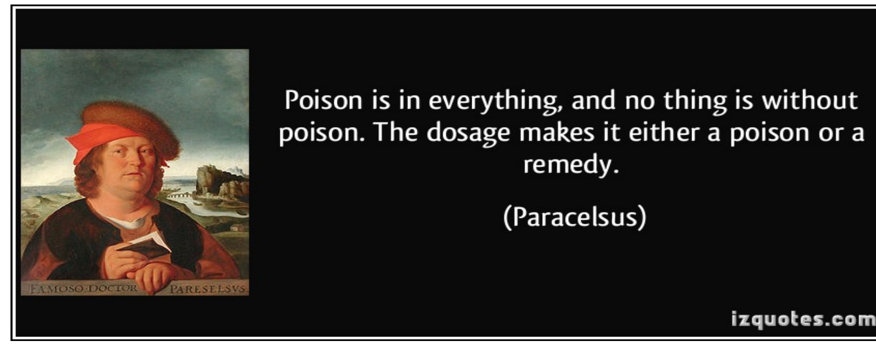
Presented for:
PFAS and Other Emerging Contaminants Conference
April 23-24, 2019

How I think engineers view the world

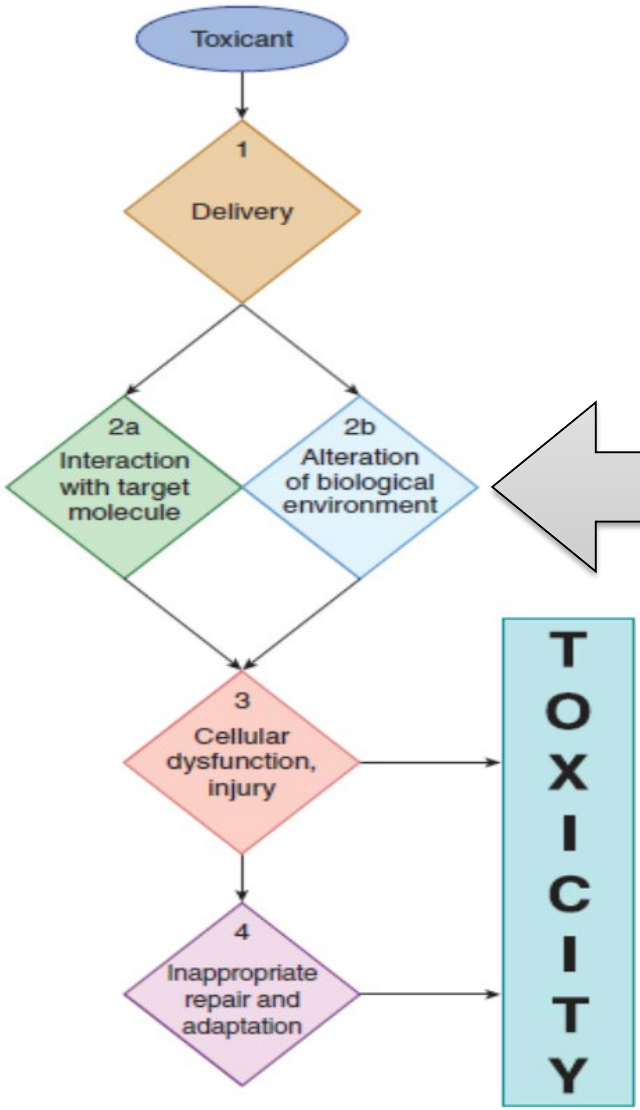


How I think people think toxicologists view the world



Everything can be toxic, it's "the dose that makes the poison."

How toxicologists view the world



Yes, there has to be sufficient DOSE for interaction and alteration but it is more than just the dose that makes the poison.

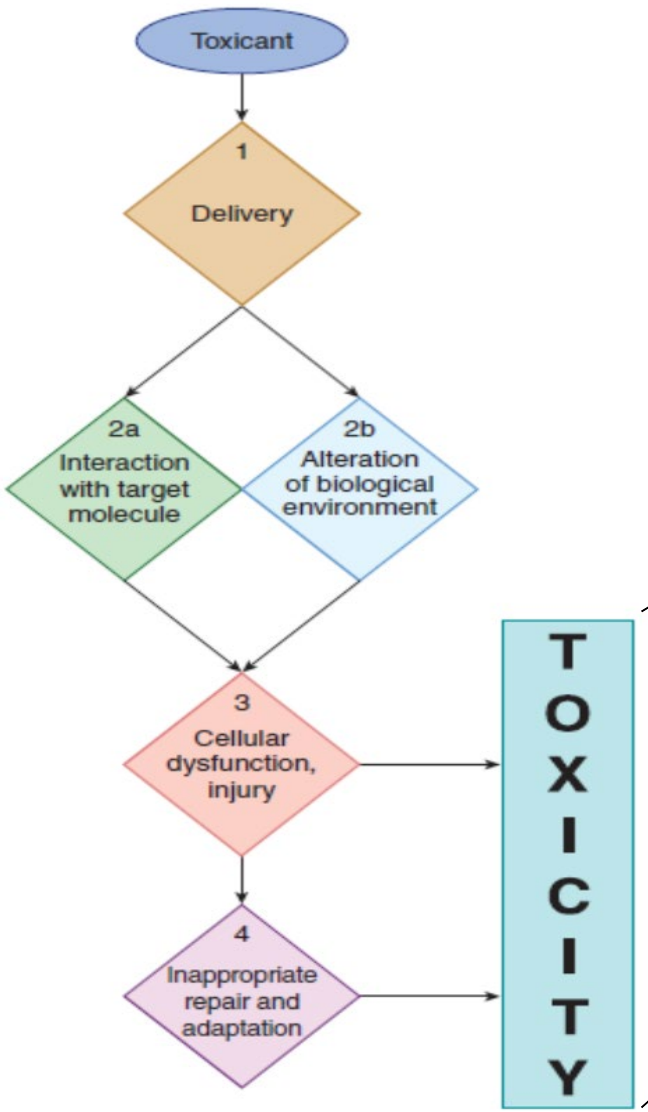
Figure adapted from Casarett & Doull's Essentials of Toxicology, 3rd Edition.

Factors affecting toxicity

- Chemical composition of toxicant
- The exposure scenario
  - ✓ Frequency, duration, route
- Species/strains/race/ethnicity
- Factors relating to exposed individual
  - ✓ Age
  - ✓ Sex
  - ✓ Nutritional/health status
  - ✓ Genetic make-up

These factors also influence toxicity, in addition to the dose.

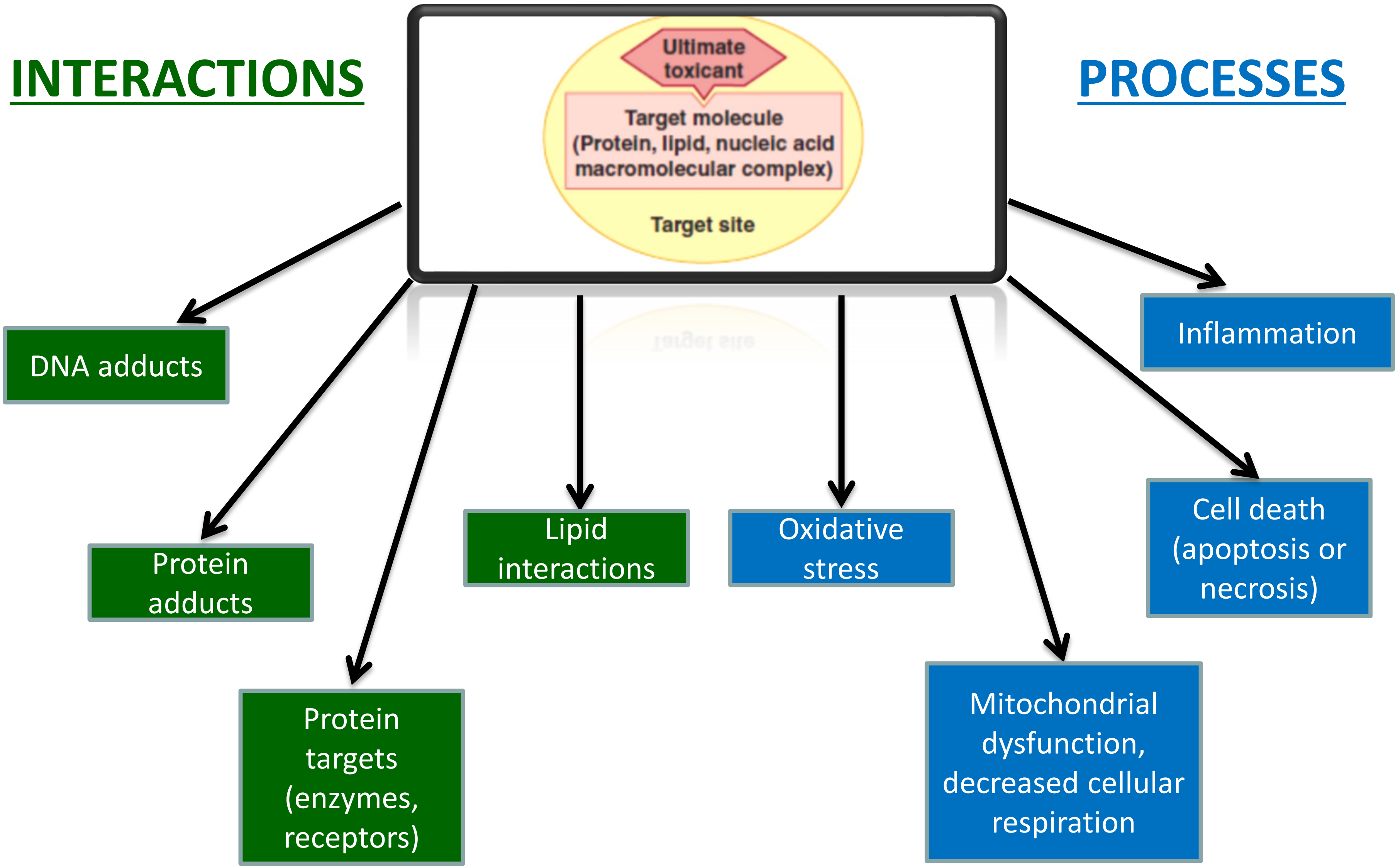
Toxicity defined (finally)



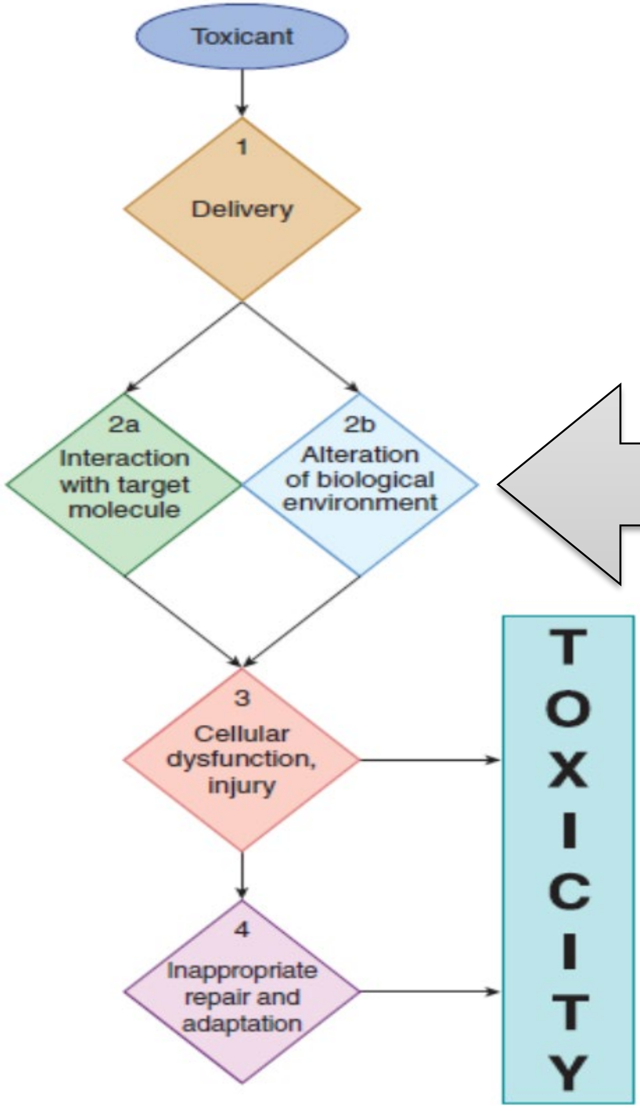
Undesirable effects that also are <u>deleterious</u> (i.e., adverse or toxic).

Figure adapted from Casarett & Doull's Essentials of Toxicology, 3rd Edition.

Types of toxic effects



How toxicologists view the world



Dose can be **external**, i.e., what someone takes in, or **internal**, i.e., what is inside of the body.

This matters a great deal for PFAS.

Figure adapted from Casarett & Doull's Essentials of Toxicology, 3rd Edition.

Ex: Dose or “relative potency” of GenX to PFOA

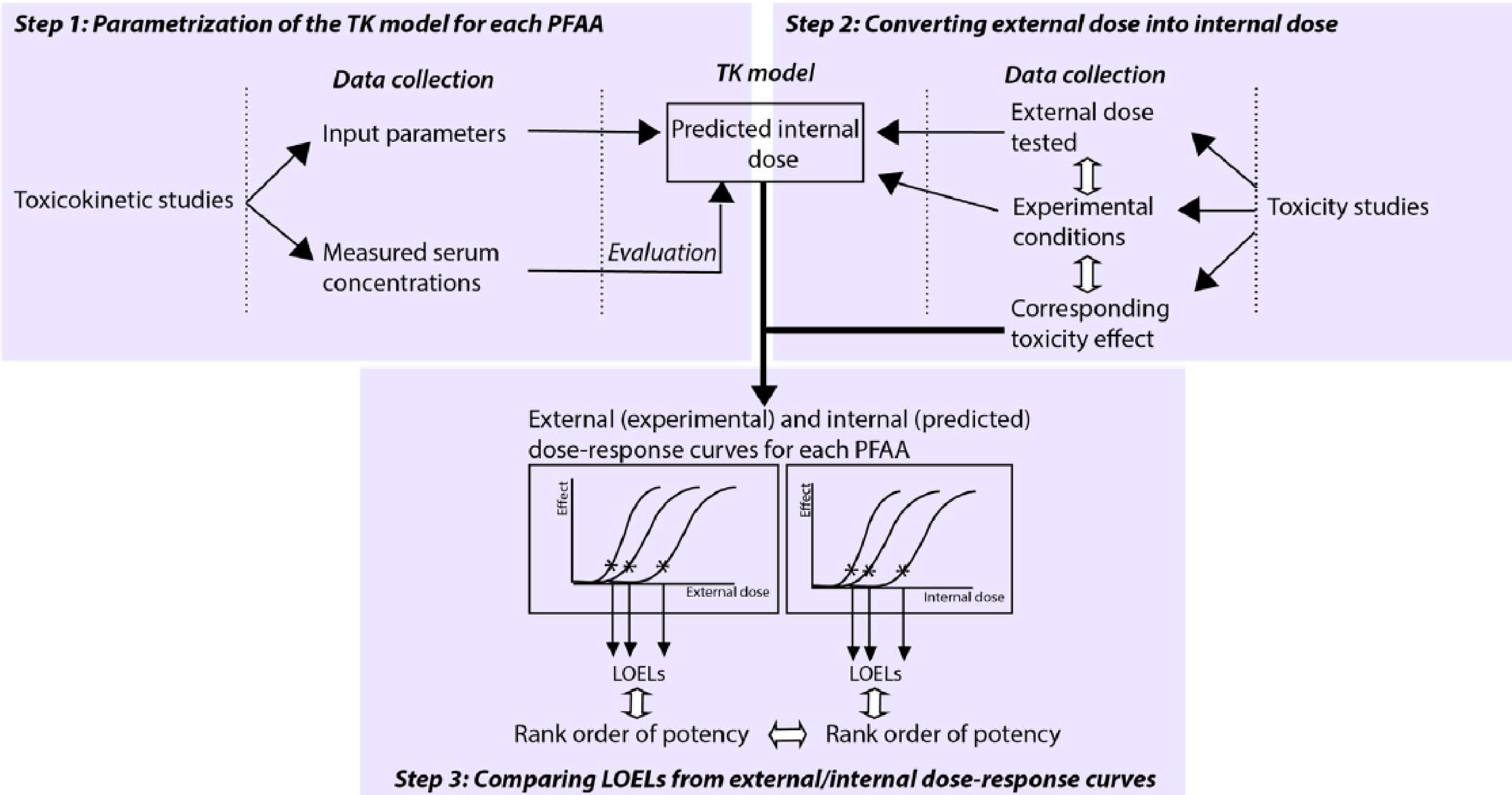


Figure from: Gomis et al. 2018. Env. Int.

Ex: Dose or "relative potency" of GenX to PFOA

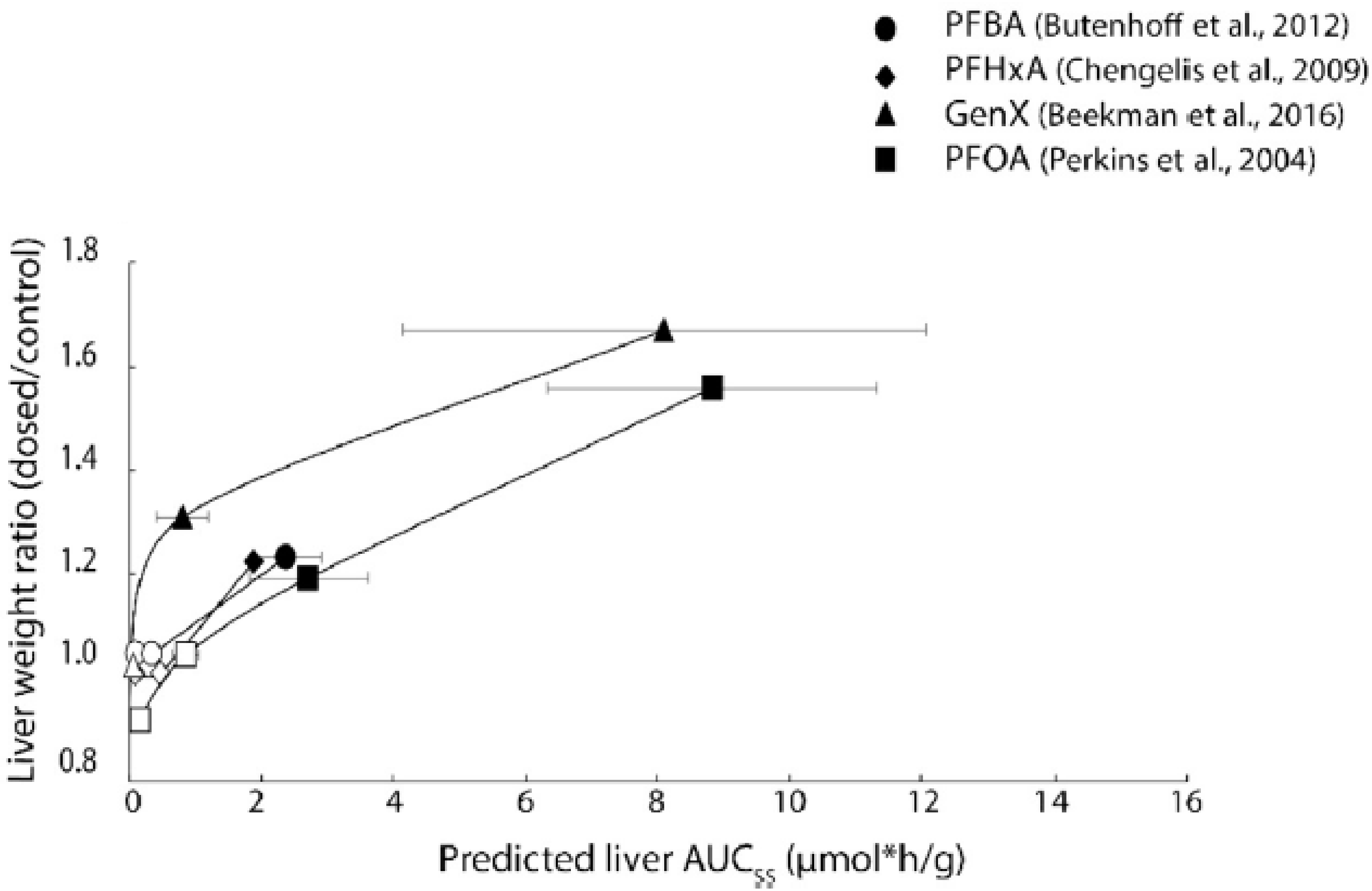


Figure from: Gomis et al. 2018. Env. Int.

Major conclusions of Gomis et al. (2018):

- GenX appears less toxic than PFOA because it is eliminated more rapidly and has lower relative distribution to the liver.
- *However*, the concentration of GenX at the target site (i.e., liver), which can be calculated from the internal dose, is what really determines toxicity.
- *Therefore*, GenX is more potent than PFOA at inducing increases in liver weight, on an internal dose basis.

Figure from: Gomis et al. 2018. Env. Int.

What this all means for public health protection

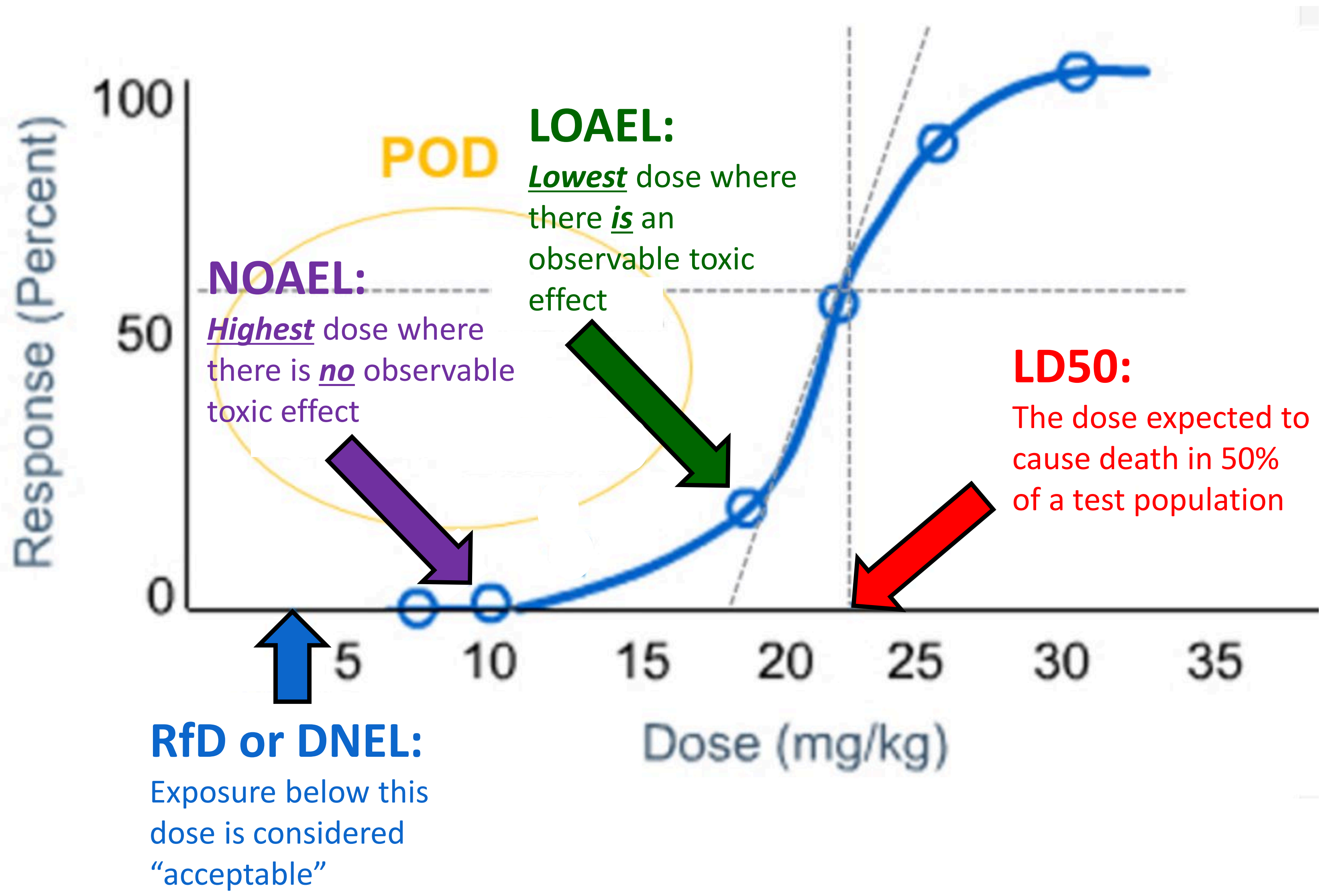


Figure adapted from http://www.chemsafetypro.com

EPA | United States Environmental Protection Agency | Office of Water Mail Code 4304T | EPA 822-R-16-003 May 2016

Health Effects Support Document for Perfluorooctanoic Acid (PFOA)

↓

Reference dose = 0.00002 mg/kg/day

derived from a study by Lau et al. (2006) demonstrating *developmental toxicity* in an *rodent model*.

Critical point

RfD was based on "human equivalent dose" rather than administered dose.

For example:

Lau et al. (2006) reported a LOAEL of 1.0 mg/kg/day with an average serum concentration of 38 mg/L. This corresponds to a human equivalent dose of 0.0053 mg/kg/day.

Why is this important for PFOA and other PFAS?

This value represents translation of rodent data to humans. For PFOA, was based largely on differences in "half-life" or elimination of PFOA from serum.

It takes much longer for PFOA to leave humans compared to rodents.

https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final_508.pdf

U.S. EPA health advisory level for PFOA (and PFOS) in drinking water

FACT SHEET
PFOA & PFOS Drinking Water Health Advisories

EPA's 2016 Lifetime Health Advisories, continued

To provide Americans, including the most sensitive populations, with a margin of protection from a life-time of exposure to PFOA and PFOS from drinking water, EPA established the health advisory levels at 70 parts per trillion. When both PFOA and PFOS are found in drinking water, the combined concentrations of PFOA and PFOS should be compared with the 70 parts per trillion health advisory level. This health advisory level offers a margin of protection for all Americans throughout their life from adverse health effects resulting from exposure to PFOA and PFOS in drinking water.

EPA's health advisory levels were calculated to offer a margin of protection against adverse health effects to the most sensitive populations: fetuses during pregnancy and breastfed infants. The health advisory levels are calculated based on the drinking water intake of lactating women, who drink more water than other people and can pass these chemicals along to nursing infants through breastmilk.

Health advisory levels were based on the RfD for PFOA (and for PFOS) derived in the health effects documents.

What DO we know about PFAS toxicology?

Undesirable effects that also are deleterious
(i.e., adverse or toxic).

The immune system as an example.

Immunotoxicity defined

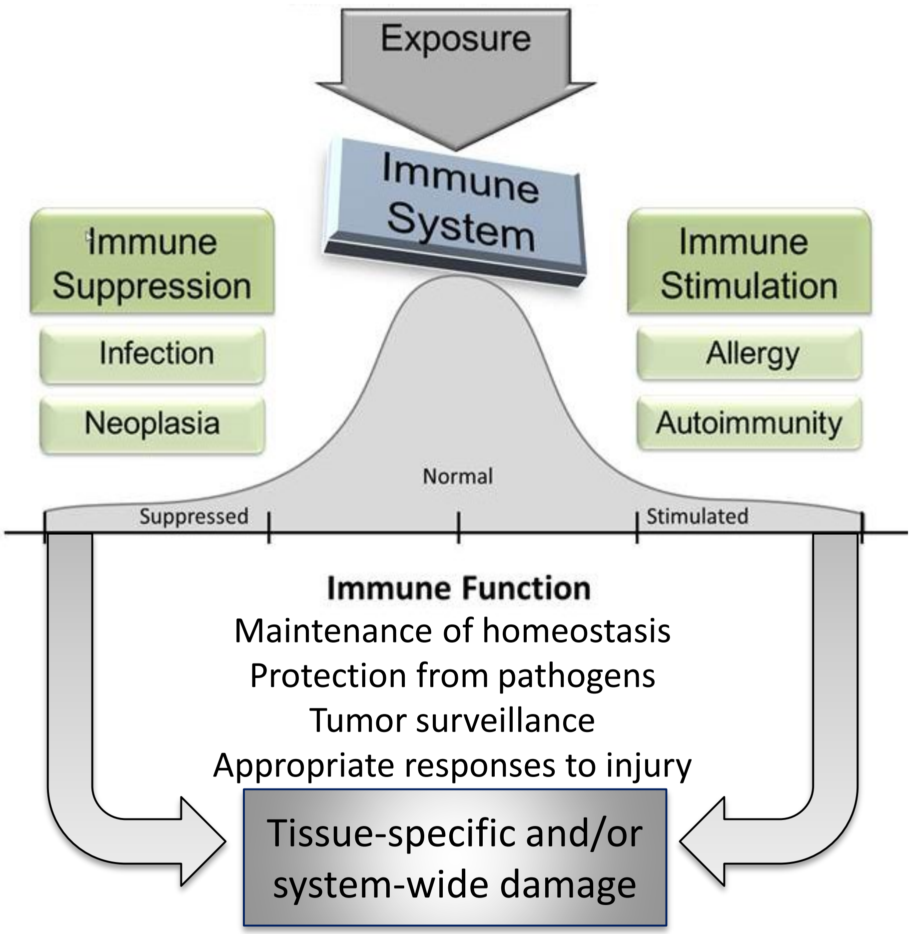


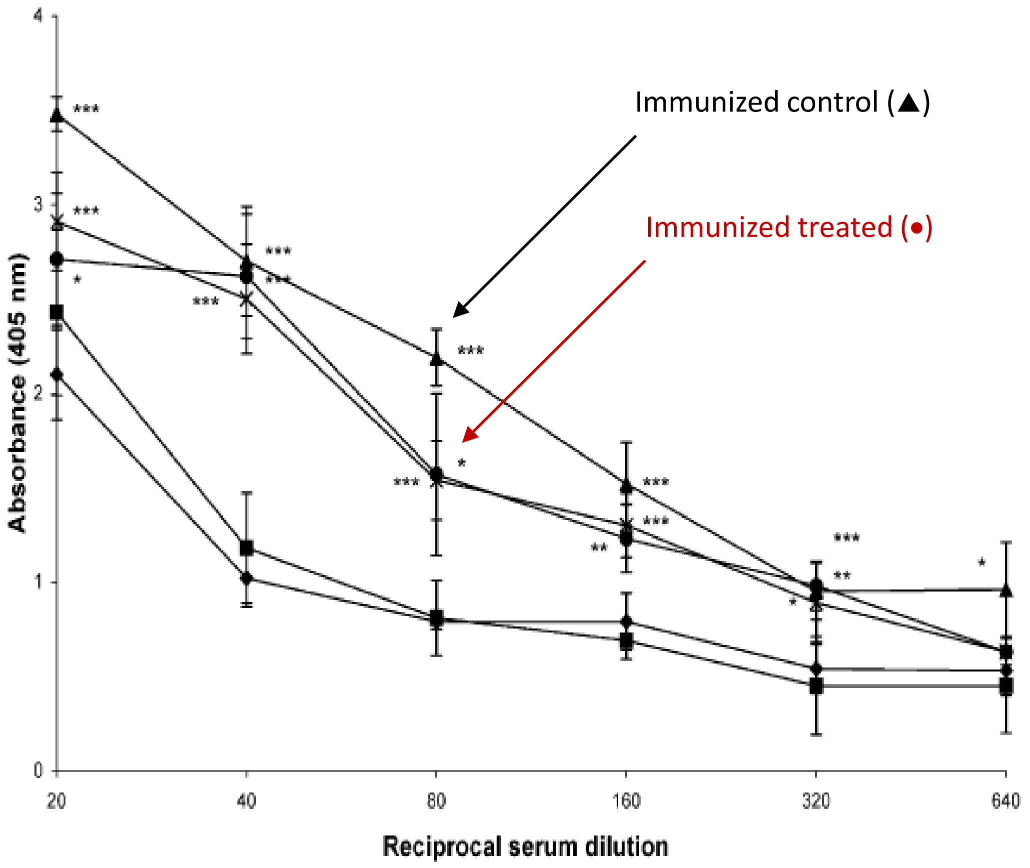
Figure courtesy of Dr. Andrew Rooney, NTP/NIEHS/OHAT.

According to the National Toxicology Program:

Immunotoxicity is defined in the context that **immune responses can be enhanced or suppressed by toxicants**. As such, dose-related effects consistent with immunosuppression and immunostimulation will be considered in hazard identification.

- **Functional effects**…should usually be weighed more heavily than observational parameters such as alterations in cell counts.
- Increases in severity and/or prevalence (more individuals with the effect) as a function of dose generally strengthen the level of evidence, keeping in mind that the specific manifestation may be different with increasing dose.
- Biological plausibility for immunotoxicity must be considered in the context of the nature of the response, the magnitude of the response, and the pattern of the response, as well as the current understanding of immune system structure and function.

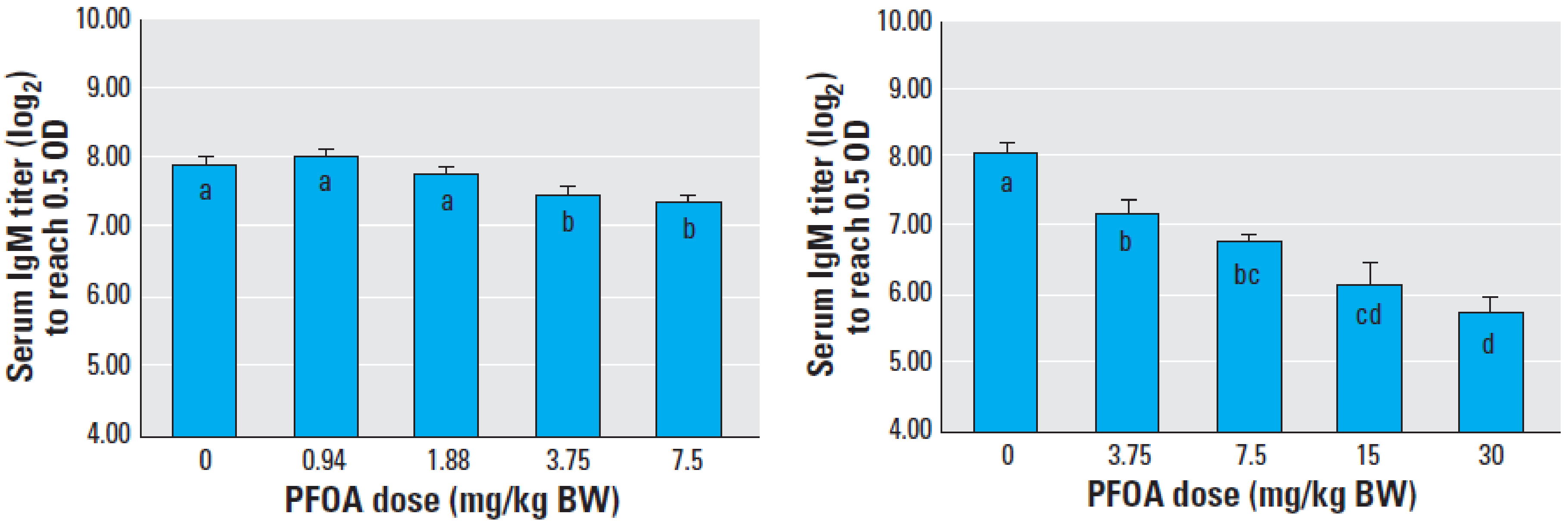
Back in the early 2000s: Immunotoxicity identified as endpoint of special concern by Science Advisory Board review of the U.S. EPA's preliminary PFOA risk assessment.



Observation: Suppression of adaptive immune function at a single dose of PFOA in a rodent model.

From: Yang et al. 2002. Int. Immunopharm.

Observation:
Dose-responsive suppression of adaptive immune function by PFOA in a rodent model.



From: DeWitt et al. 2008. EHP.

Table 4

Differences in Tetanus and Diphtheria Antibody Concentrations at Age 5 Years Prebooster and Age 7 Associated With a Doubled Concentration of PFCs for Maternal Pregnancy Serum and Age-5 Serum in a Structural Equation Model

	Tetanus, % Change (95% CI)	*P* Value	Diphtheria, % Change (95% CI)	*P* Value	*P* Value for Same Effect[a]	Joint Change, % (95% CI)	*P* Value
Age 5 prebooster							
Maternal PFC	−20.2 (−49.2 to 25.2)	.33	−47.9 (−67.7 to −15.9)	.008	.17	−31.1 (−56.8 to 9.8)	.12
PFC at age 5 y	−20.5 (−44.4 to 13.6)	.21	−7.9 (−38.0 to 37.0)	.69	.47	−15.6 (−38.5 to 15.8)	.29
PFC at age 5 y[b]	−17.2 (−42.1 to 18.5)	.30	−1.2 (−33.6 to 46.8)	.95	.39	−11.0 (−35.2 to 22.3)	.47
Age 7							
Maternal PFC	35.1 (−25.4 to 144.6)	.32	−42.0 (−66.1 to −0.8)	.047	.007		
PFC at age 5 y	−55.2 (−73.3 to −25.0)	.002	−44.4 (−65.5 to −10.5)	.02	.42	−49.4 (−66.7 to −23.0)	.001
PFC at age 5 y[b]	−58.8 (−76.0 to −29.3)	.001	−45.5 (−66.9 to −10.3)	.02	.31	−51.8 (−68.9 to −25.1)	.001

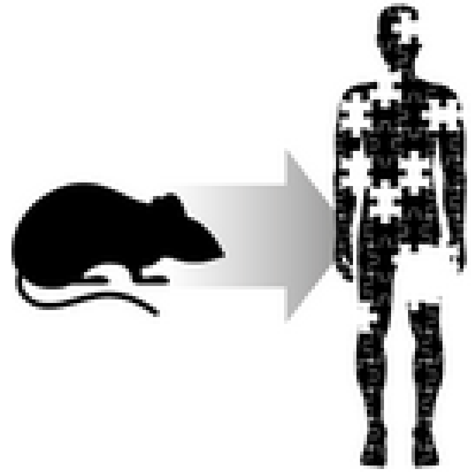
Abbreviation: PFC, perfluorinated compound.

[a]Determined by likelihood ratio test for the same effect of PFC on the 2 types of antibodies.
[b]Adjusted for the PFC concentration in maternal pregnancy serum.

Observation:

Suppression of adaptive immune function by PFOA (and PFOS) in humans from an environmentally-exposed population.

From: Grandjean et al. 2012. JAMA.



Observation:
Dose-responsive suppression of adaptive immune function by PFOA in a rodent model.

Observation:
Suppression of adaptive immune function by PFOA (and PFOS) in humans from an environmentally-exposed population.

Concordance between observations in rodents and humans = support for biological plausibility of adverse findings.

Image from: http://www.mouse2man.org/

National Toxicology Program
U.S. Department of Health and Human Services

SYSTEMATIC REVIEW OF IMMUNOTOXICITY ASSOCIATED WITH EXPOSURE TO PERFLUOROOCTANOIC ACID (PFOA) OR PERFLUOROOCTANE SULFONATE (PFOS)

Interpretation:
Based on the weight of the evidence (more than the previous three slides), PFOA and PFOS are presumed to be immune hazards to humans.

PFOA suppresses the TDAR in experimental models (high level of evidence) and humans (moderate level of evidence).

PFOS suppresses the TDAR in experimental models (high level of evidence) and humans (moderate level of evidence).

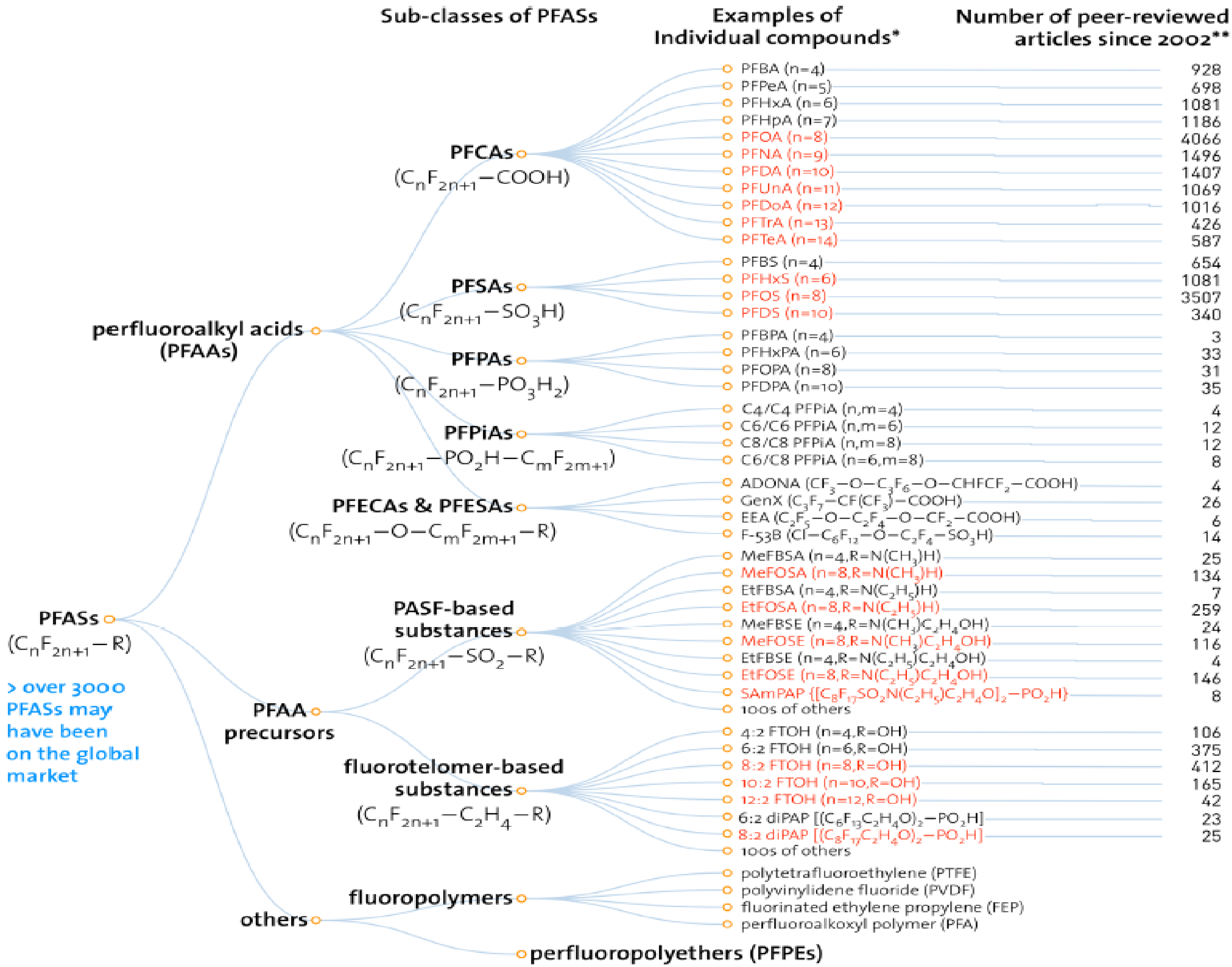
Other immune effects determined relevant to this classification:

- Increased hypersensitivity-related outcomes
- Suppression of innate immune responses (i.e., NK cell function)
- Alterations in disease resistance/infectious disease outcomes
- Autoimmunity

Adapted from: National Toxicology Program Systematic Review of PFOA and PFOS Immunotoxicity. 2016.

However, PFOA and PFOS are only **two** among **thousands** of compounds classified as PFAS.

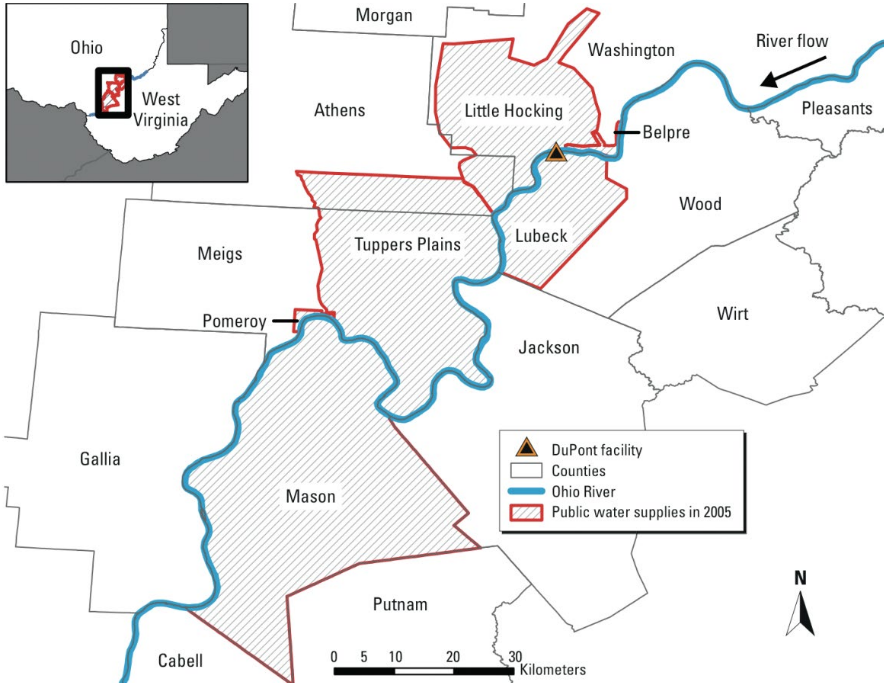
The immune system isn't the only system affected by exposure to PFAS.



* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).
** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Figure 1. "Family tree" of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAs and their major precursors.).

Figure from: Wang et al. 2017. ES&T.

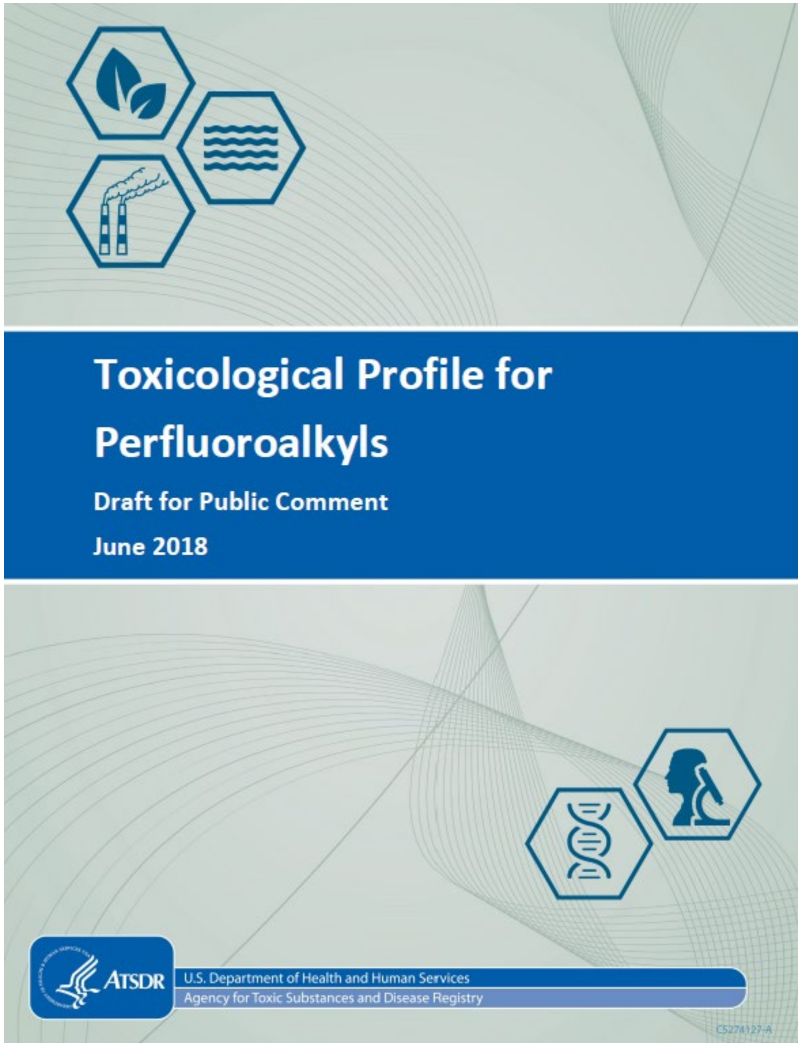


C8 Science Panel

http://www.c8sciencepanel.org

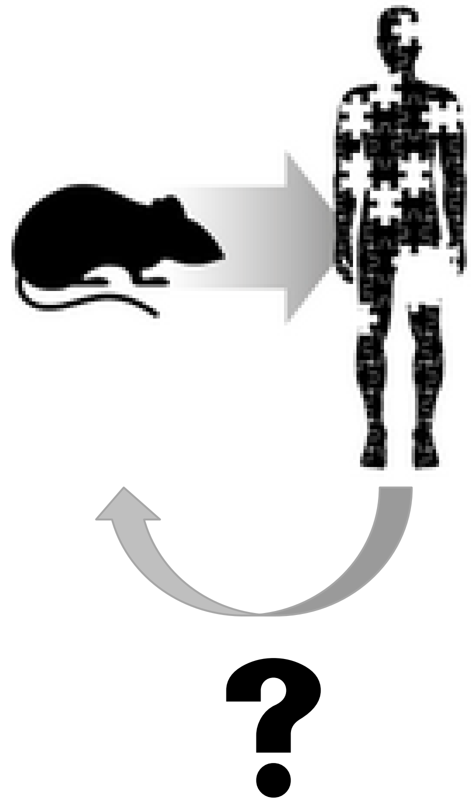
Health effects considered probable links *in this human population* exposed to PFOA in drinking water included:

- Cancer - kidney and testicular
- Diagnosed elevated cholesterol
- Pregnancy-induced hypertension and preeclampsia
- Thyroid Disease
- Ulcerative colitis



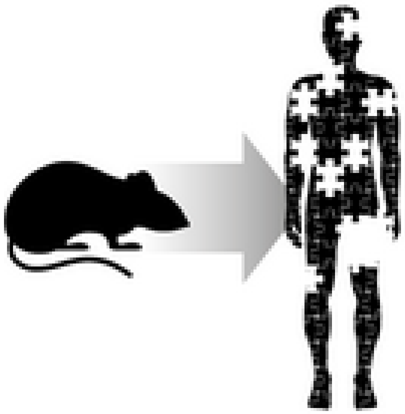
- Pregnancy-induced hypertension and preeclampsia (**PFOA, PFOS**)
- Liver damage, including increases in serum enzymes and decreases in serum bilirubin levels (**PFOA, PFOS, PFHxS**)
- Increases in serum lipids, particularly total cholesterol and low density lipoprotein cholesterol (**PFOA, PFOS, PFNA, PFDeA**)
- Increased risk of thyroid disease (**PFOA, PFOS**)
- Decreased antibody response to vaccines (**PFOA, PFOS, PFHxS, PFDeA**)
- Increased risk of asthma diagnosis (**PFOA**)
- Increased risk of decreased fertility (**PFOA, PFOS**)
- Small decreases in birth weight (**PFOA, PFOS**)

These findings are from studies of people who worked with PFAS, lived near a PFOA manufacturing facility with high levels of PFOA in water, and/or who were members of the general population.



Where are we now with other observations of these adverse findings that have been summarized by the C8 Health Science Panel and the ATSDR?

Image from: http://www.mouse2man.org/



Rodents typically exhibit the “tumor triad” (liver, pancreatic, and testicular tumors) ← *Cancer - kidney and testicular*

Rodents tend to have *decreased* cholesterol ← *Diagnosed elevated cholesterol*

Rodents develop changes in thyroid hormone levels ← *Thyroid disease*

Reproductive & developmental toxicity have been observed in rodents ← *Pregnancy-induced hypertension and pre-eclampsia*

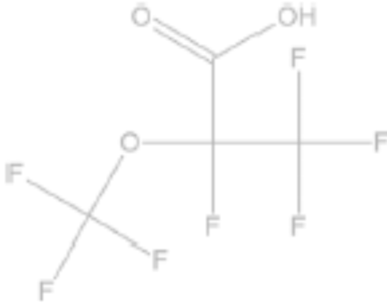
Autoimmune/inflammatory alterations have been observed in rodents ← *Ulcerative colitis*

Image from: http://www.mouse2man.org/

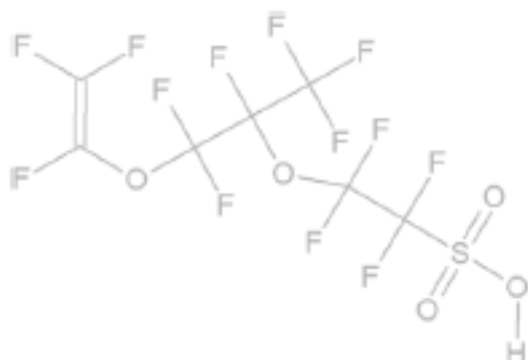
“Given the large number of substances in the PFAS family, the participants agreed that actions need to address groups of PFASs rather than individual chemicals and that such a grouping approach needs to be scientifically sound.”

--Zurich Statement on Future Actions of Per- and Polyfluoroalkyl Substances (PFASs)

Figures from: Hopkins et al. 2018. Journal AWWA. Quote from: Ritscher et al. 2018. EHP.



“To critically evaluate the idea that PFASs are essential in modern society, The essentiality of PFASs should be carefully tested against the available evidence for each of their uses.”

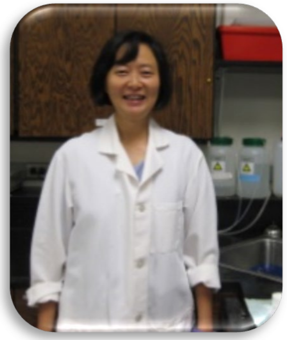


Figures from: Hopkins et al. 2018. Journal AWWA. Quote from: Cousins et al. 2019. Under review at ESPI.

Acknowledgements

Luebke Lab at the U.S. EPA

PFOA



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GenX

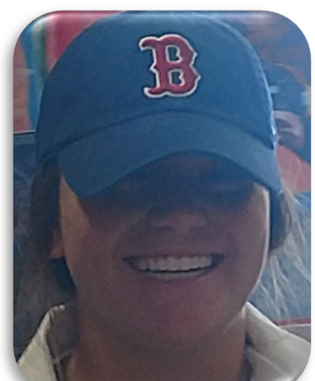
Chastity Ward (UG)

Dr. Chris Higgins
CO School of Mines

AFFF

Dr. Detlef Knappe
NC State

PFAST Network



Sam Vance (MS), Katie Ferris (UG), Dr. Tracey Woodlief (postdoc)

Thank you for listening.

Image from: Wang et al. 2017. ES&T.

Geosyntec consultants

engineers | scientists | innovators

Prioritization of Exposure Pathways at Sites Impacted by PFAS

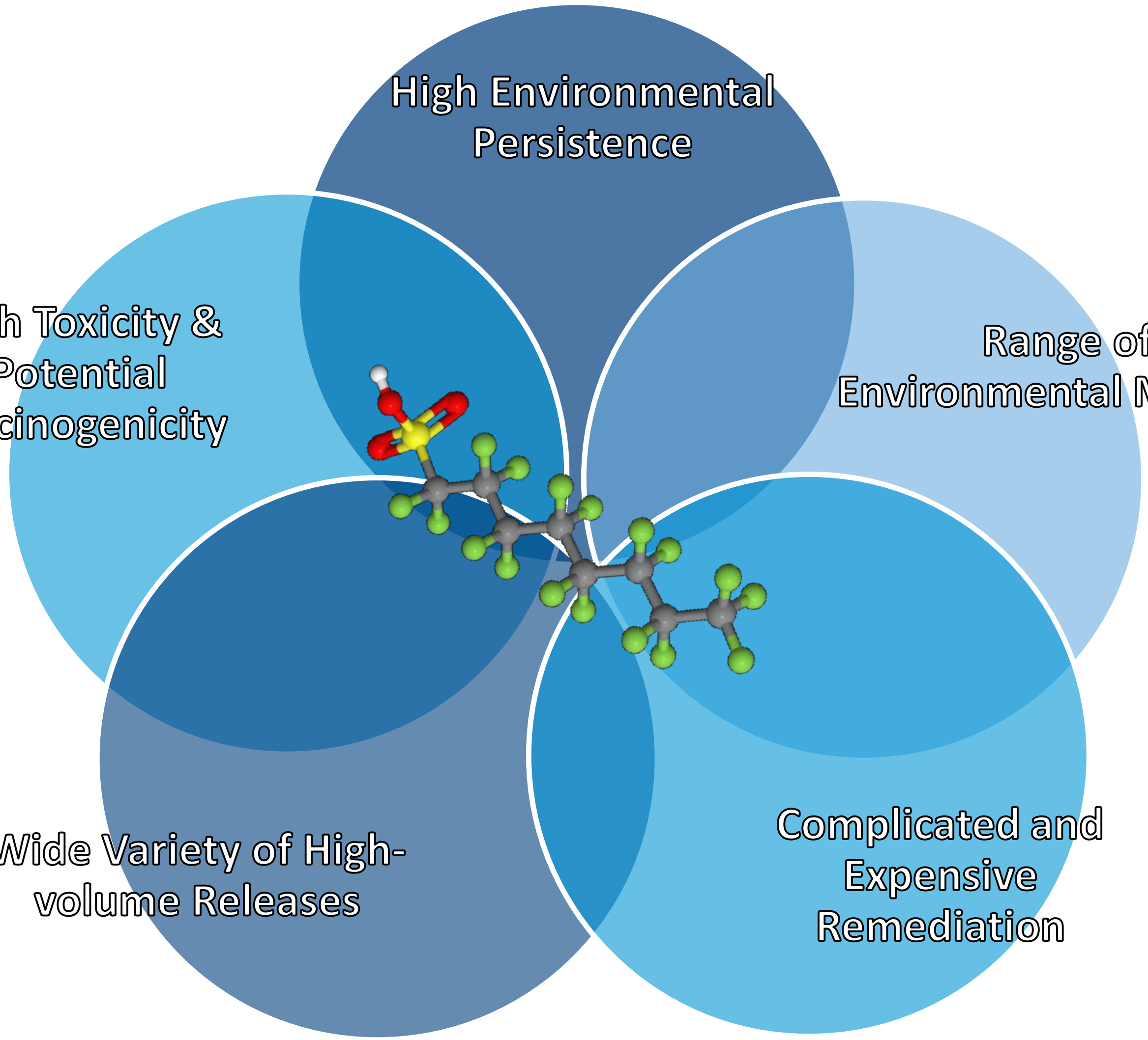
Jennifer Arblaster

June, 2019

Why PFAS?

Geosyntec consultants

A Perfect Storm of Environmental Challenges



Chemical Type Affects Bioaccumulation

Functional Group

Carboxylates PFCAs (e.g., PFOA, PFNA)

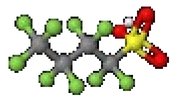
Less bioaccumulative

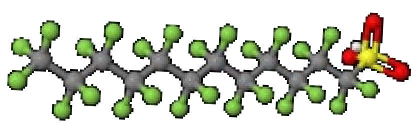
↓

Sulfonate PFSAs (e.g., PFOS, PFDS)

More Bioaccumulative

Perfluorinated-carbon Chain Length



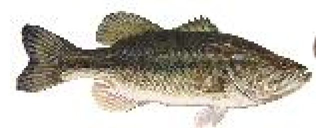


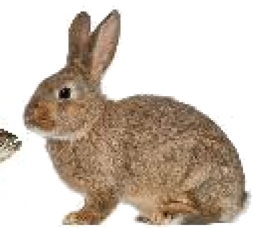
More bioaccumulative

↓

Less bioaccumulative

Less bioaccumulative



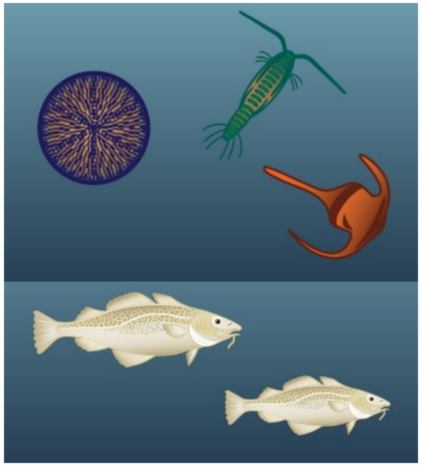


↓

More bioaccumulative

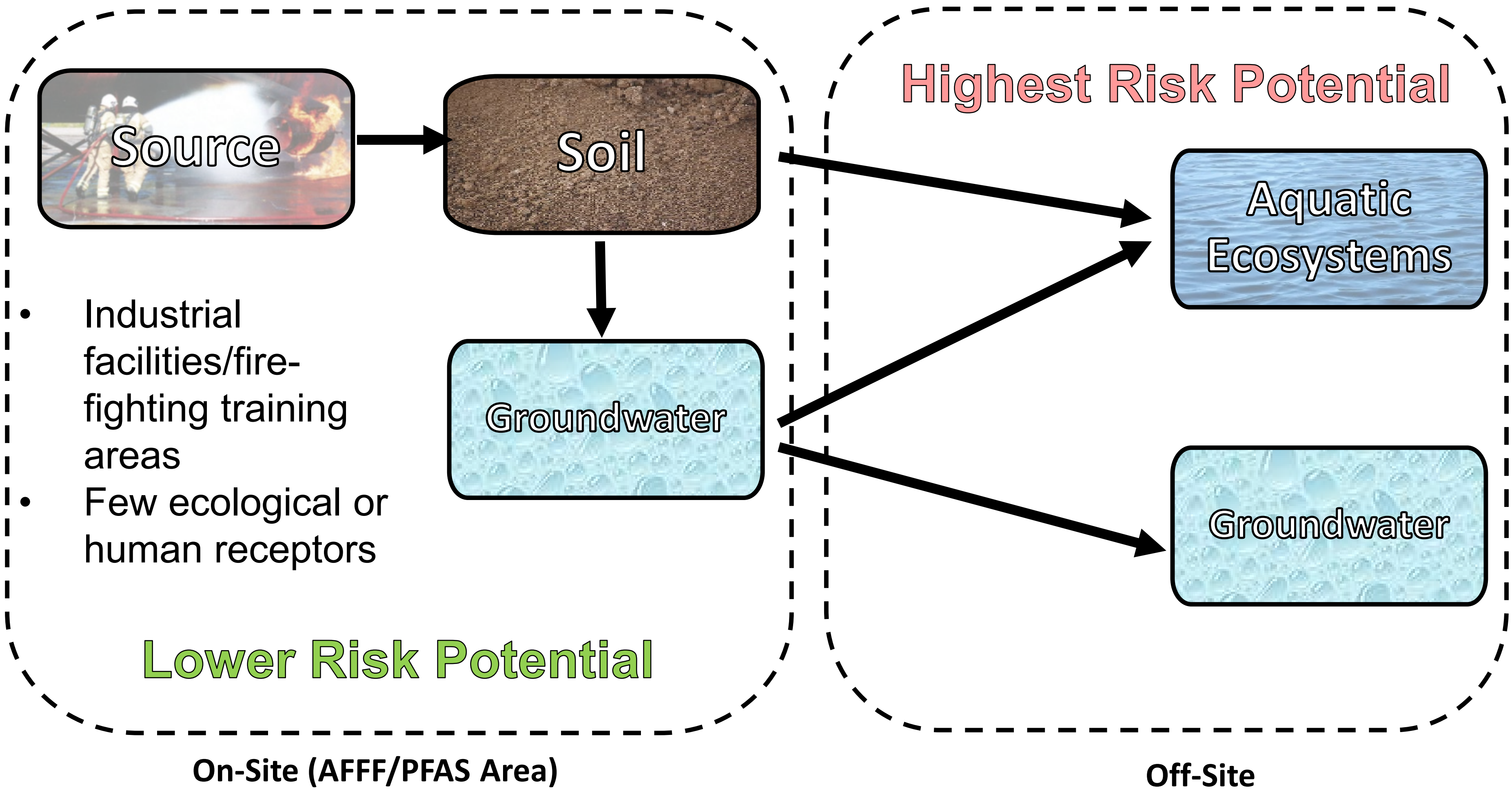
Toxicology of PFAS to Ecological Receptors

- Wildlife effects (mammals and birds)
  - Effects on liver and kidney
  - Reproduction
- Plants and soil invertebrates
  - Relatively insensitive – effects occur in the mg/kg range (higher than other concerns)
- Aquatic toxicity data (fish, invertebrates)
  - Most direct toxic effects occur at concentrations much higher than other concerns (e.g., drinking water), but high uncertainty/controversy



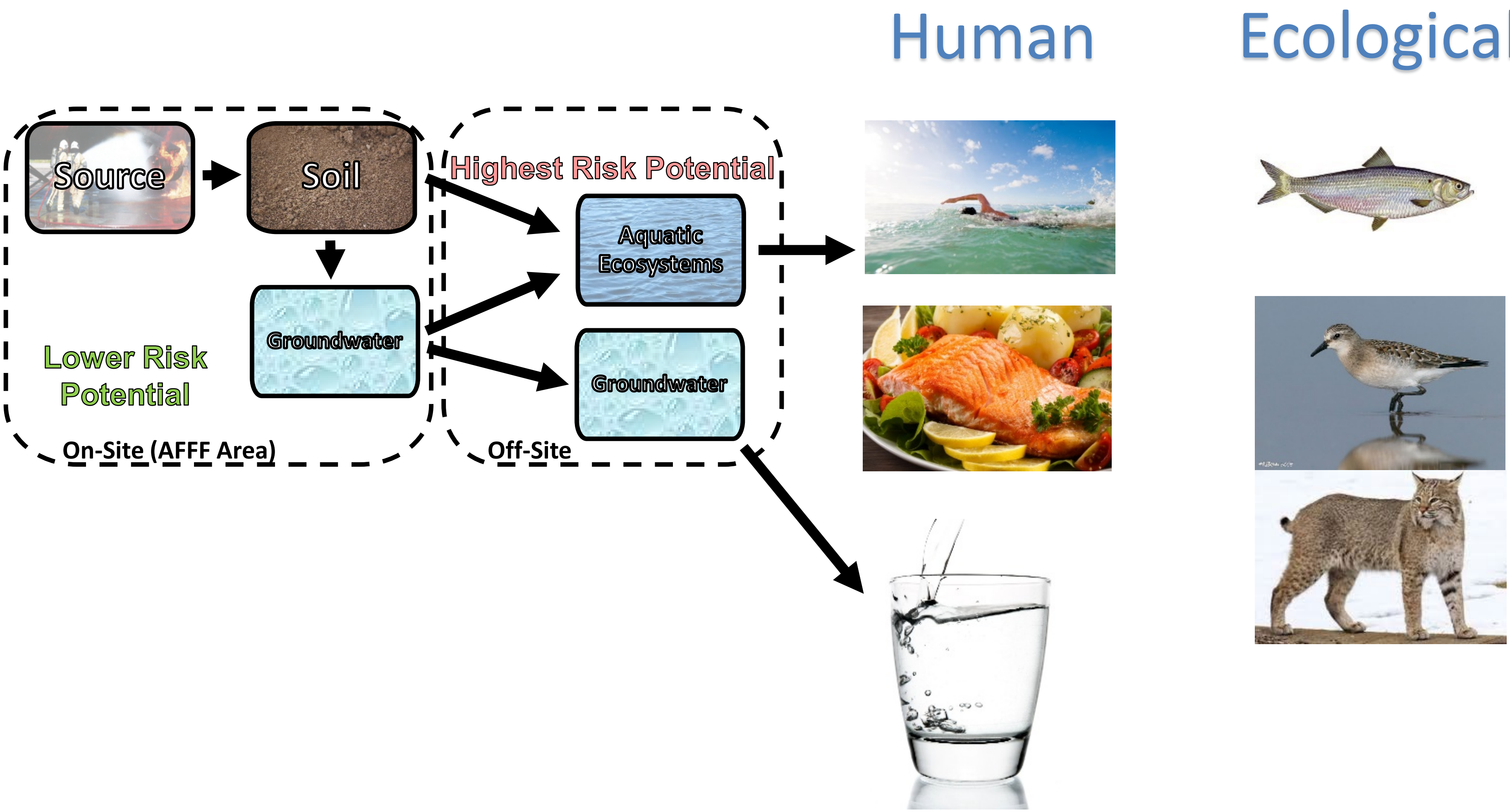
Conceptual Site Model for PFAS Site

Geosyntec consultants



- Industrial facilities/fire-fighting training areas
- Few ecological or human receptors

Exposure Pathways at PFAS Sites



Ecological Risk Modeling: Aquatic-dependent Birds and Mammals

Geosyntec consultants

- 5 example AFFF case study sites
- 7 PFAS tracked:
  - PFCA: PFHxA, PFOA, PFNA, PFDA
  - PFSA: PFHxS, PFOS, PFDS
- Model Input, measurements of:
  - PFAS in sediment and water
  - PFAS in fish (2 sites)
  - Organic carbon content in sediment
- Model Output, predictions of:
  - PFAS Total Daily Intakes (TDIs) for 4 avian & 2 mammalian receptors, Fractions of TDIs from sediment/water/diet
- More details in Larson et al. 2018

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

Modeling avian exposures to perfluoroalkyl substances in aquatic habitats impacted by historical aqueous film forming foam releases

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[b] Geosyntec Consultants, 2100 Main Street, Suite 150, Huntington Beach, CA 92648, USA

HIGHLIGHTS

- We modeled the exposure of 7 PFASs to birds in aquatic ecosystems impacted by AFFF.
- Modeled exposures exceeded levels of potential concern for 3 of 5 model scenarios.
- Perfluoroalkyl sulfonic acids, especially PFOS, comprised >90% of PFAS exposures.
- Sediment, not water, represented the primary abiotic source of PFAS exposure.

GRAPHICAL ABSTRACT

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Aqueous Film Forming Foam (AFFF)
Perfluorooctane sulfonic acid/perfluorooctane sulfonate (PFOS)
Ecological risk assessment
Bioaccumulation

ABSTRACT

Releases of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) associated with Aqueous Film Forming Foams (AFFFs) have the potential to impact on-site and downgradient aquatic habitats. Dietary exposures of aquatic-dependent birds were modeled for seven PFASs (PFHxA, PFOA, PFNA, PFDA, PFHxS, PFOS, and PFDS) using five different scenarios based on measurements of PFASs obtained from five investigations of sites historically-impacted by AFFF. Exposure modeling was conducted for four avian receptors representing various avian feeding guilds: lesser scaup (*Aythya affinis*), spotted sandpiper (*Actitis macularia*), great blue heron (*Ardea herodias*), and osprey (*Pandion haliaetus*). For the receptor predicted to receive the highest PFAS exposure (spotted sandpiper), model-predicted exposure to PFOS exceeded a laboratory-based, No Observed Adverse Effect Level exposure benchmark in three of the five model scenarios, confirming that risks to aquatic-dependent avian wildlife should be considered for investigations of historic AFFF releases. Perfluoroalkyl sulfonic acids (PFHxS, PFOS, and PFDS) represented 94% (on average) of total PFAS exposures due to their prevalence in historical AFFF formulations, and increased bioaccumulation in aquatic prey items and partitioning to aquatic sediment relative to perfluoroalkyl carboxylic acids. Sediment-associated PFASs (rather than water-associated PFASs) were the source of the highest predicted PFAS exposures, and are likely to be very important for understanding and managing AFFF site-specific ecological risks. Additional considerations for research needs and site-specific ecological risk assessments are discussed with the goal of optimizing ecological risk-based decision making at AFFF sites and prioritizing research needs.

1. Introduction

With the ongoing investigations of Perfluoroalkyl and

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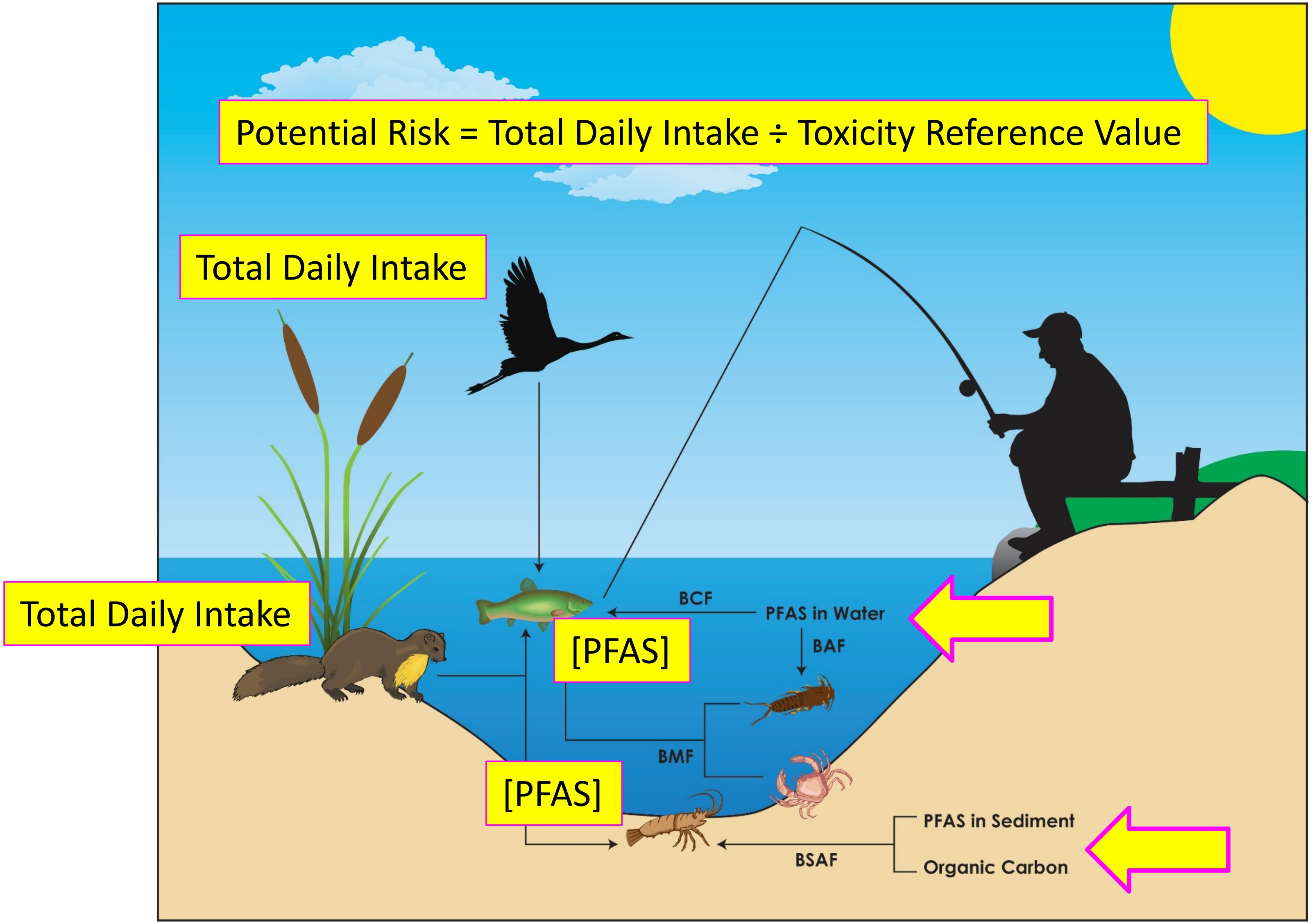
https://doi.org/10.1016/j.chemosphere.2018.03.004
0045-6535/

Larson, E.S., Conder, J.M., Arblaster, J.A. 2018. Modeling avian exposures to perfluoroalkyl substances in aquatic habitats impacted by historical aqueous film forming foam releases. Chemosphere 201:335-341.

Modeling to Understand Ecological Risk Drivers

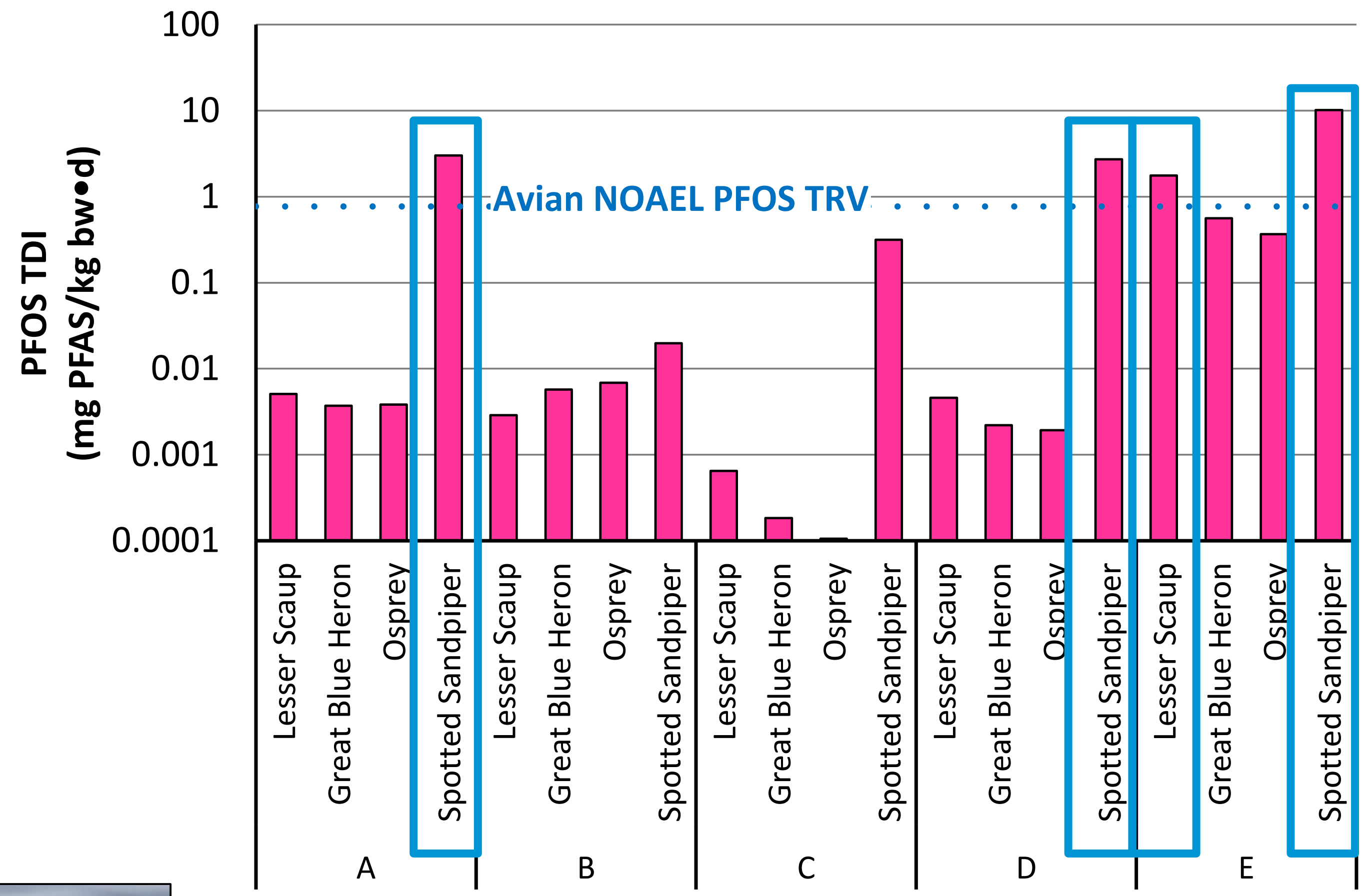
Geosyntec consultants



Modeling to Understand Ecological Risk Drivers - Avian

Geosyntec consultants

- PFOS exposure highest for scaup and sandpiper
  - Small home ranges
  - Benthic invertebrate diet exposure
- Potential risk to birds at 3 Sites



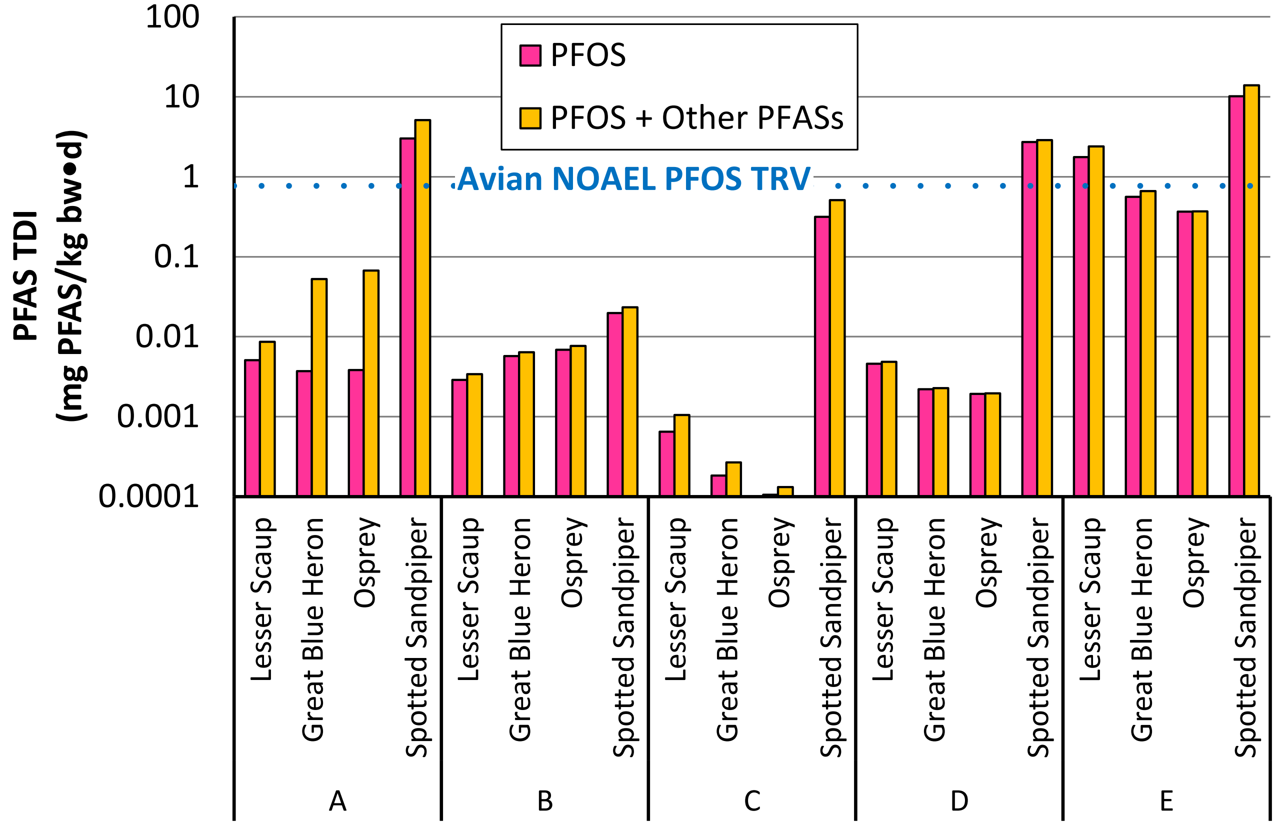
engineers | scientists | innovators

Toxicity Reference Value – Newsted et al. 2007

Modeling to Understand Ecological Risk Drivers - Avian

Geosyntec consultants

- Same conclusion with ΣPFAS
- PFOS is the driver
  - PFOS 73% of PFAS exposure
- Runners-up: other PFSA
  - PFHxS (10%)
  - PFDS (2-15%)



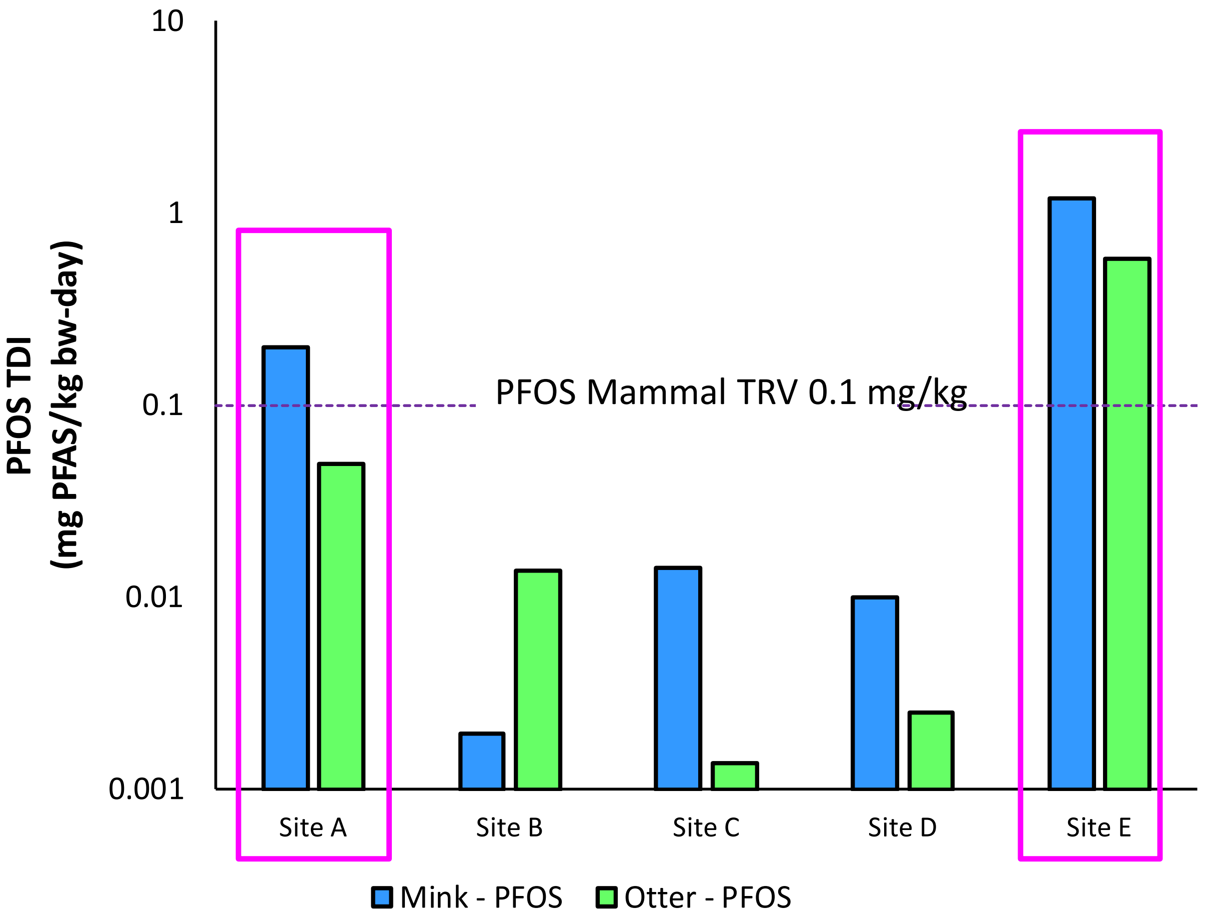
engineers | scientists | innovators

Toxicity Reference Value – Newsted et al. 2007

Modeling to Understand Ecological Risk Drivers – Small Mammals

Geosyntec consultants

- Estimated exposures for Mink and Otter
  - Mink = 50% fish, 50% benthic invertebrate diet
  - Otter = 100% fish diet
- Higher exposure for Mink
  - Smaller home ranges
  - Consumption of benthic invertebrates
  - Higher incidental sediment ingestion rate

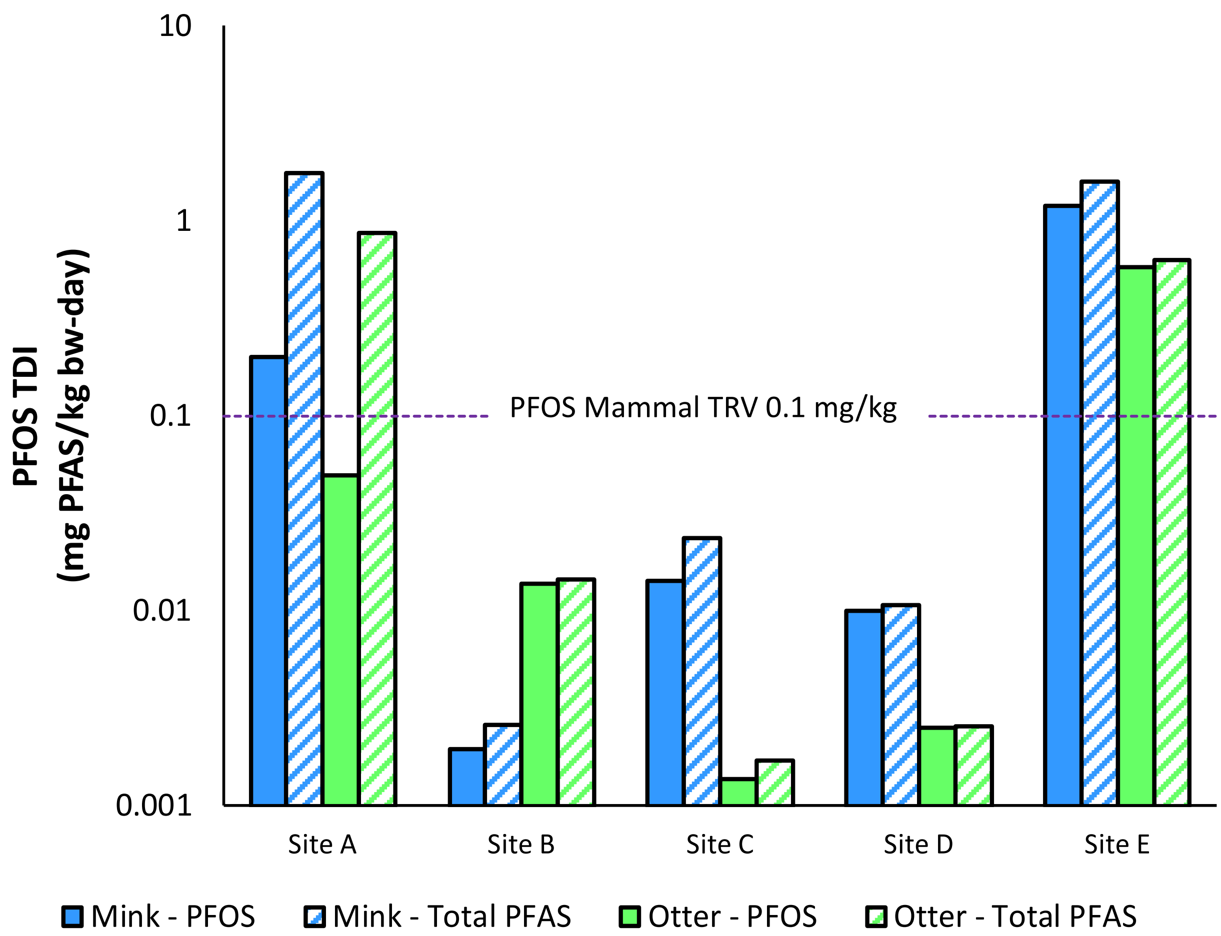


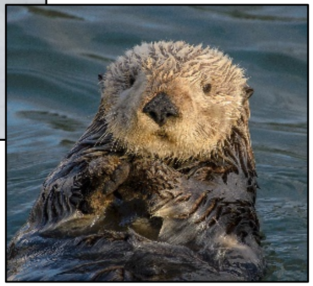
TRV = NOAEL used for USEPA POD for LHA (USEPA 2016)

Modeling to Understand Ecological Risk Drivers – Small Mammals

Geosyntec consultants

- PFOS is the driver
  - PFOS 63% (11% to 95%) of PFAS exposure
- Runners-up: other PFSAs
  - PFHxS (5 - 20%)
  - PFDS (6 - 83%)



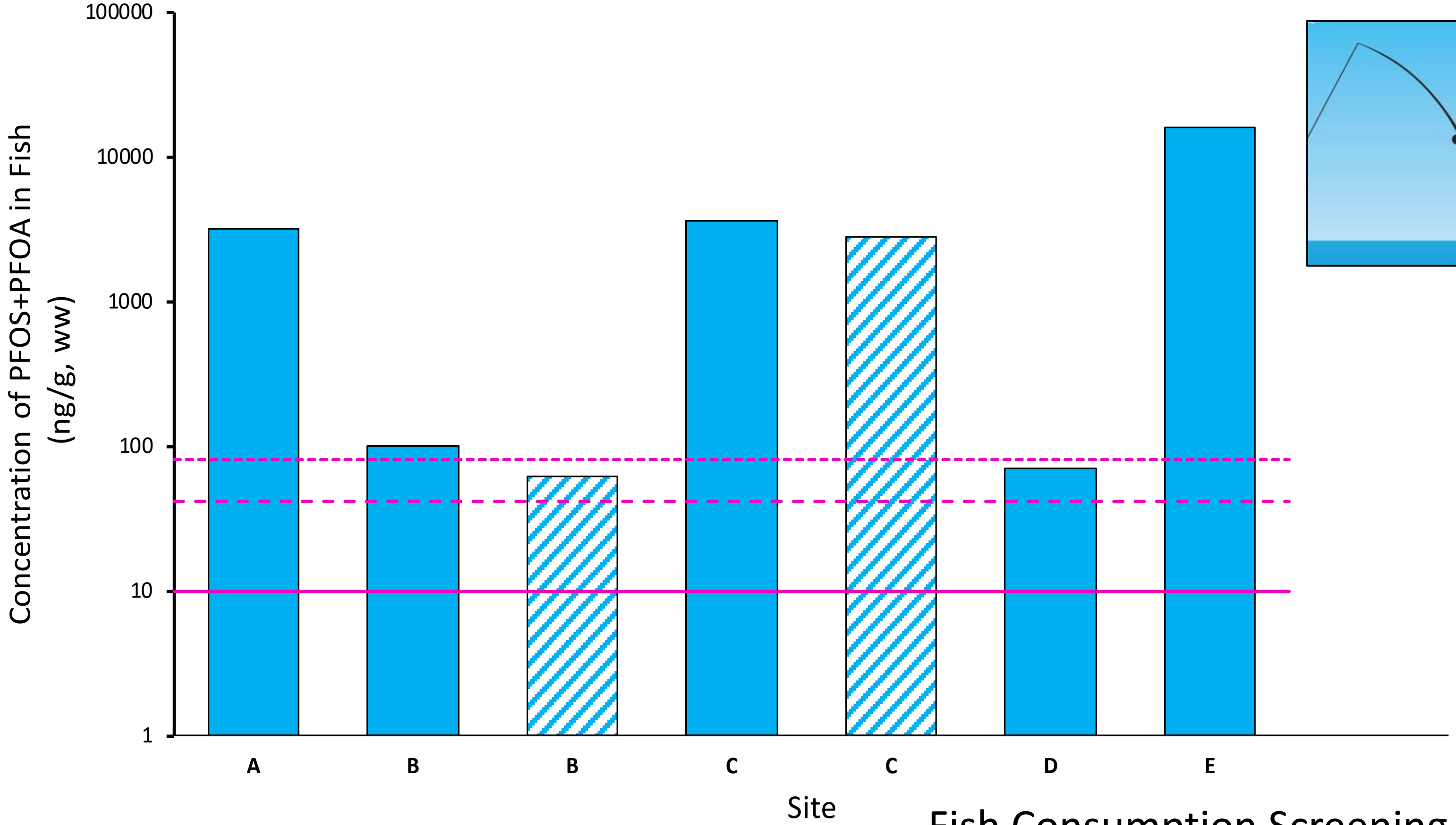


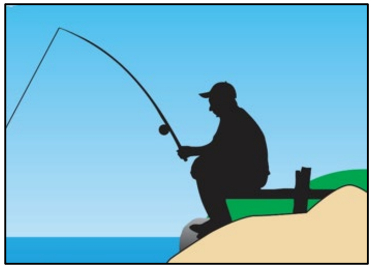
engineers | scientists | innovators

TRV = NOAEL used for USEPA POD for LHA (USEPA 2016)

Human Health Risks from Fish Consumption

Geosyntec consultants





Modeled

Measured

Fish Consumption Screening Levels:

Ontario (80 ng/g)

Australia (41 ng/g)

Minnesota (10 ng/g)

Aquatic Life Benchmarks

Geosyntec consultants

- Screening levels based on protection of aquatic life for PFOS only
- Based on Species Sensitivity Distributions:
  - ~~Australia (2016) = **0.00023 µg/L**~~
  - Canada (2018) = **6.8 µg/L**
  - Giesy et al., (2010) = **5.1 µg/L**
  - Qi et al., = **6.66 µg/L**
  - Arblaster et al., (2017) = **5.7 µg/L**
  - SERDP T&E Guidance (in press) = **5.8 µg/L** based on NOECs

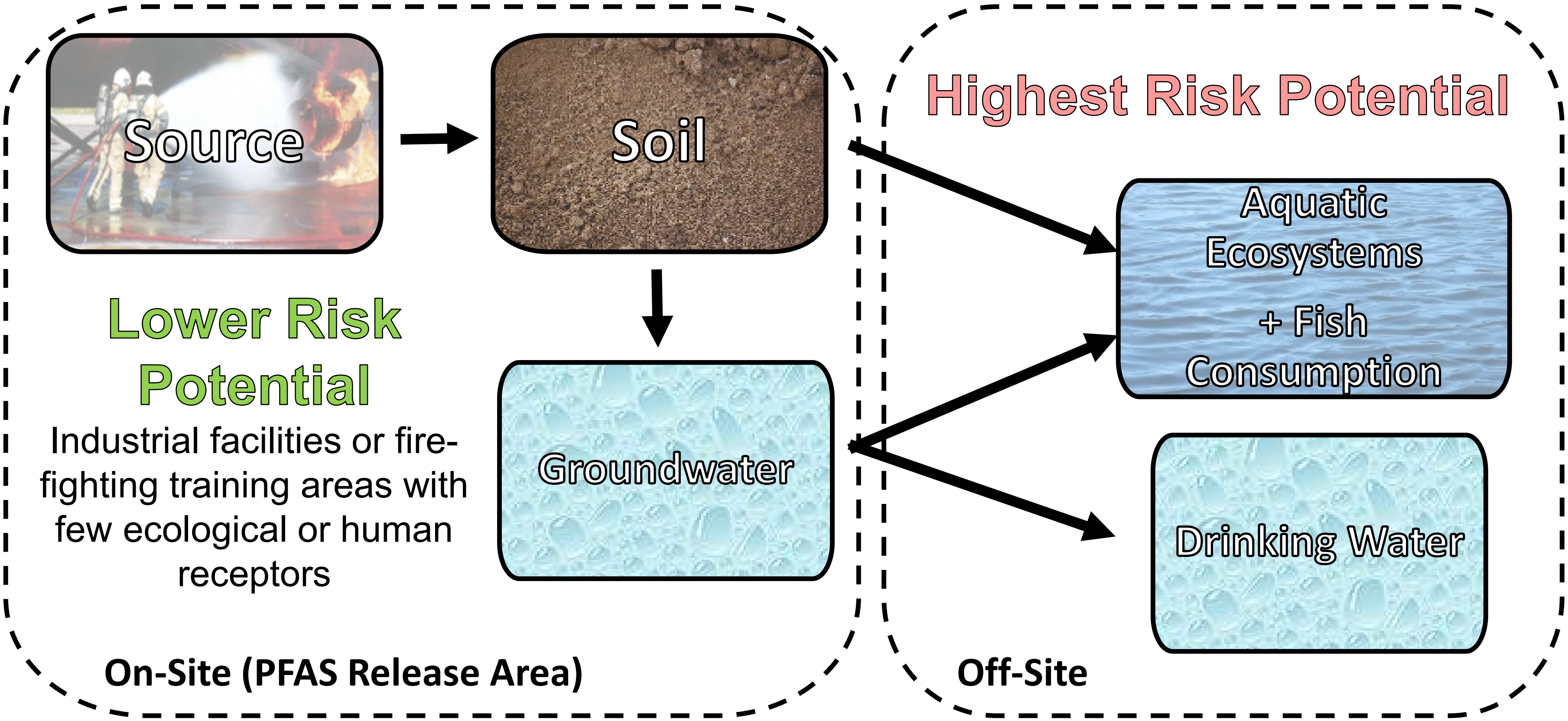
Freshwater Aquatic Life Benchmark ≈ 5 µg/L

Key Exposure Pathways

Site	Aquatic Toxicity in Surface Water	Birds	Mammals	Human Health
	Exceedance of PFOS Effect Concentrations (> 6.8 µg/L)?	Predicted Exceedance of PFOS NOAEL?	Predicted Exceedance of PFOS NOAEL?	Exceedance of PFOS Fish Criteria?
A	No	Yes	Yes	Yes
B	No	No	No	Yes
C	No	No	No	Yes
D	Yes	Yes	No	Yes
E	No	Yes	Yes	Yes

Evaluation of aquatic life risks would miss potential risks to birds, mammals, and human health

Key Exposure Pathways



Uncertainties - Mixtures

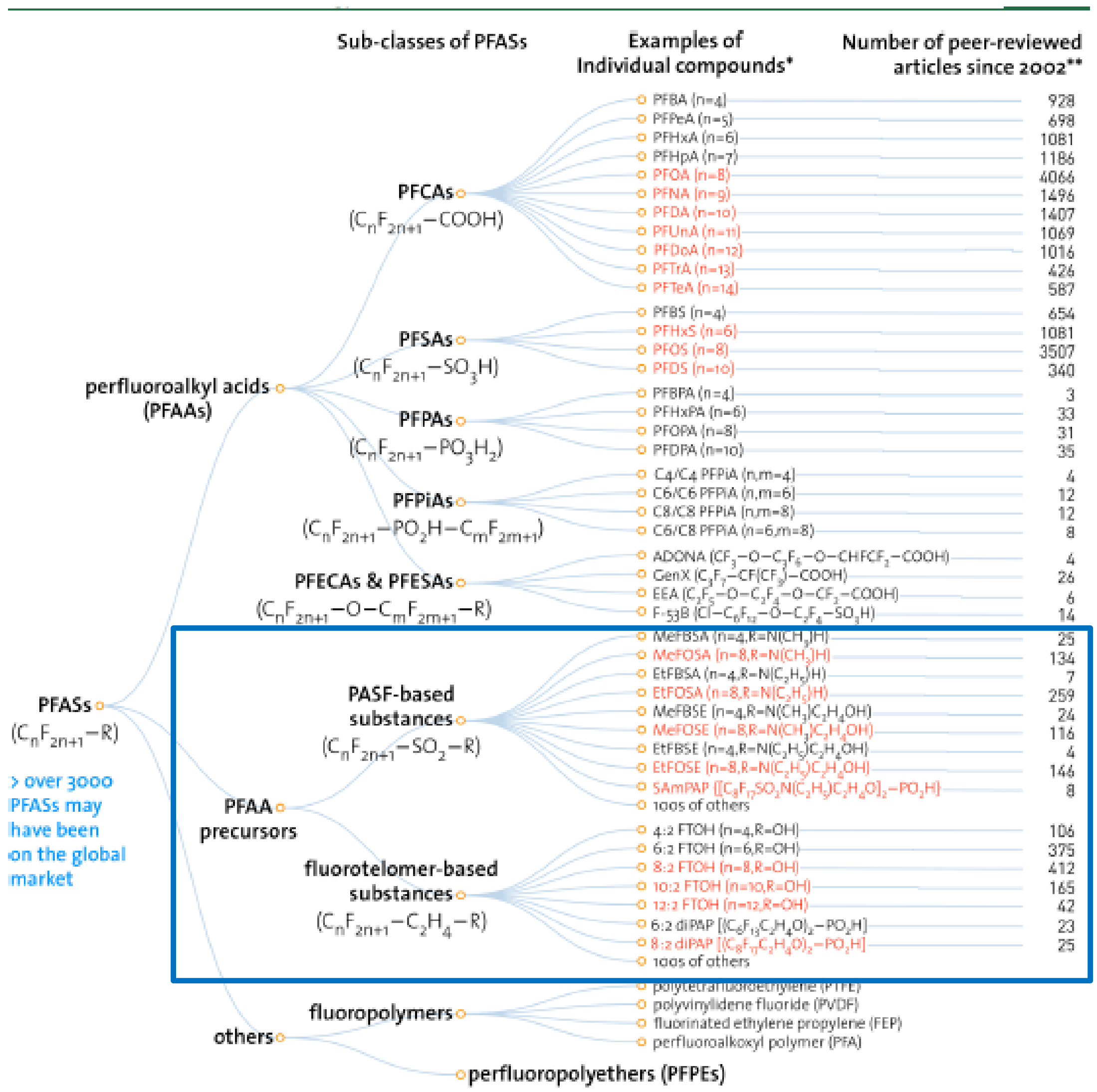
Geosyntec consultants

- PFAS > 3000 compounds, but toxicity data on < 20
- Addressing mixture toxicity varies by location:
  - Toxicity Equivalency Approach (RIVM)
    - Relative Potency Factors to PFOA based on liver toxicity
  - PFOS + PFOA (USEPA approach)
  - PFOS + PFHxS (Australia approach)
- As a <u>*conservative*</u> approach ΣPFAS can be compared to toxicity benchmarks for PFOS
- Research on potential effects of other PFAS is needed

Uncertainties - PFAA Precursors

Geosyntec consultants

- Can be quantified using TOPA
  - Results don't represent the true exposure
- Useful for source zone identification or total PFAS mass analyses
- Need to be considered when evaluating remedial designs as some technologies may transform precursors



Conclusions

Geosyntec consultants

- Ecological and human health risk potential at PFAS-impacted/AFFF sites will drive concerns
  - Drinking water is not the only pathway to consider
- Key risk considerations:
  - Bioaccumulation is likely to drive risk
  - Ambient exposures should be characterized to understand site related risks
  - Data gaps (toxicity for many PFAS, mixtures, precursors) need to be addressed
  - Standard (and reasonable!) screening levels and risk assessment/management practices are needed

Thank you!

Academic Research: Developing the science to help answer community questions

NC STATE UNIVERSITY
Center for Human Health and the Environment

Duke UNIVERSITY

NORTH CAROLINA PFAS Testing Network

Detlef Knappe[1] and Lee Ferguson[2]

(knappe@ncsu.edu)

[1] Dept. of Civil, Construction, and Environmental Engineering, NC State University

[2] Dept. of Civil and Environmental Engineering, Duke University

PFAS and Other Emerging Contaminants Conference
Raleigh, NC; April 23, 2019

Toxin taints CFPUA drinking water

▲ HIDE CAPTION

A 2000 aerial photo of Fayetteville Works on the Cumberland-Bladen county line. The site, home to several plants, one of which makes GenX, is about 100 miles upstream from Wilmington. [COURTESY OF THE FAYETTEVILLE OBSERVER]

Utility can't filter out chemical produced upriver at Fayetteville plant

By Vaughn Hagerty StarNews Correspondent

Posted Jun 7, 2017 at 10:31 AM
Updated Jun 8, 2017 at 10:38 AM

StarNews 150th 1867 • 2017

Chemours: GenX polluting the Cape Fear since 1980

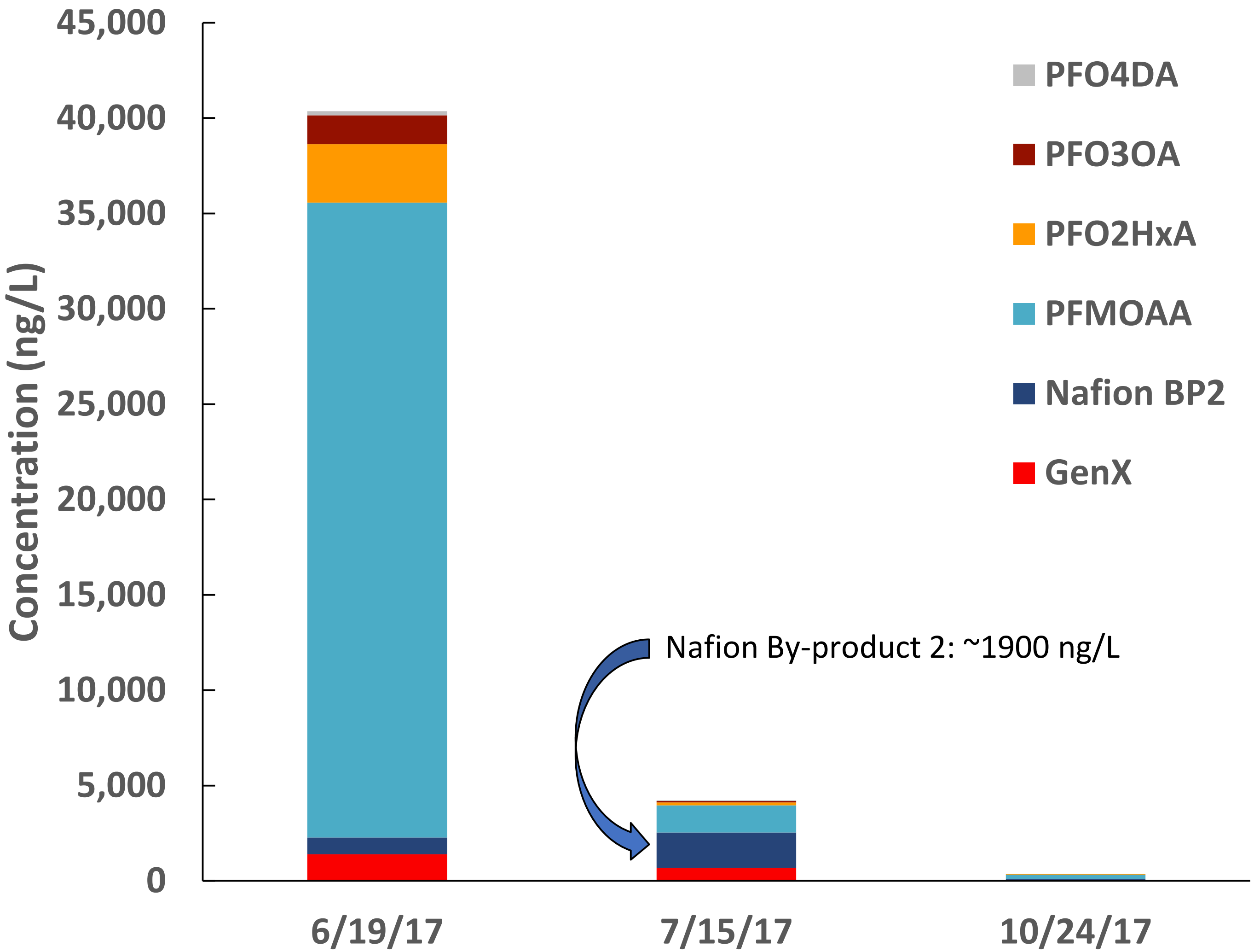
By Adam Wagner and Tim Buckland GateHouse Media

Posted Jun 15, 2017 at 2:00 PM
Updated Jun 16, 2017 at 12:06 AM

Wilmington-area officials demand answers, action during invitation-only meeting with company

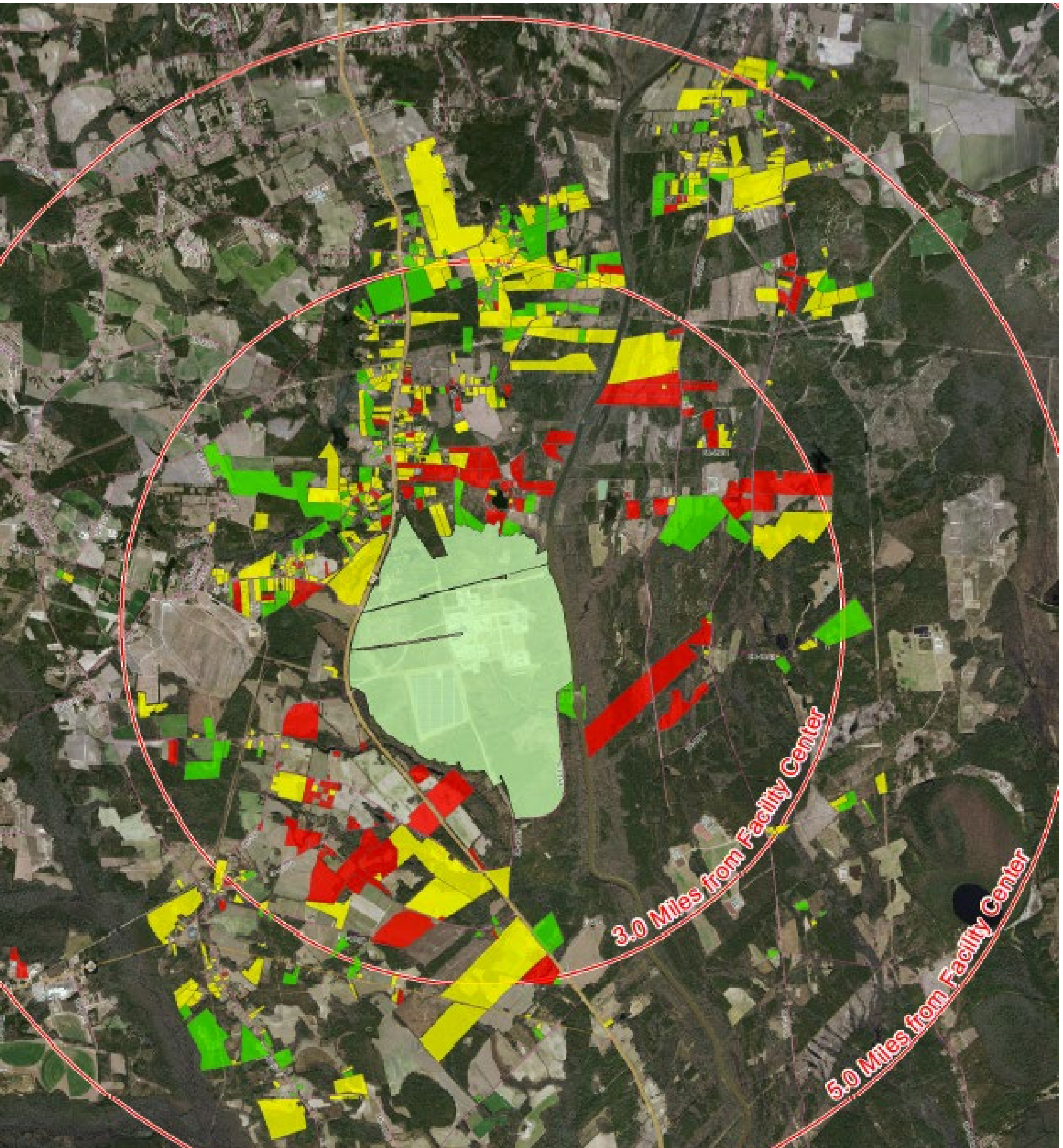
WILMINGTON -- A former DuPont plant has been discharging an unregulated toxic chemical into the Cape Fear River since 1980, company officials revealed Thursday at a meeting with local and state officials.

PFAS concentrations at drinking water intake have dropped dramatically since mid-June 2017



Hopkins et al. JAWWA 2018

GenX detected in private drinking water wells >5 miles from plant



Red: >140 ng/L
Yellow: detect-140 ng/L
Green: non-detect

~1,000 wells analyzed:

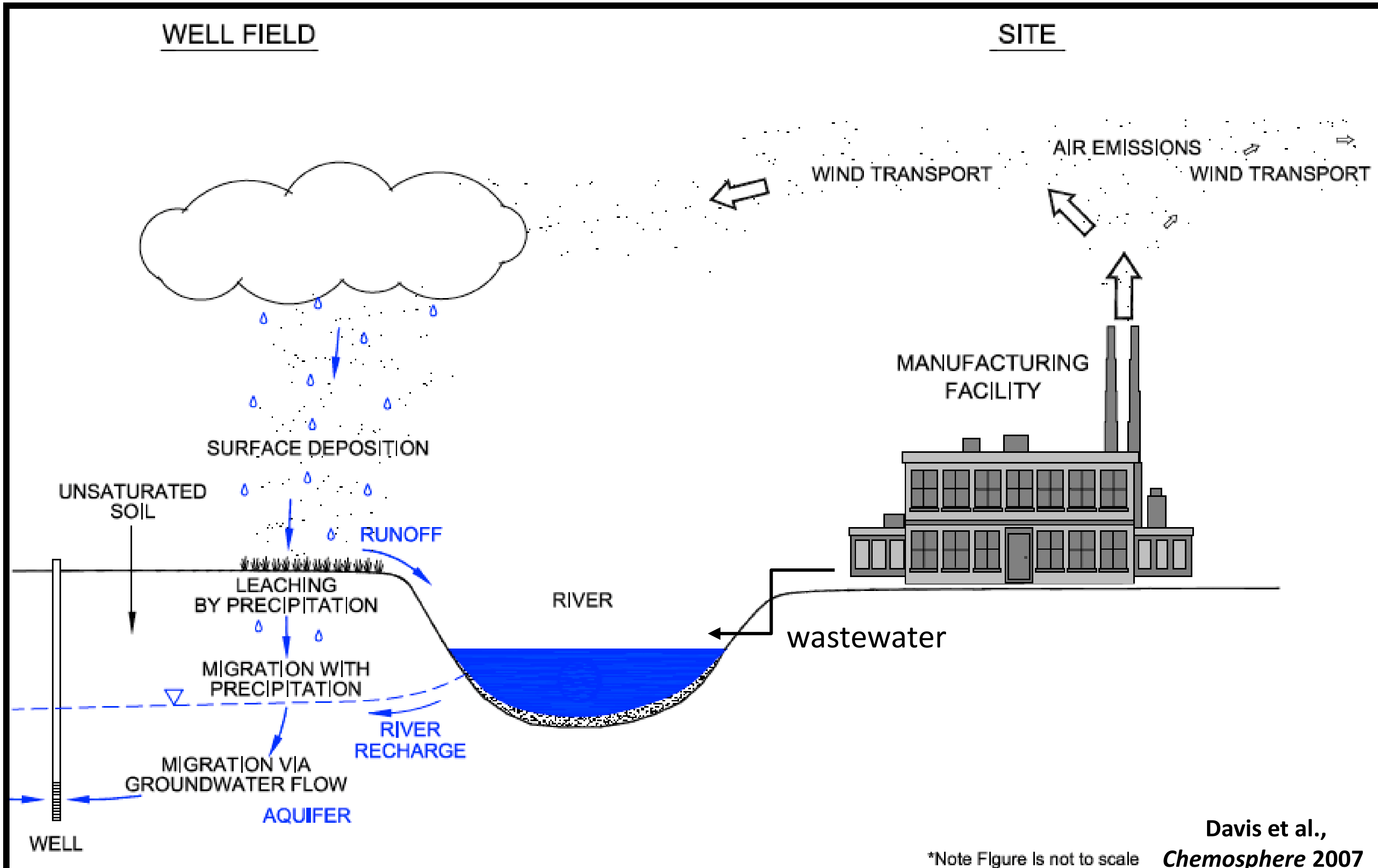
GenX >140 ng/L: 225
Detect – 140 ng/L: 538
Non-detect: 231

Max. GenX: 4,000 ng/L

GenX detections in 3 counties

https://files.nc.gov/ncdeq/GenX/Presentation_May29InfoSession_StPaulsMiddleSchool.pdf

Fluorochemical manufacturers and industries using fluorochemicals **emit PFAS to air and water**



Davis et al.,
Chemosphere **2007**

Key Community Questions

- Are PFAS in my drinking water? Are there PFAS that standard methods do not detect?
- Are PFAS in the fish I catch? …the food I grow in my garden?
- Are PFAS in me? At what levels? What are the health effects?
- How can I get PFAS out of my water?

Research Expertise and Teams identified across NC Universities to address NC PFAS questions

NC PFAS Testing Network

NORTH CAROLINA PFAS Testing Network

NC Legislature

NC Collaboratory
Warren

Program Director
Surratt (UNCCH)

Executive Advisory Committee
Ferguson (Duke) – ***Co-chair***
Knappe (NCSU) – ***Co-chair***
DeWitt (ECU)
MacDonald-Gibson (UNCCH)
Mead (UNCW)
Sun (UNCC)

Scientific Program Analyst
Bodnar (UNCCH)

Program Assistant
Khan (UNCCH)

Research Teams & Leads

PFAS Sampling & Analysis
Ferguson (NCSU)
Knappe (Duke)

Private Well Risk Modeling
Genereux (NCSU)
MacDonald-Gibson (UNCCH)

PFAS Removal Performance Testing
Coronell (UNCCH)
Sun (UNCC)

Air Emissions & Atmospheric Deposition
Mead (UNCW)
Turpin (UNCCH)

Applied Research Opportunities
DeWitt (ECU)
Fry (UNCCH)

Support Teams & Leads

Communications
Gray (UNCCH)
Hoppin (NCSU)
Weintraub (Duke)

Data Management
Center for Geospatial Analytics (NCSU)
Renaissance Computing Institute/Lenhardt (UNCCH)

Synthetic Organic Chemistry
Zhang (UNCCH)

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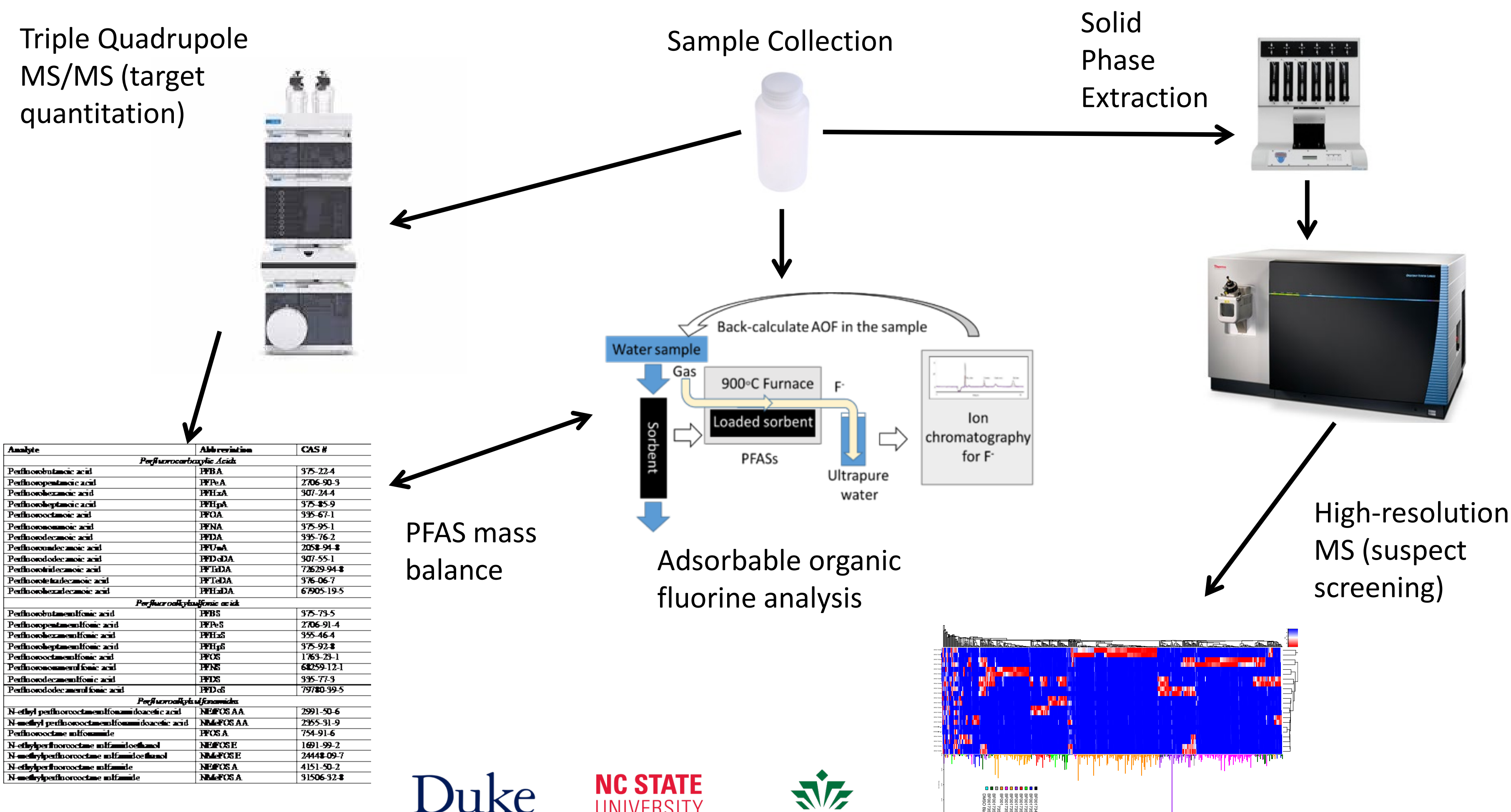
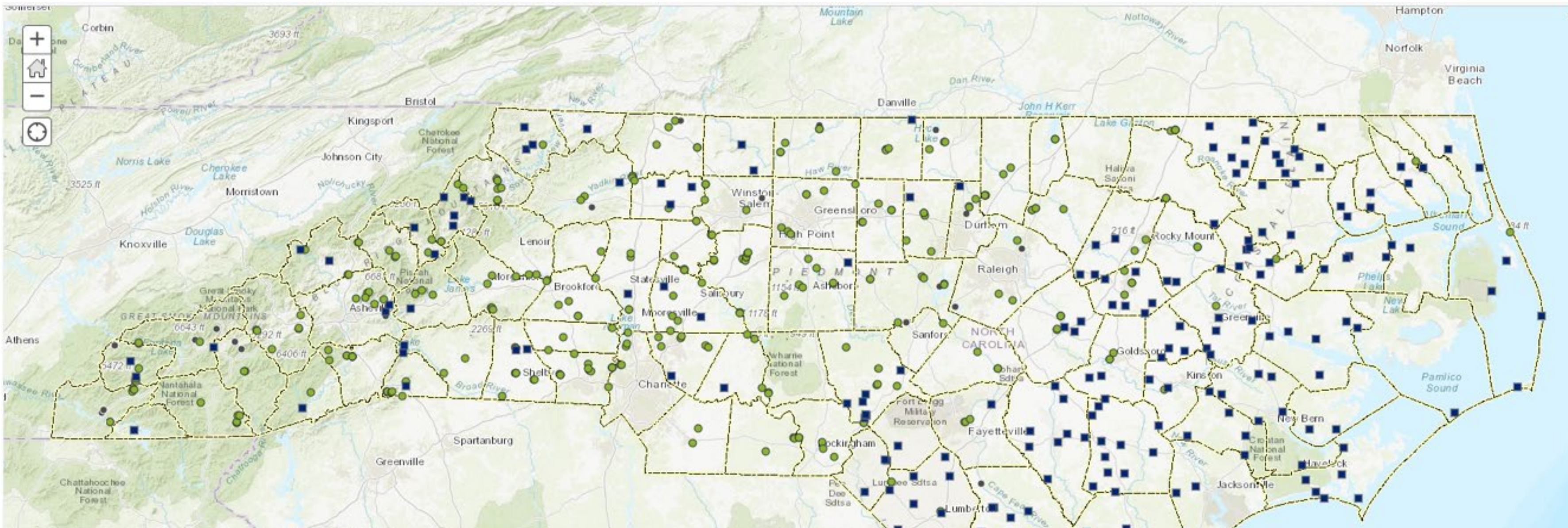
Are PFAS in my drinking water? Are there PFAS that standard methods do not detect?



Analyte	Abbreviation	CAS #
Perfluorocarboxylic Acids		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoDA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorohexadecanoic acid	PFHxDA	67905-19-5
Perfluoroalkylsulfonic acids		
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorododecanesulfonic acid	PFDoS	79780-39-5
Perfluoroalkylsulfonamides		
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorooctane sulfonamide	PFOSA	754-91-6
N-ethylperfluorooctane sulfamidoethanol	NEtFOSE	1691-99-2
N-methylperfluorooctane sulfamidoethanol	NMeFOSE	24448-09-7
N-ethylperfluorooctane sulfamide	NEtFOSA	4151-50-2
N-methylperfluorooctane sulfamide	NMeFOSA	31506-32-8

We will sample sources of all municipal water systems in NC (191 surface water sources, 149 well water sources) at least twice this year



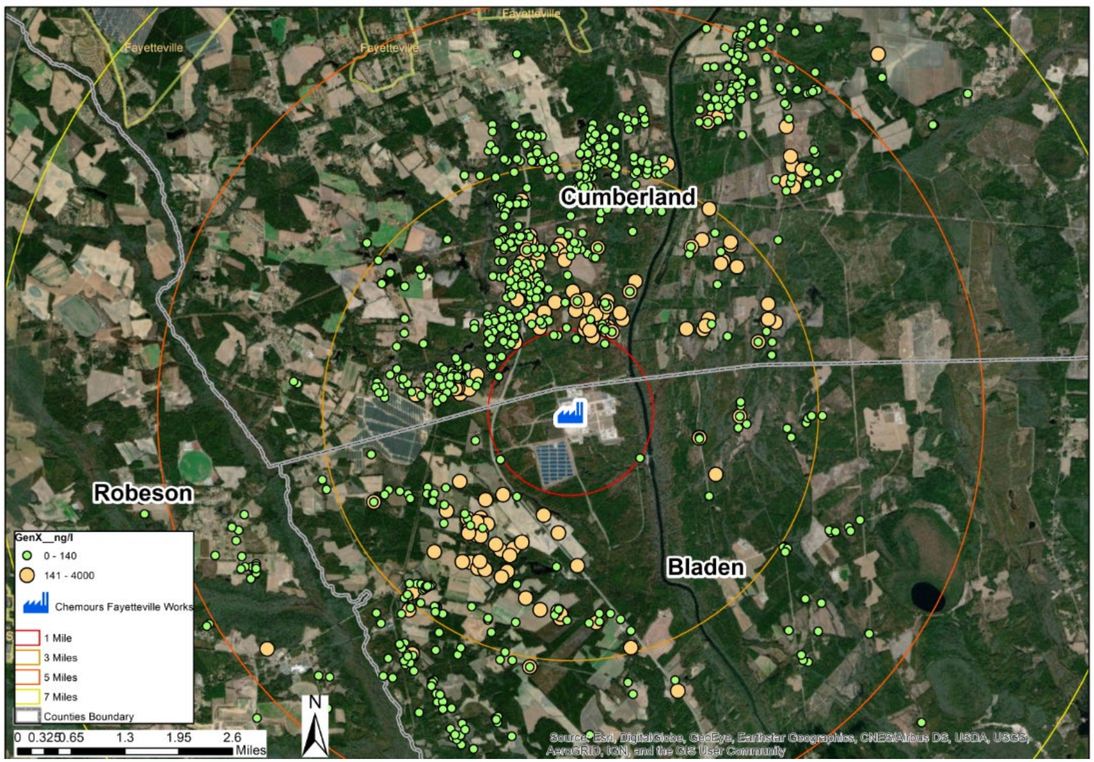
Abigail Joyce, CEE, Duke University
Noelle DeStefano, CCEE, NCSU

Surface (green circle) and ground water (blue square) sampling sites for drinking water sources to be analyzed for PFAS.

Predicting Which Private Wells Are at Risk

Jackie MacDonald
ESE, UNC-CH

- We are using PFAS occurrence data from 1220 private well water samples to predict which wells are at risk.
- We will use a machine-learning approach to discover what factors influence risk.



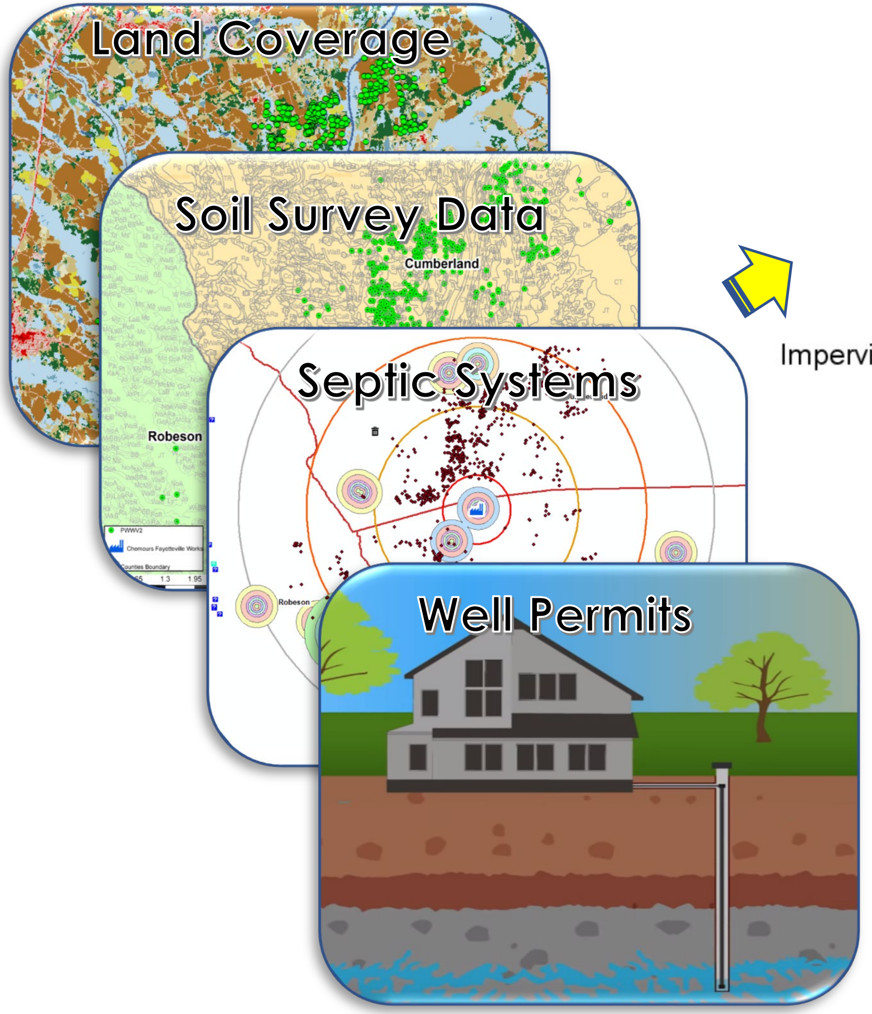
GenX concentrations vary widely from well to well.

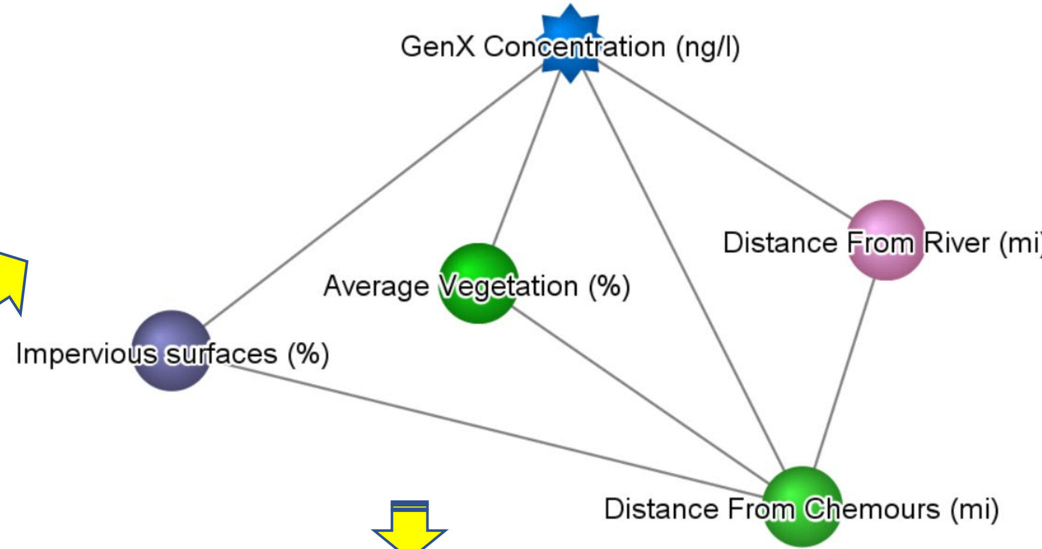
We are building a curated data set of potential influential factors:

- Proximity to Chemours
- Proximity to airports
- Fire incidents
- Proximity to wastewater treatment plants and septic systems
- Forest coverage
- Well construction records
- Soil type
- Meteorological variables

UNC GILLINGS SCHOOL OF GLOBAL PUBLIC HEALTH

Our Curated Data Set Forms the Basis for a Machine-Learned Risk Model





Machine-learned model to identify other wells at risk

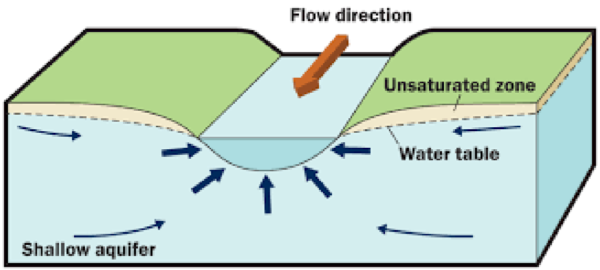
Preliminary results show an **84%** overall precision in our results

UNC | GILLINGS SCHOOL OF GLOBAL PUBLIC HEALTH

How long will it take for the PFAS to flush out of the aquifer near Chemours?

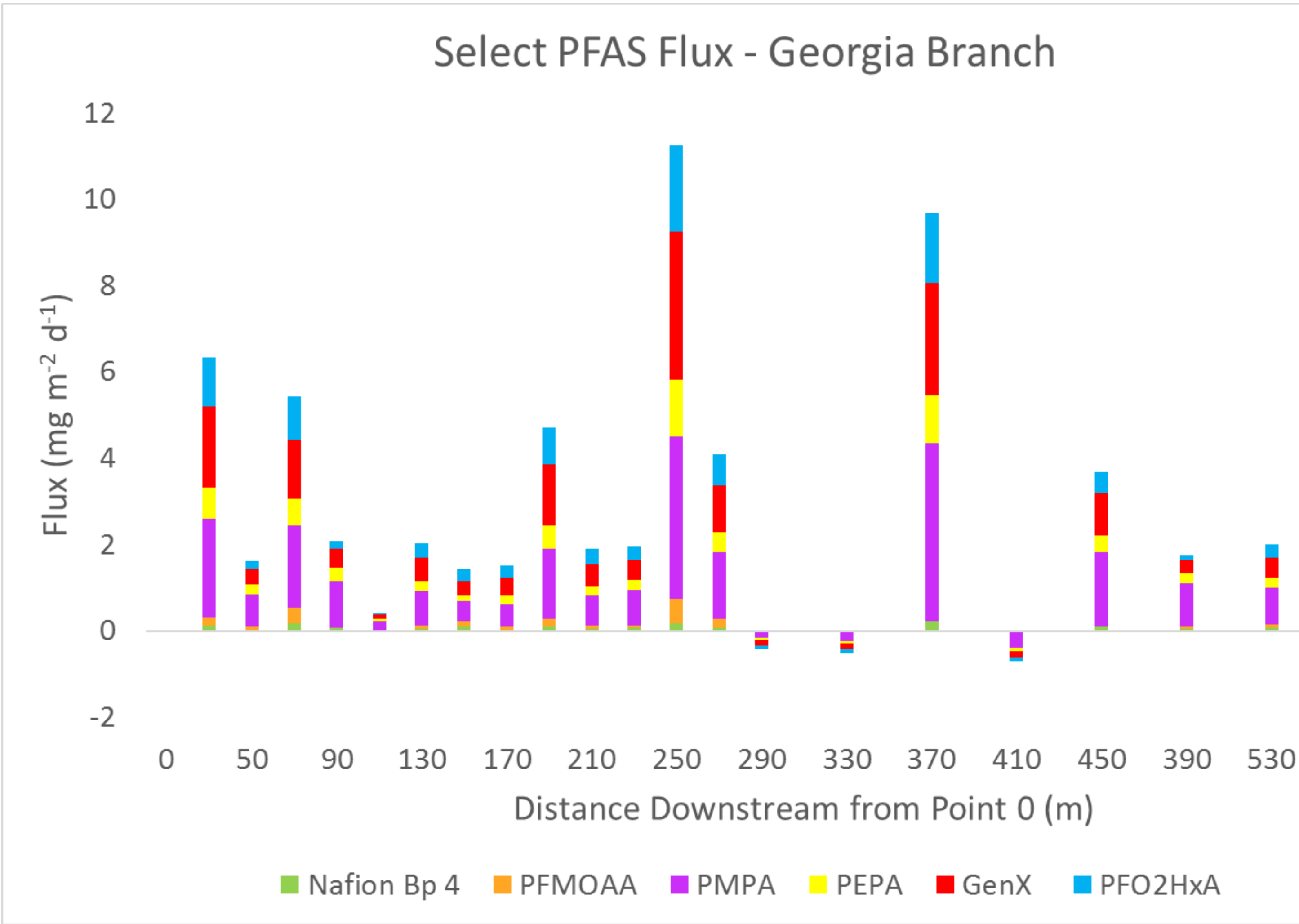
David Genereux
MEAS, NCSU

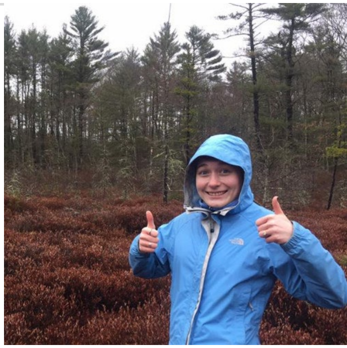
- Natural groundwater flow slowly flushes PFAS from contaminated surficial aquifer to streams (tributaries of the Cape Fear River)
- Good (eventually) for residents near Chemours with contaminated wells, not so good for downstream Cape Fear users



- Research questions:
  - What are the PFAS concentrations in groundwater discharging to streams?
  - What is the rate of PFAS discharge from groundwater to streams?
  - What effect might this have on PFAS concentrations in the Cape Fear River?

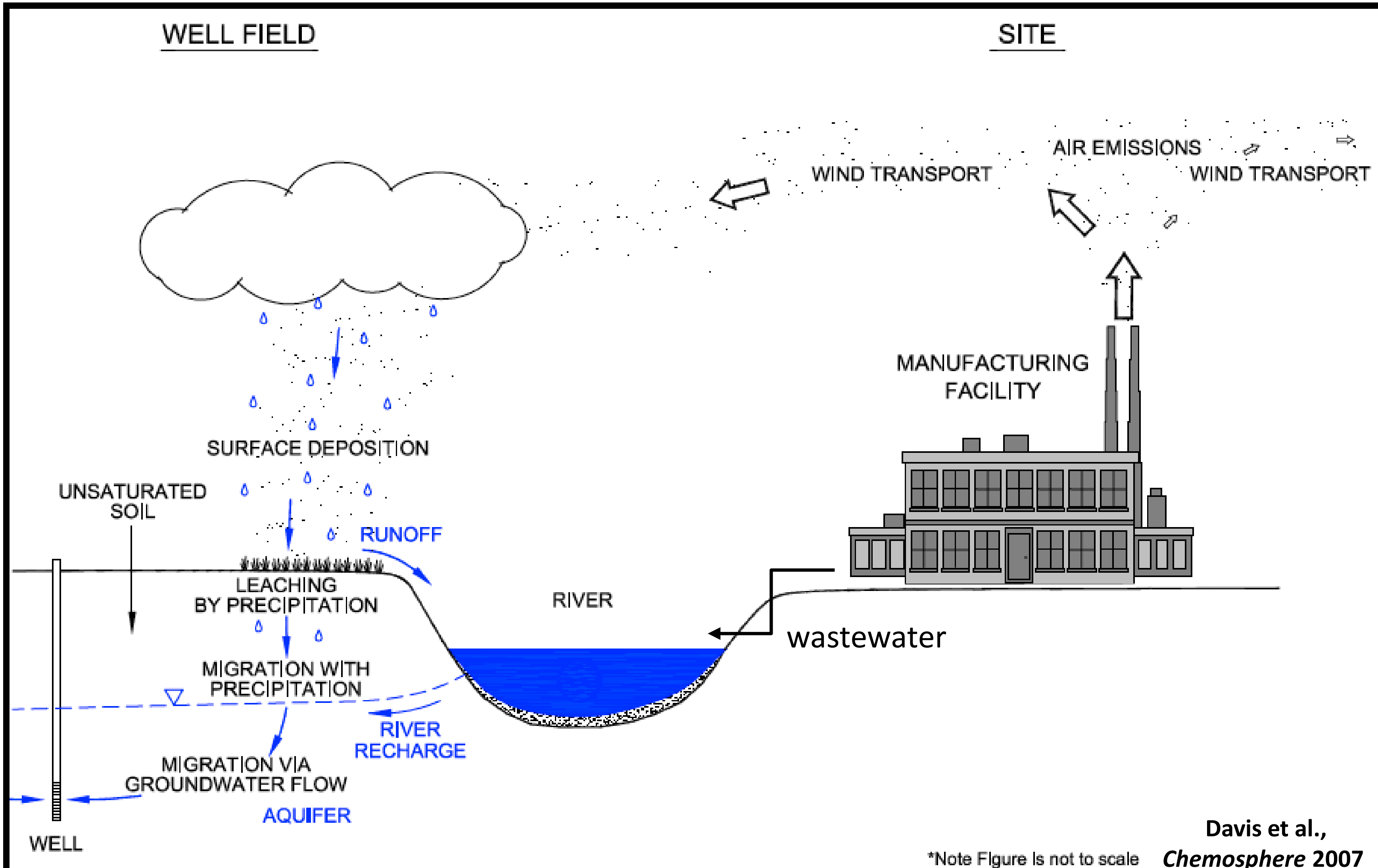
On October 22, 2018, PFAS mass discharge from aquifer to stream (and then to Cape Fear) was about 60 g/day



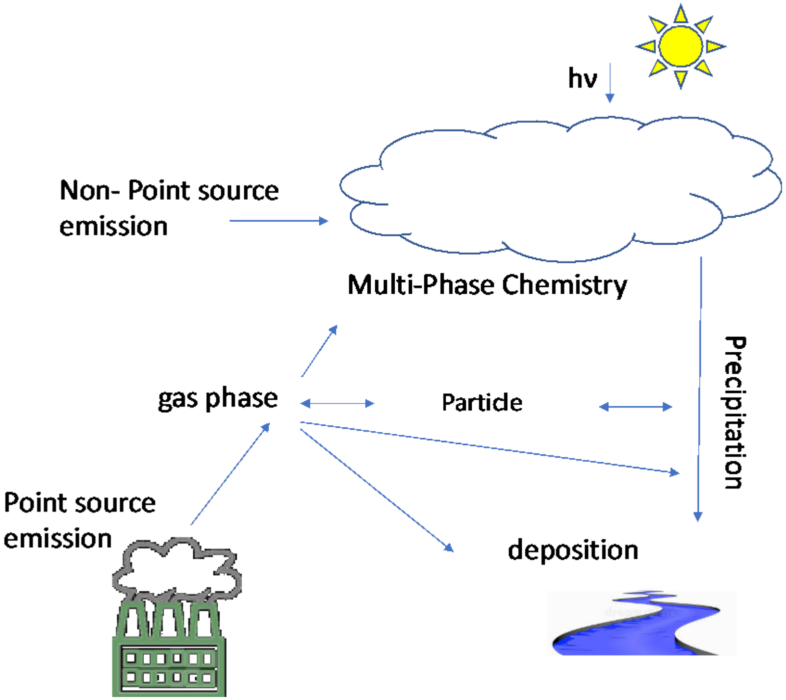


Lydia Koropeckyj-Cox
MS student, MEAS, NCSU

Fluorochemical manufacturers and industries using fluorochemicals **emit PFAS to air and water**



Davis et al., *Chemosphere* 2007



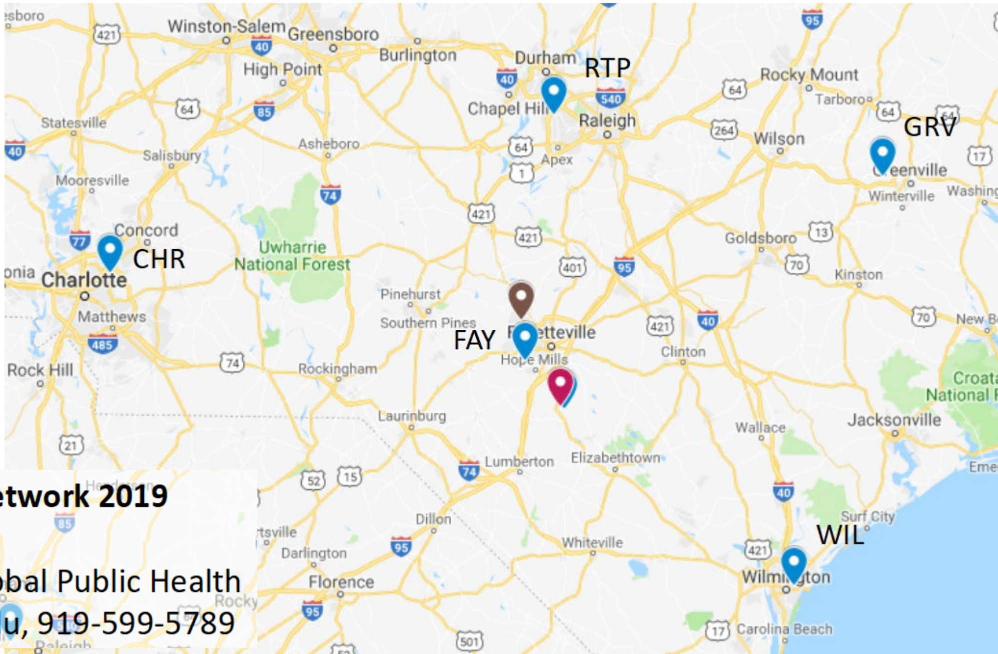
Ralph Mead,
Chem, UNC-W

Barbara Turpin,
ESE, UNC-CH

Determine the wet/dry deposition of GenX and other PFAS

Measure atmospheric gas- and particle-phase concentrations of PFAS

Examine the multiphase chemistry (or reactive uptake) of hexafluoropropylene oxide (HFPO) with atmospheric aerosol



Aerosol Sampling Sites for the North Carolina PFAS Testing Network 2019

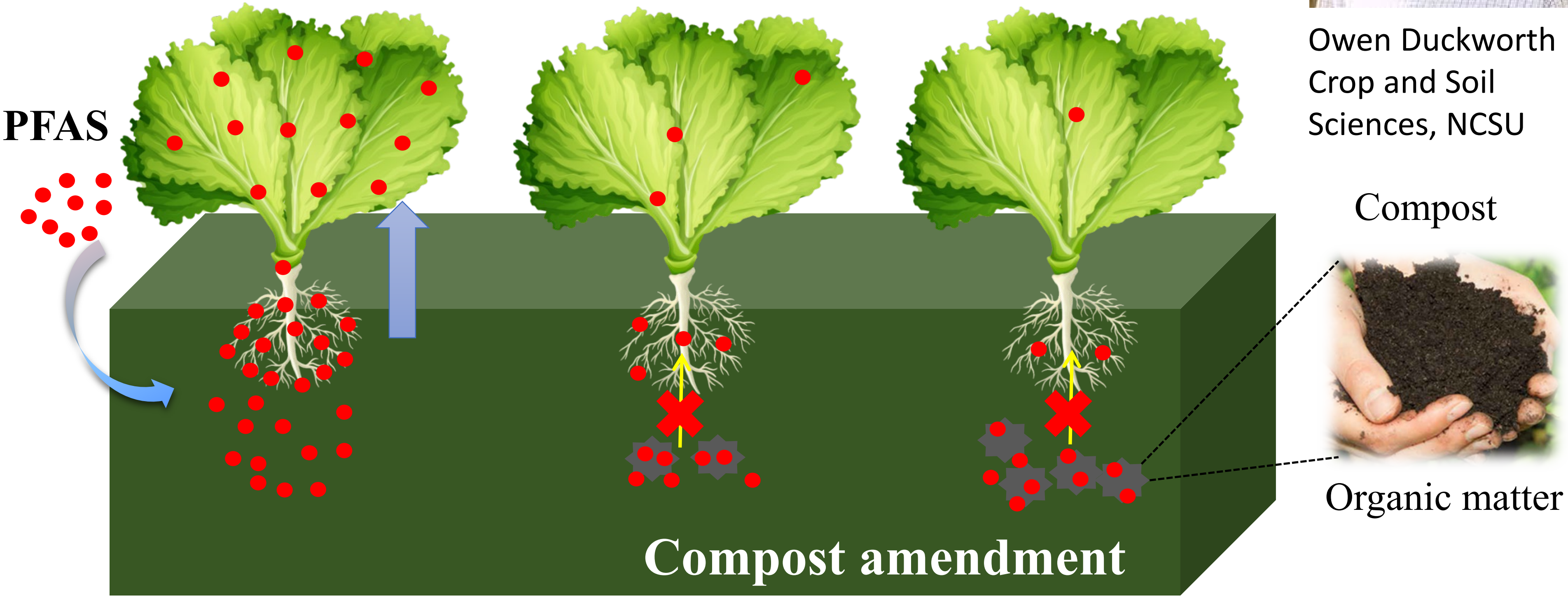
POC: Dr. Karsten Baumann

Environmental Sciences and Engineering, Gillings School of Global Public Health

University of North Carolina at Chapel Hill, kbaumann@unc.edu, 919-599-5789

Effects of compost addition on reducing the plant uptake of PFAS from soil

Owen Duckworth
Crop and Soil Sciences, NCSU



Hypothesis: Increasing the compost content could increase the sorption of PFAS chemicals thus reduce plant uptake.

Assessment of novel and legacy PFAS in larger aquatic vertebrates of Cape Fear River, NC

Scott Belcher,
Biology, NCSU

Theresa Guillette,
Biology, NCSU

Study Goals:

1) Characterize levels of PFASs in American alligator, catfish, and striped bass blood/plasma and tissue by sex, size, and location in different sites along the Cape Fear River watershed / "Reference" sites

2) Determine the relationship between individual and total PFAS load and indicators of health outcomes to identify biomarkers of PFAS exposure (morphometrics, blood chemistry and blood cell counts, and lipid, cholesterol, hormone and liver enzymes)

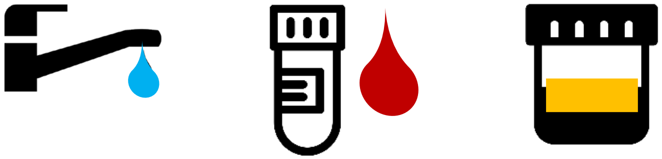
NC STATE UNIVERSITY
Center for Human Health and the Environment

The GenX Exposure Study: Characterizing PFAS exposure in the Lower Cape Fear River Basin

Funding: NIEHS 1R21ES029353-01

Chemours Plant, Fayetteville, NC

Wilmington, NC



Jane Hoppin, CHHE, NCSU

Detlef Knappe, CCEE, NCSU

Nadine Kotlarz, CHHE, NCSU

Community concerns motivated the GenX Exposure Study

Research Questions:

What chemicals are in water, blood or urine?

What factors predict the chemical levels?

How long do these chemicals stay in the body?

Are chemical levels associated with health effects?

Key findings in Wilmington blood

1. Recently identified long-chain fluoroethers detected in a majority of serum samples

2. GenX was not detected

3. Serum levels of fluoroethers decreased after six months

PFAS research in the DeWitt Lab at East Carolina University

Does exposure to PFAS impact markers of immune function in a rodent model?

Objectives:

- **Assess functional responsiveness of the adaptive immune system** (T cell-dependent antibody response targeting B cells) following exposure to selected PFASs
- **Asses functional responsiveness of the innate immune system** (NK cell cytotoxicity) following exposure to selected PFASs
- **Determine effects of selected PFASs on major immune cell subpopulations** in primary (thymus) and secondary (spleen) lymphoid organs

Together, these measures will provide a robust assessment of the immunotoxic potential of the evaluated PFAS.

ECU

How can we remove PFAS from water?

Experimental Design

Mei Sun, CEE, UNC-C

Orlando Coronell, ESE, UNC-CH

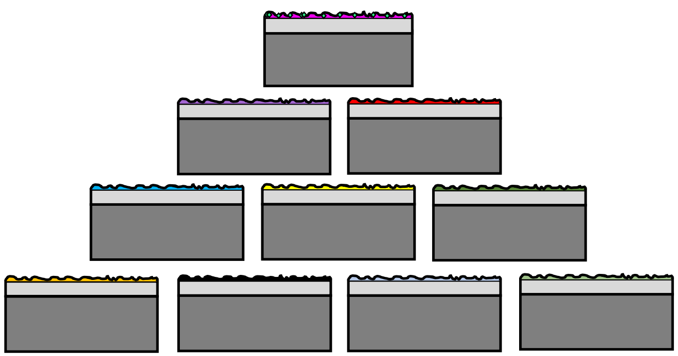
Detlef Knappe, CCEE, NCSU

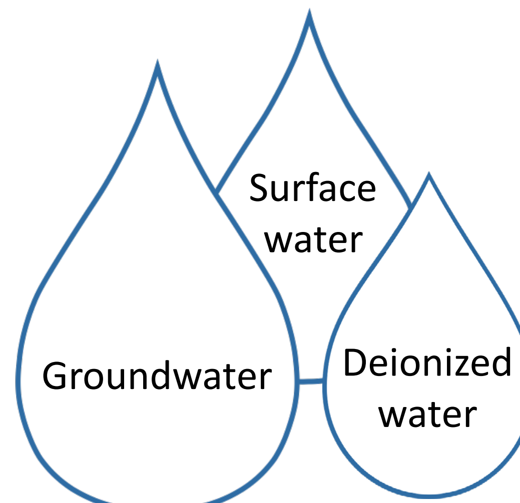
10 types of:

- High-pressure membranes
- Ion exchange resins
- Granular activated carbons

29 PFAS

3 types of water





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UNC CHARLOTTE

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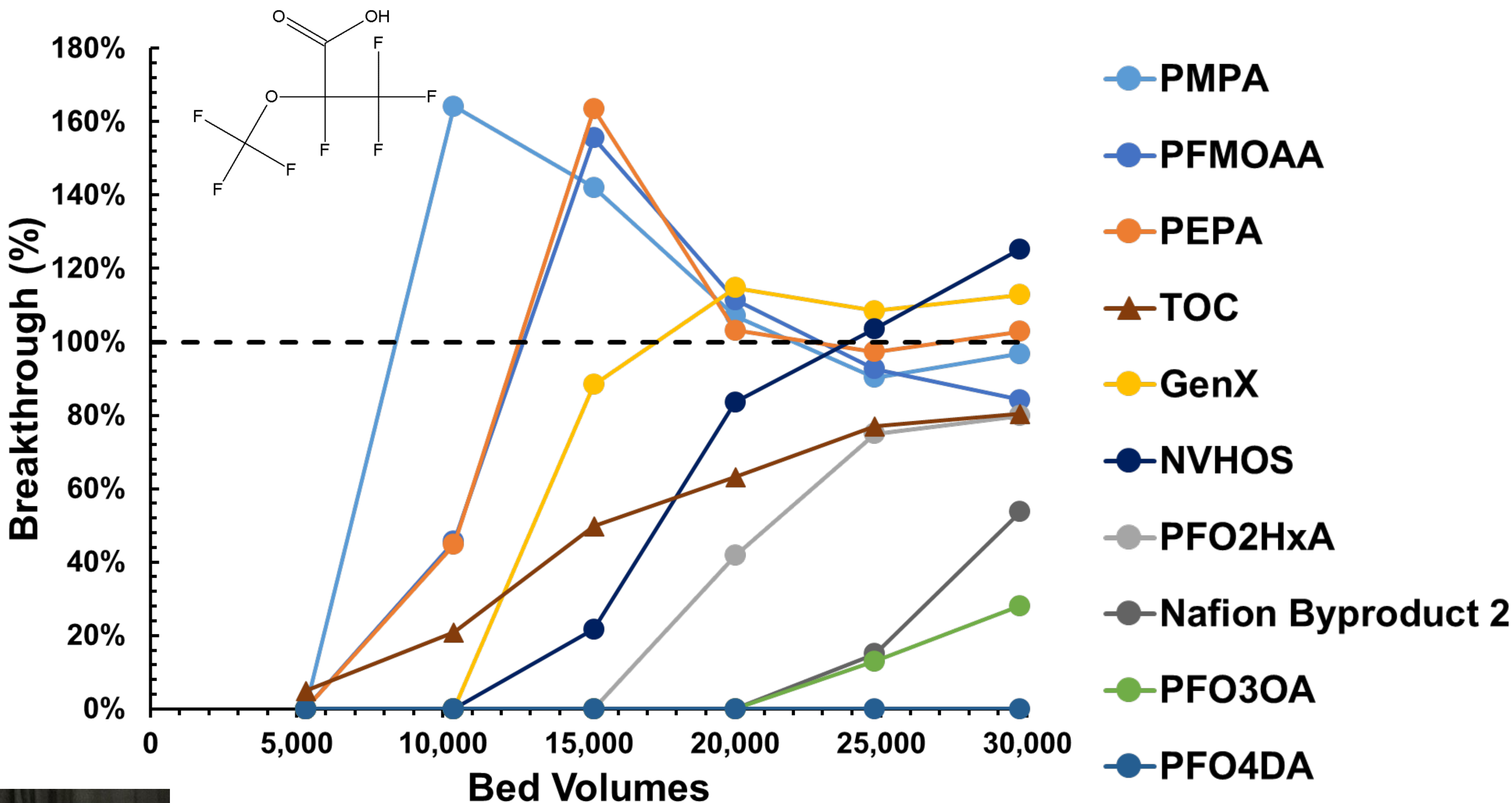
Adsorbability of PFAS varies widely



Zack Hopkins, PhD student
CCEE, NCSU

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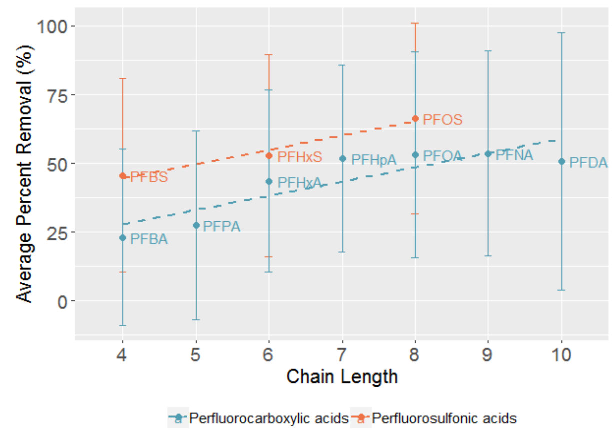
Reverse Osmosis (RO) based systems nearly completely removed all PFAS examined, while activated carbon (AC) based systems showed significantly more variability. AC systems showed an improved removal efficiency for longer chain length PFAS.

Summary of Percent Removal for PFAA and PFPE compounds by Filter Class. Note: Values <MDL after filtering were consider 100% removal for this analysis.

			Activated Carbon				
	Reverse Osmosis	2-Stage Filter	Faucet Filter	Pitcher Filter	Refrigerator Filter	Whole House Filter	Average AC-POU[1]
n =	12	4	7	12	22	6	12
Gen-X	100%	100%	55%	46%	56%	21%	53%
PFBS	99%	100%	98%	70%	34%	19%	55%
PFHxS	100%	100%	95%	59%	68%	34%	69%
PFOS	100%	100%	99%	71%	64%	78%	70%
PFBA	100%	99%	29%	36%	47%	-34%	41%
PFPA	100%	100%	60%	47%	37%	-85%	42%
PFHxA	100%	100%	61%	43%	60%	-63%	55%
PFHpA	100%	100%	58%	44%	66%	-37%	58%
PFOA	100%	100%	66%	69%	73%	20%	71%
PFNA	100%	100%	68%	58%	78%	39%	71%
PFDA	100%	100%	82%	61%	61%	44%	65%

[1]The average AC-POU includes all Faucet, Pitcher and Refrigerator filters



Average percent removal compared to chain length of PFAA chemicals for activated carbon based point-of-use filters

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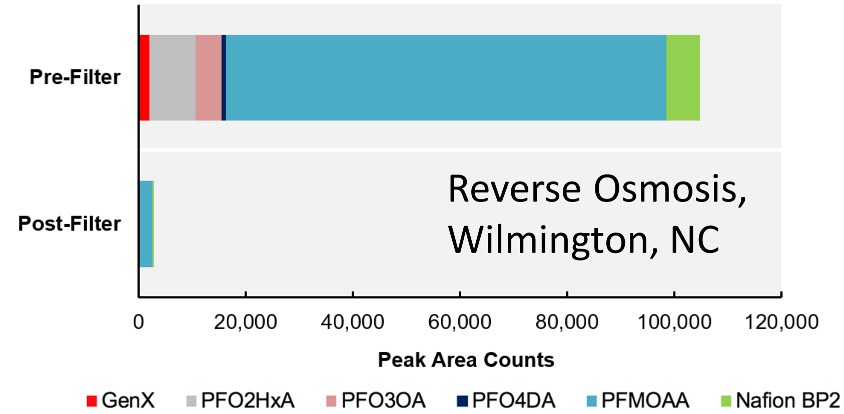
John Merrill, CCEE, NCSU

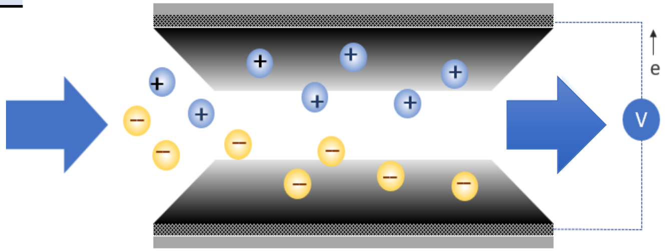


Duke UNIVERSITY

Heather Stapleton,
Nicholas School of the Environment

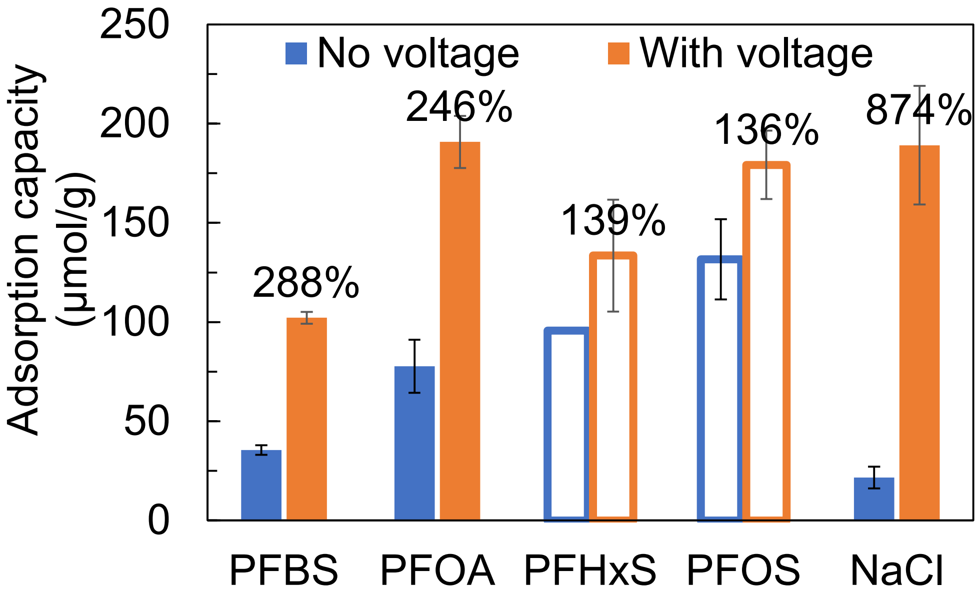
Can we electrically enhance PFAS adsorption on AC?

PFAS	pK_a
PFOA	-0.5~4.2
PFOS	< 1.0
PFHxS	0.14
PFBS	-3.31



Hypothesis: applying an electrical voltage between two AC electrodes will increase adsorption of ionic PFAS relative to identical electrodes with no applied voltage.

- At environmentally relevant pH values, many PFAS occur as charged ions.



Doug Call, CCEE, NCSU

Detlef Knappe, CCEE, NCSU

Shan Zhu, CCEE, NCSU

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Take Home Messages

- In the Cape Fear River watershed of NC, previously unknown PFAS were discharged into air and water for almost 40 years
- Once drinking water contamination became widely known, PFAS emissions to air and water were drastically reduced
- Environmental fate and transport of recently identified PFAS largely unknown (new EPA project)
- Exposure pathways other than drinking water are not well understood: food (new EPA project), air
- Health effects of recently identified PFAS are largely unknown
- Remediation of PFAS is challenging (persistent, short-chain PFAS difficult to remove from water) – new Water Research Foundation and ESTCP projects

Emerging Compounds – GenX Case

Julie Woosley and Mike Abraczinskas

North Carolina Department of Environmental Quality

April 22, 2019

GenX – Not a Generational Thing

- GenX = C3 Dimer Acid = $C_6HF_{11}O_3$
- GenX is a trade name for a man-made and unregulated chemical used in manufacturing nonstick coatings and for other purposes.

- An *emerging compound* in a family of chemicals known as per- and poly-fluorinated alkyl substances (PFAS)
- Produced and emitted by one company in NC – Chemours (formerly Dupont)
- Has been discharged into the Cape Fear River for 30+ years.
- Until the past couple of years, labs couldn't measure it.

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Emerging Compounds

What do we mean when we say Emerging Compounds?

- No specific limit in environmental regulations.
- Sparse knowledge about how they behave in the environment.
- Little known about their effects on human health and environment.

Emerging compounds pose significant challenges for regulatory agencies.

- How to prioritize?
- Research?
- Minimize impacts?
- *Communicate?*

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Emerging Compounds – GenX Case History

- **Early-mid 2017:** focus on surface water issues
- **Mid 2017:** groundwater issues discovered
- **Mid-late 2017:** air emission contributions

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GenX in Water

Emerging Compounds – GenX Case History

DEQ Sampling – Cape Fear River

GenX was first identified in the Cape Fear River by researchers at North Carolina State University.

Analysis of surface waters identified multiple PFAS compounds, including GenX, in the Cape Fear River at higher levels below than above the Chemours facility.

Water Resources began sampling:

- Process area sampling at Chemours
- Weekly composite sampling at the Chemours wastewater Outfall 002
- Weekly sampling of finished drinking water downstream of the Chemours facility

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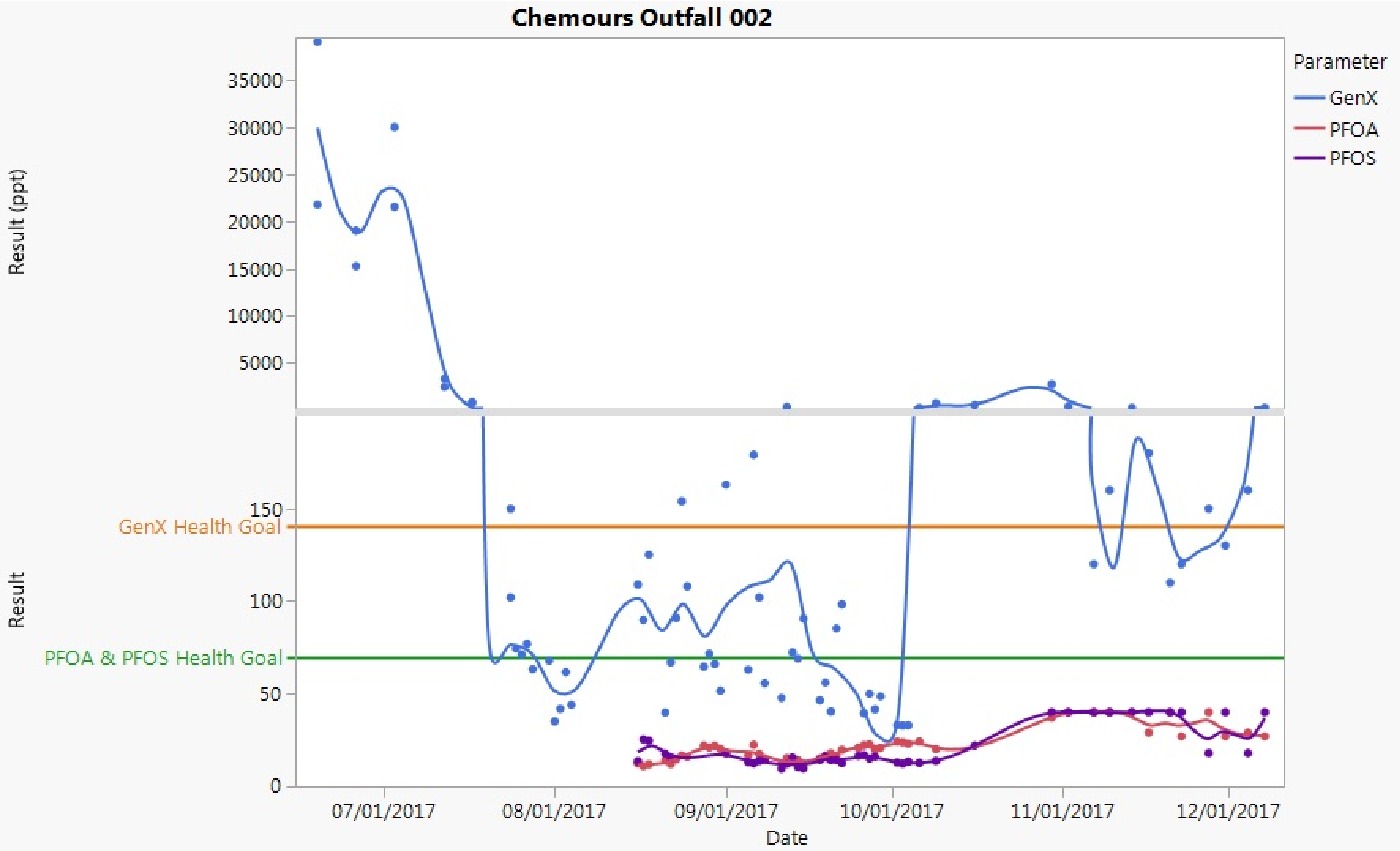
Data at Chemours Outfall 002

GenX (parts per trillion)



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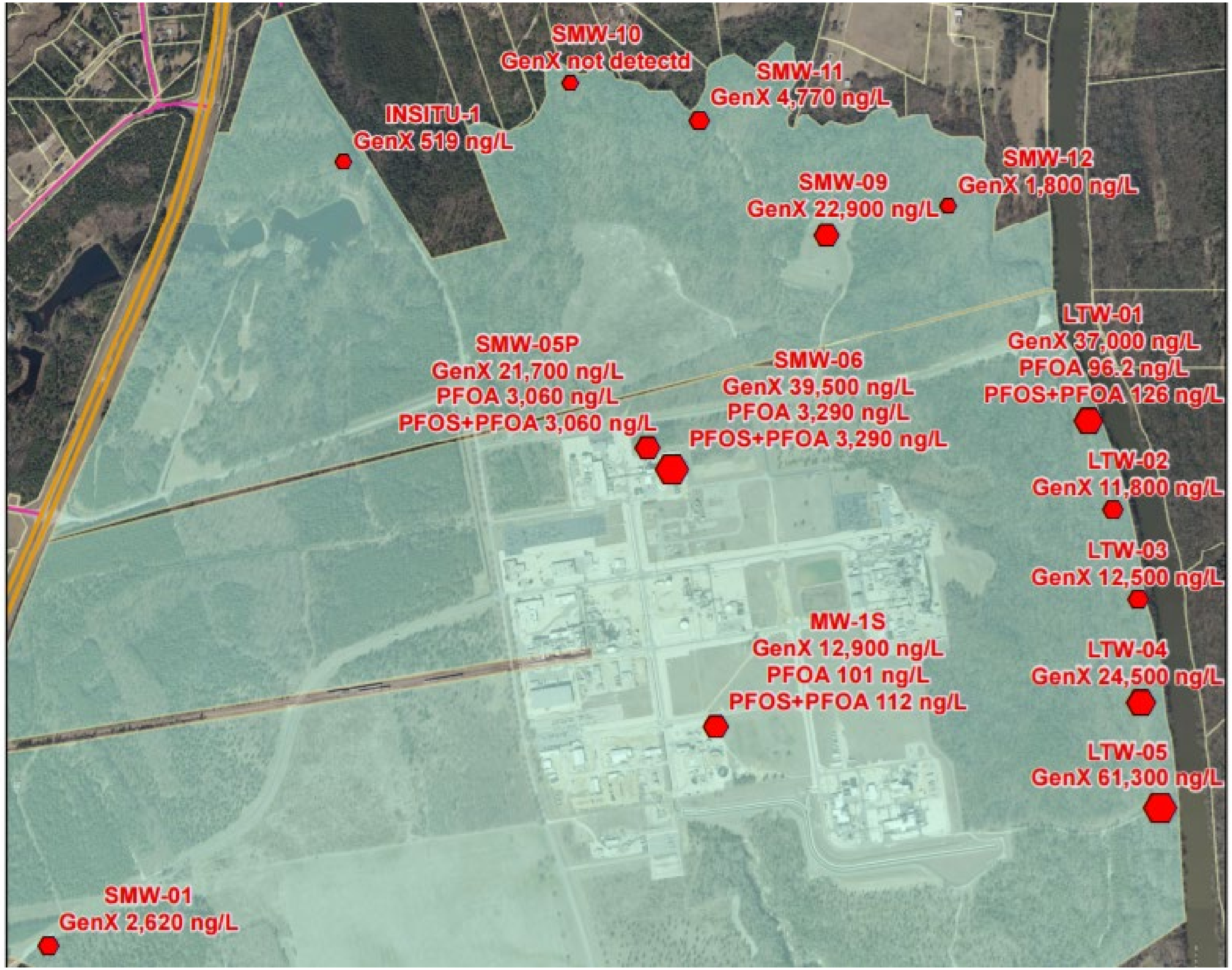
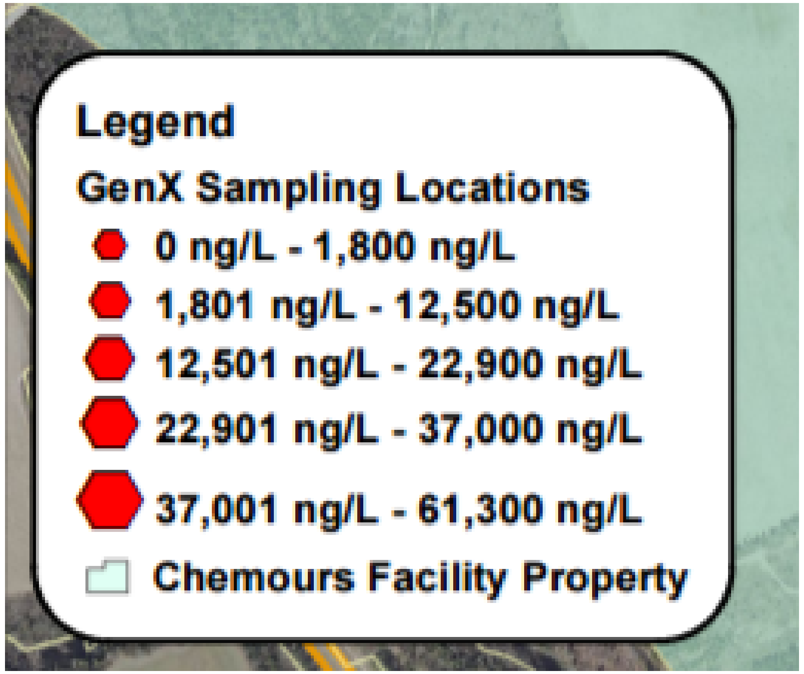
Onsite Groundwater Testing at Chemours





Found high levels of PFAS compounds in onsite monitoring wells

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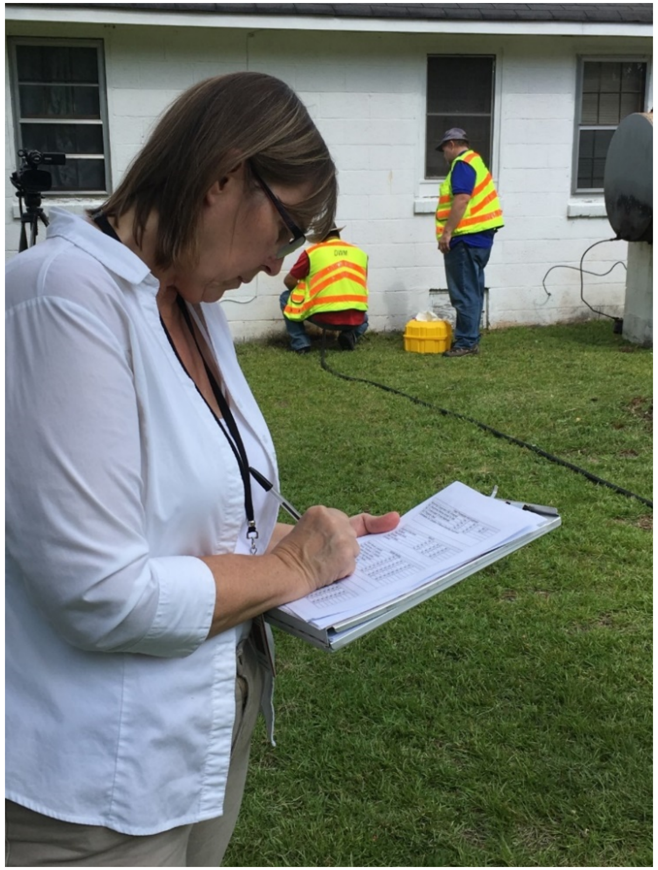
Offsite Groundwater Testing

- NC DHHS established a GenX drinking water health goal of 140 ppt
- Because of high levels of PFAS compounds found in onsite monitoring wells, DEQ tested wells on properties adjacent to Chemours first and found high levels
- Asked Chemours to test additional wells in the area to determine extent of contamination



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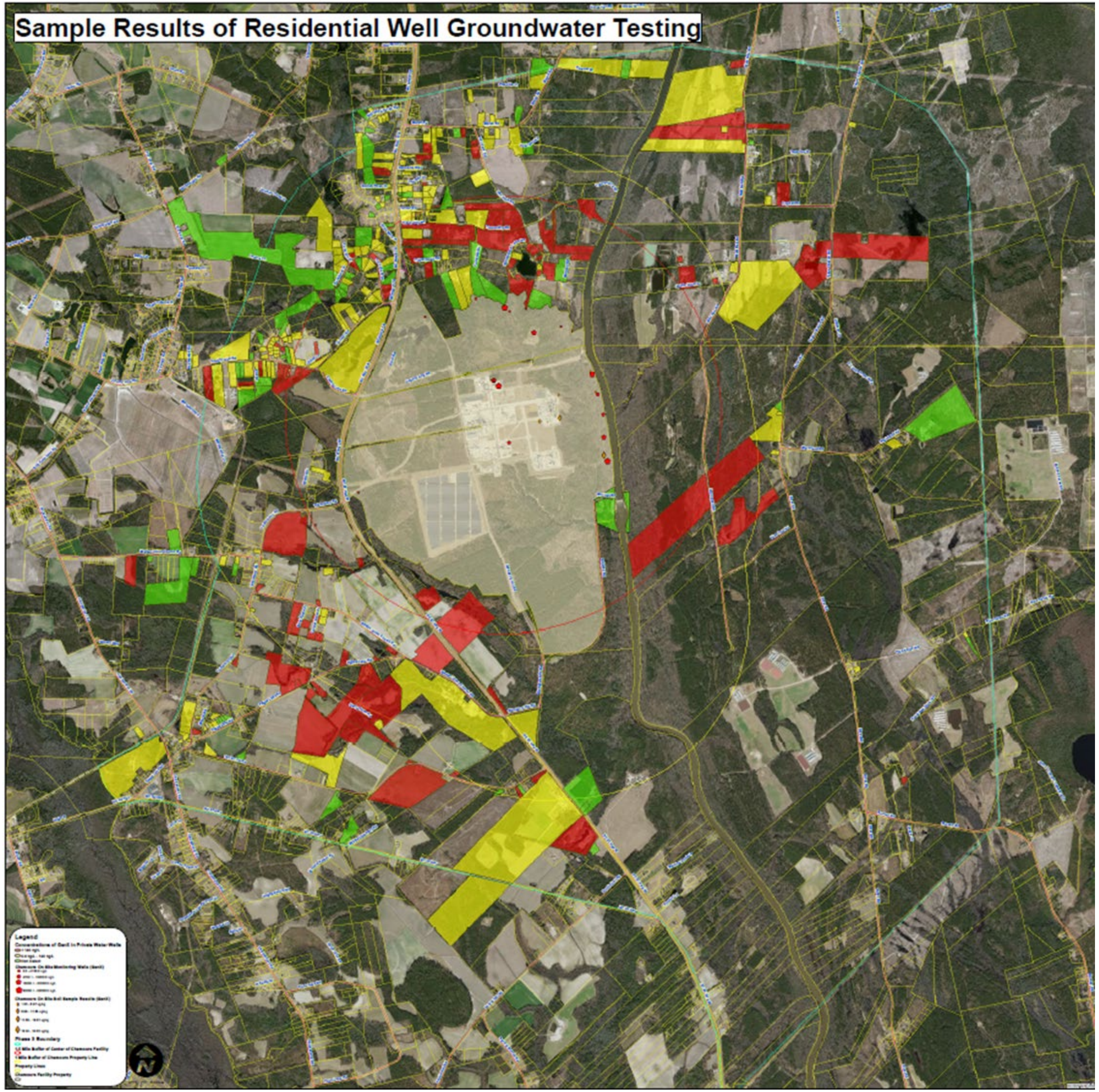

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GenX Private Well Summary Data

Combined Phase I, II, III , IV (partial) Private Well PFAS Data, also Includes Robeson Co. and DEQ-collected Data

Private Well Water GenX Summary	Combined Well Data
Distance from Chemours' border	Up to 5.5 miles
Well Collection Dates	9/6/2017 – 6/13/18
Number of Wells tested	823
Number of Exceedances of the GenX Provisional Health Goal	164
Number of Not-Detected ("ND") GenX Analyses	220
Number of GenX Detections Less than the Health Goal [a]	439
Maximum Detected GenX Concentration	4000 ng/L

a. The NC DHHS Provisional Drinking Water Health Goal for GenX is 140 ng/L (July 2017)

Other – Fish Testing

- Fish tissue testing found short-chain PFAS but no GenX in two species in a nearby pond (Largemouth Bass and RedEar Sunfish).
  - GenX at 700-1,000 ppt in goundwater and surface water at pond
- Truck spill results – EPA assistance
- Post-hurricane sampling report

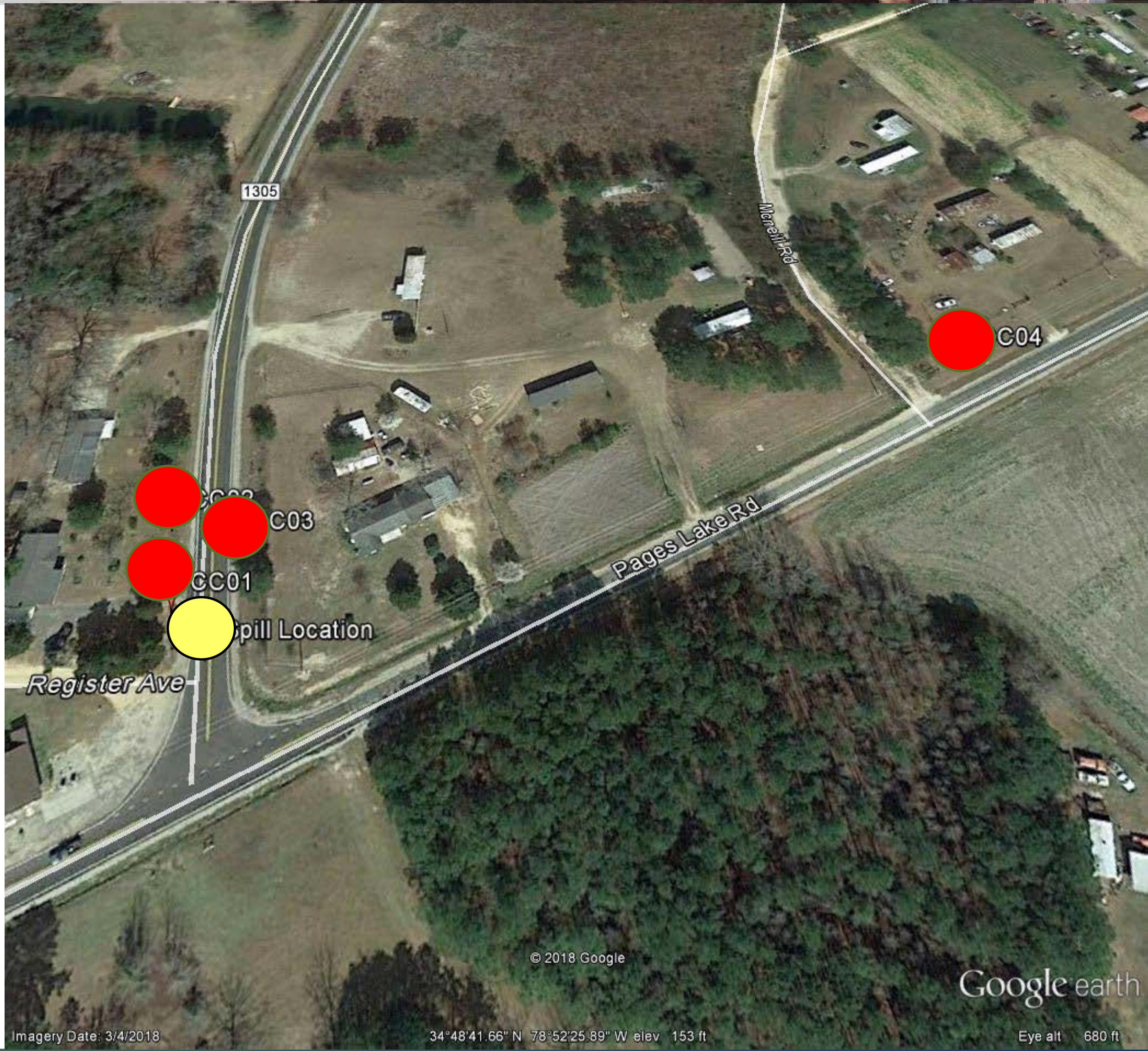
Other – Truck Spill

- A truck leaving the Chemours facility spilled liquid on the road near the intersection of Tobermory Rd. and Register Ave.

Liquid samples: collected by waste-receiving facility and a concerned citizen.

Soil samples: collected by DEQ and EPA staff.

Multiple PFAS at high levels in liquid; a few PFAS near background levels in soil



Chemours – Addressing Contamination

Consent Order Feb 2019

- DEQ signed a Consent Order with Chemours 2/26/19: https://deq.nc.gov/news/hot-topics/genx-investigation

- $12M civil penalty and $1M in investigative costs.

- Requirement to achieve maximum reductions of all remaining PFAS contributions to the Cape Fear River on an accelerated basis, including groundwater.

- Additional penalties will apply if Chemours fails to meet the conditions and deadlines established in the order.

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Chemours – Addressing Contamination

Consent Order Feb 2019: Groundwater

Sample Wells and Provide Drinking Water:

- Sample drinking water wells
  - ¼ mile beyond the closest well that had PFAS levels above 10 parts per trillion as well as annually retest wells that were previously sampled.

- Provide permanent drinking water supply
  - For those with GenX above 140 parts per trillion or applicable health advisory.
  - Public waterline connection or whole building filtration system

- Provide, install and maintain up to three under-sink system per residence
  - Reverse osmosis drinking water systems for:
    - Combined PFAS levels above 70 parts per trillion or
    - Any individual PFAS compound above 10 parts per trillion.

Chemours – Addressing Contamination

Consent Order Feb 2019

- Assess and remediate PFAS contamination, on- and offsite.
  - Complete receptor survey
- Fund 3rd party assessments of fate and transport and development of analytical chemistry methods for total organic fluorine.
- Toxicity studies to determine potential health risks associated with release of PFAS compounds into the environment.
- Notify and coordinate with downstream public water utilities when potential discharge of GenX compounds into the Cape Fear River above140 ppt.
- Reporting

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Questions?

Julie S. Woosley
Hazardous Waste Section Chief
NC DEQ, Division of Waste Management

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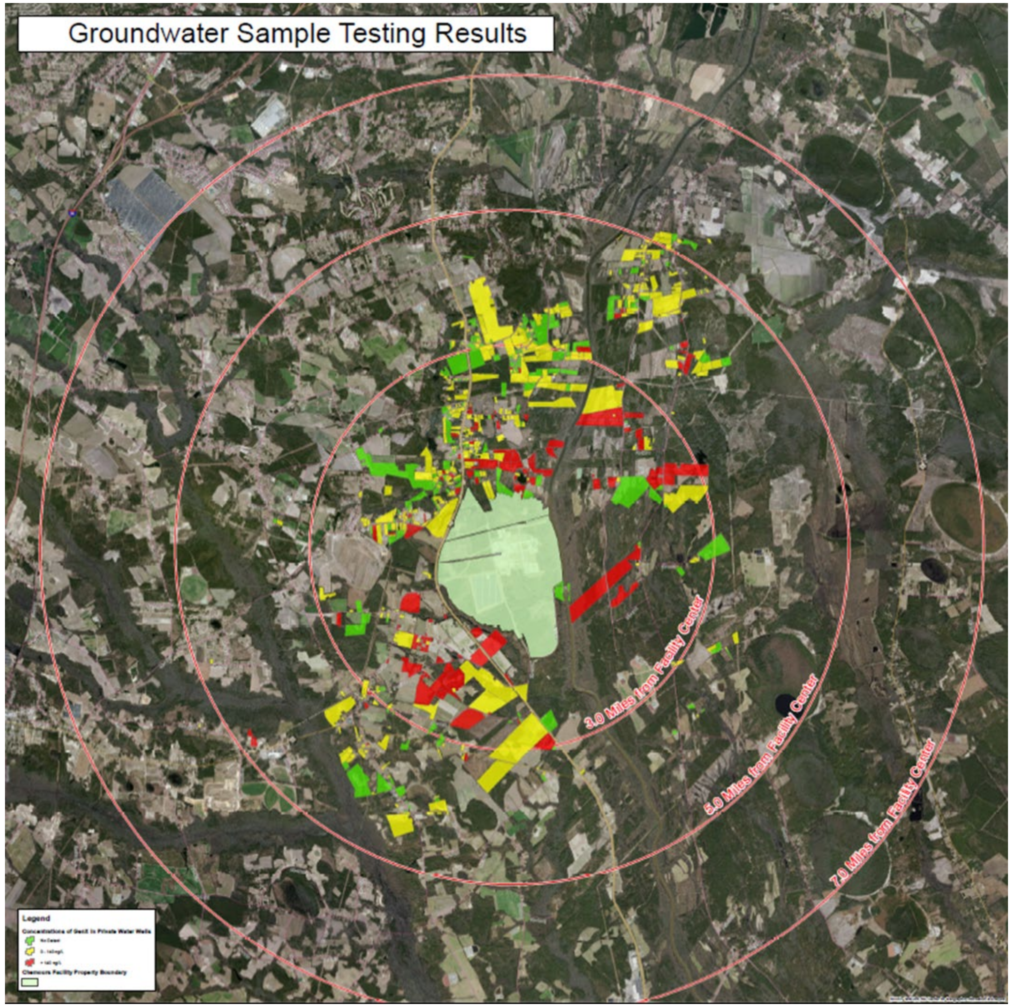
GenX in Air

Division of Waste Management
GenX Private Well Sampling



Well sampling results in the Chemours area.

Approximate distances from facility boundary:

- Northeast – 5.5 miles
- West – 1.8 miles
- Southwest – 3.9 miles
- East – 2.6 miles

GenX: NC health goal = 140 ng/l

Red = > 140 ng/l
Yellow = 0-140 ng/l
Green = Non-detect

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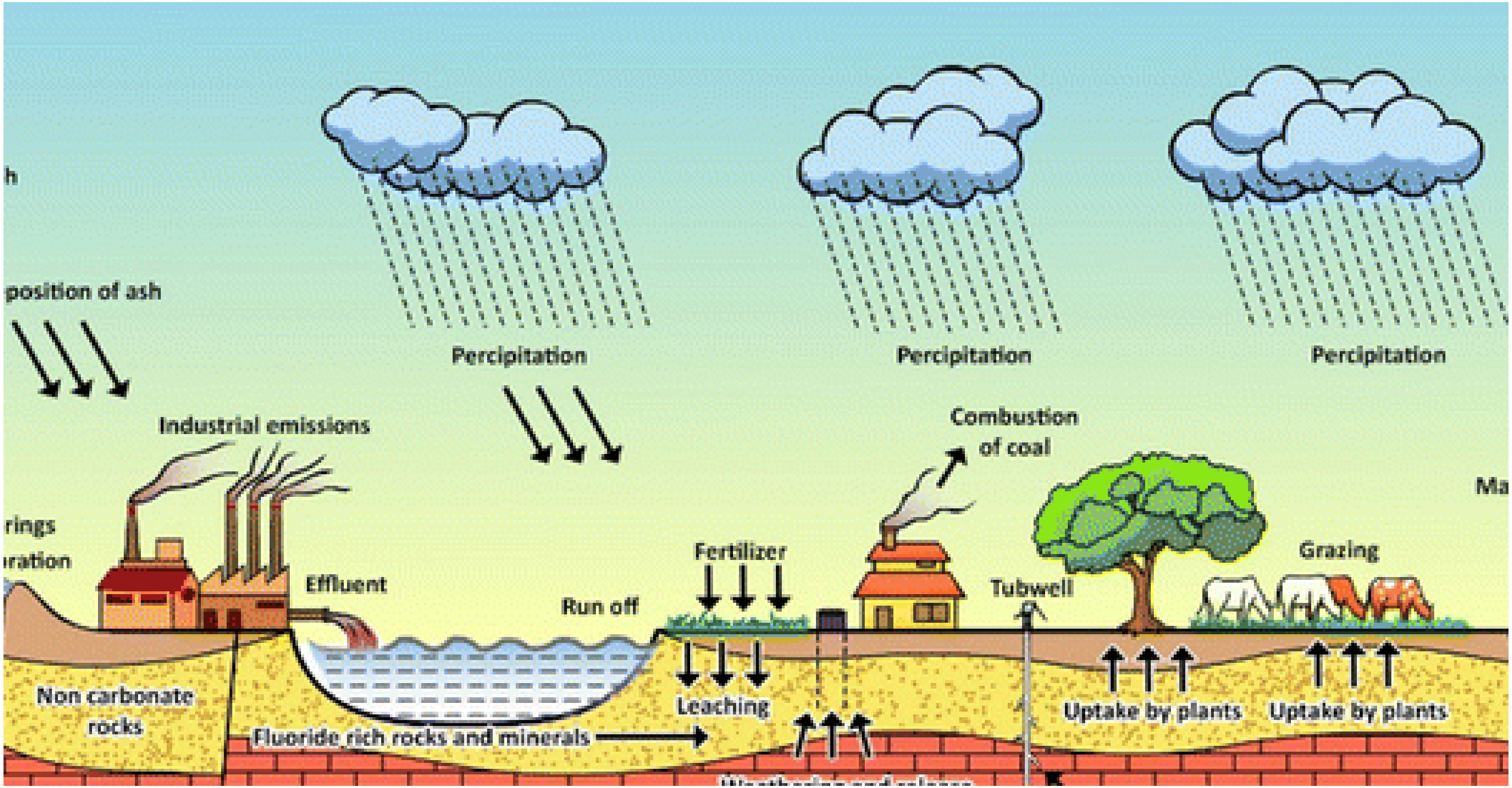

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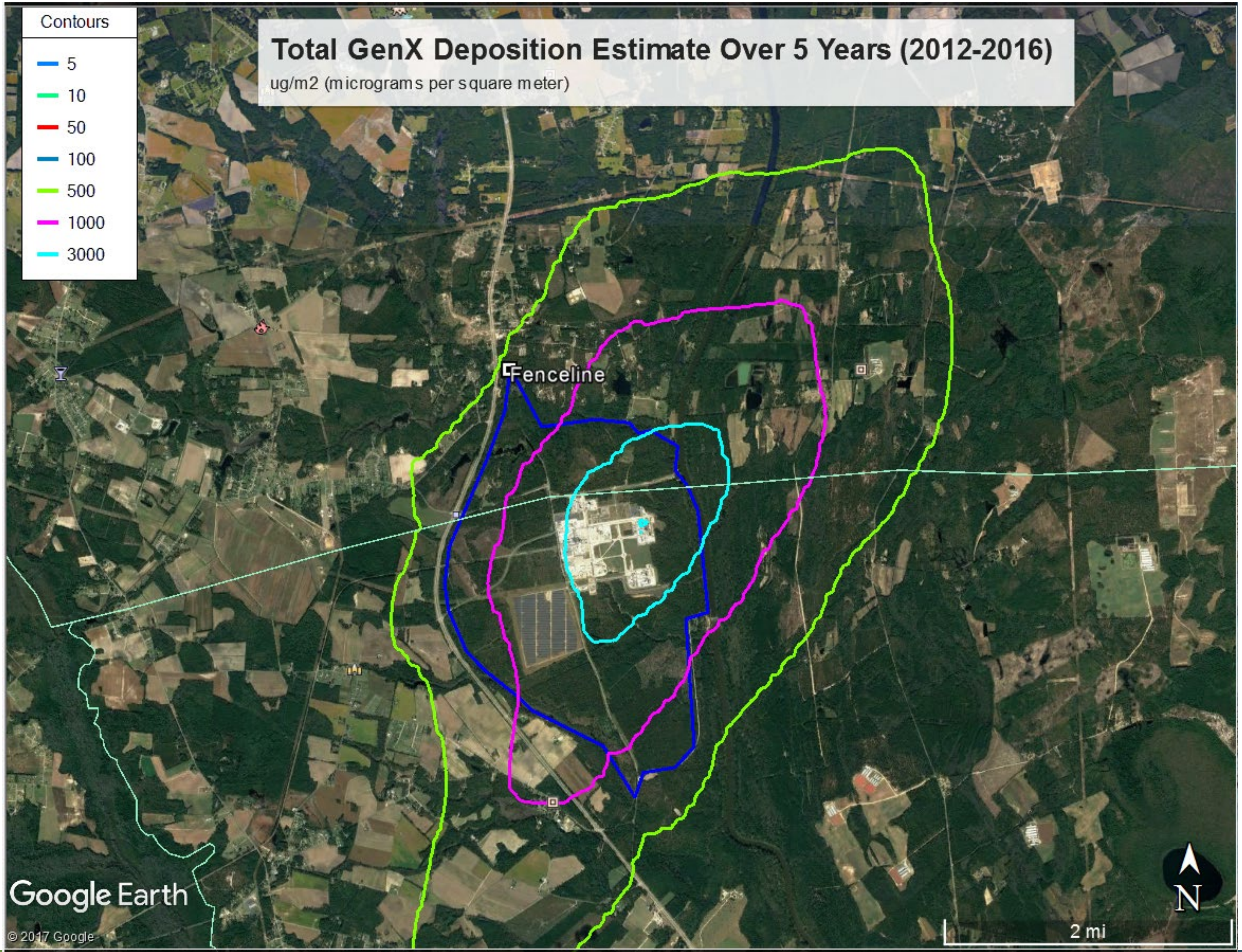
position of ash
Percipitation
Percipitation
Percipitation
Industrial emissions
Combustion
of coal
Ma
rings
ration
Fertilizer
Grazing
Effluent
Tubwell
Run off
Non carbonate
rocks
Leaching
Uptake by plants
Uptake by plants
Fluoride rich rocks and minerals

Emerging Compounds – GenX Case History



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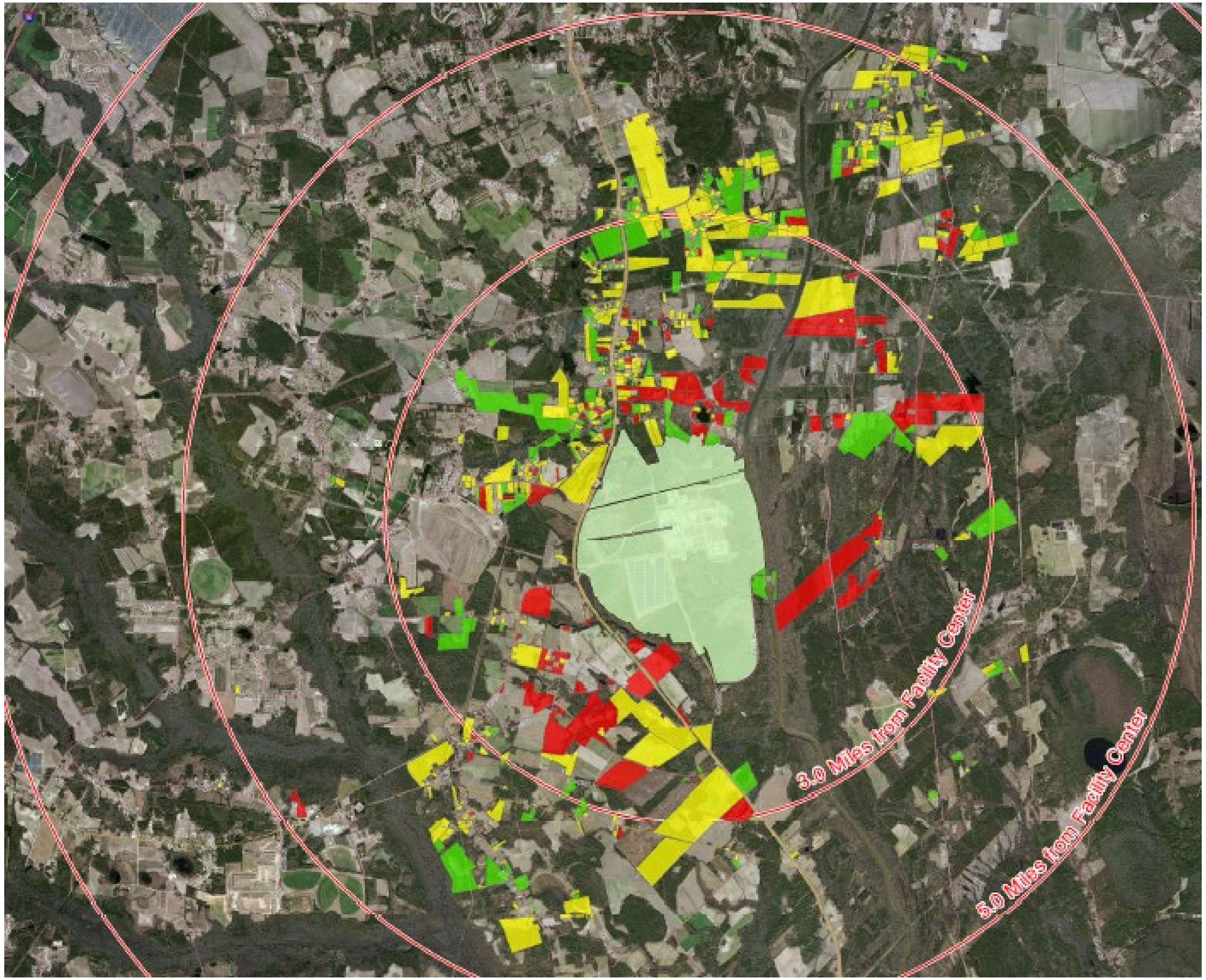
Emerging Compounds – GenX Case History



Private groundwater wells

- >140 ppt GenX
- 10-140 ppt GenX
- ND GenX

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Department of Environmental Quality

Emerging Compounds

DAQ's investigation involving GenX and other PFAS from Chemours

- GenX emissions data
  - Started with only estimates
  - Required stack tests
  - Method development
  - First of its kind measurements

Chemours 2016 emissions estimates as originally reported to DAQ	Chemours revised 2016 emissions estimates as of October 2017	Latest calculations of annual emissions, including stack test measurements
66.6 lb/yr	594 lb/yr	2302.7 lb/yr

Emerging Compounds – GenX Case History

What about ambient air measurements???

- No agreement on appropriate methods.
- But, we knew we could measure it in water.
- Why not collect rainwater samples to get a sense of atmospheric contributions groundwater issues?
- Purchased temporary rain collection equipment.
- Used lab protocols to prepare equipment.

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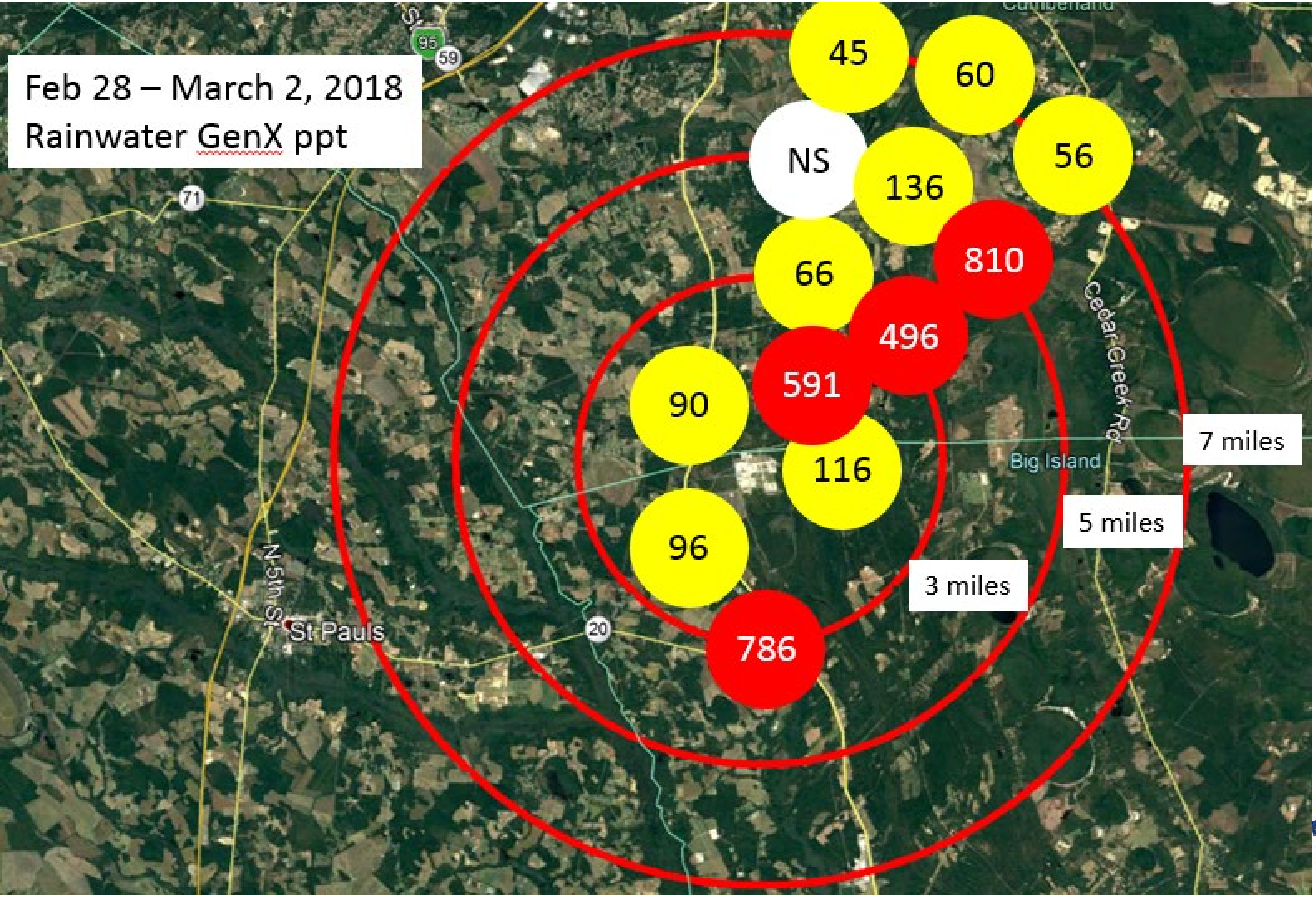

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Emerging Compounds

DAQ's investigation involving GenX and other PFAS from Chemours

Summary of facts:

- The measured air emissions of GenX compounds are significantly higher than previously understood and reported.
- DAQ has measured GenX deposition through rainfall as far as 20 miles from the facility.
- The evidence of atmospheric deposition of GenX shows a geographic footprint that is similar to the detection of GenX in groundwater samples.

DEQ
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Emerging Compounds
GenX – Review of Actions

- The data led us to confirming the linkages between air emissions and groundwater contamination.
- Drove serious discussions about air pollution controls being added in order to significantly reduce or eliminate the impacts to the water.

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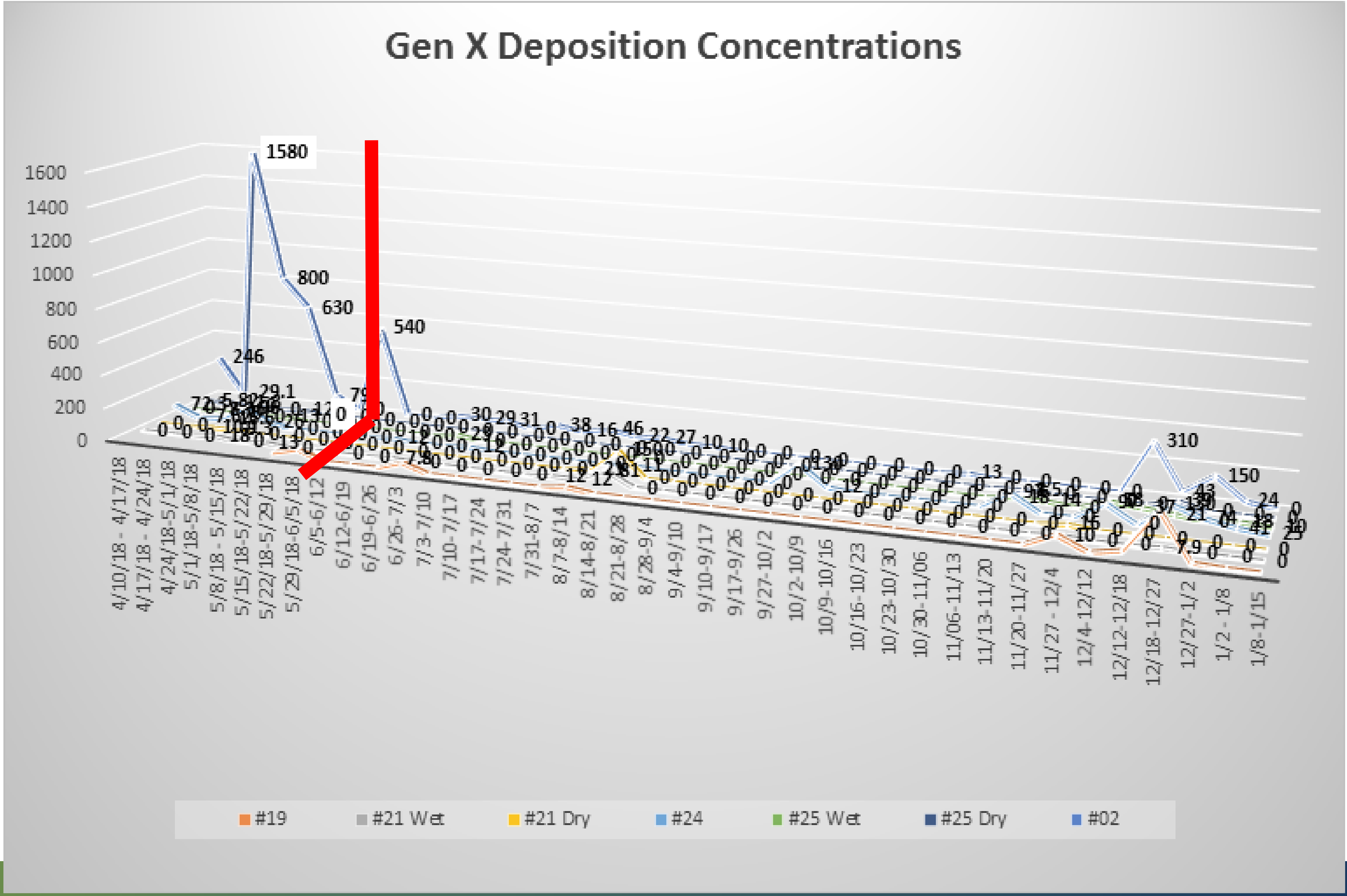
Emerging Compounds

GenX - Recent Actions | Carbon Adsorbers in place – late May 2018



Gen X Deposition Concentrations
1600
1400
1200
1000
800
600
400
200
0
1580
800
630
540
246
310
150
#19
#21 Wet
#21 Dry
#24
#25 Wet
#25 Dry
#02

Emerging Compounds
GenX – Consent Order

- Chemours will install a thermal oxidizer for control of all PFAS from HFPO, VEN, VES, RSU, TFE, MMF, IXM processes by December 31, 2019

  - Test report demonstrating 99.99% control efficiency for all PFAS within 90 days of installation/connection.

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Emerging Compounds
GenX – Consent Order

GenX Emissions Reduction Milestones

1. 82% facility-wide reduction of GenX compounds relative to 2017 total reported emissions by October 6, 2018 and 12-month period that follows.
2. 92% facility-wide reduction of GenX compounds relative to 2017 total reported emissions by December 31, 2018 and 12-month period that follows.
3. 99% facility-wide reduction of GenX compounds relative to 2017 total reported emissions by December 31, 2019 and for each consecutive 12-month period following that date.

Stipulated penalties for #1, 2 & 3: $200,000, $350,000, and $1,000,000, respectively.

Emerging Compounds: Take Home Messages

Take home messages for:

- EPA: We need each other!
  - Emissions stack test method development
    - Source attribution starts with good emissions data
  - Ambient air monitoring
    - Does EPA have capabilities that states don’t?
  - How to prioritize emerging compounds?
    - Prevalence, concentrations, toxicity.

Emerging Compounds: Take Home Messages (con't.)

Take home messages for:

- Industry: Know what is in your waste streams!
- State: Monitoring and surveillance is a must!
  - Get the resources in place!
  - Must look beyond GenX… What are the possible needs?
  - Do we have the lab and field equipment that we need?
  - Risk communication is a must !!!

NORTH CAROLINA Department of Environmental Quality

Thank you!

Fayetteville Regional Office Staff – Especially Greg Reeves, Heather Carter, Mitch Revels
Wilmington Regional Office Staff – Especially Brad Newland
Laboratory Analysis Branch Staff – Especially Jim Bowyer, Karen Clevenger, Forest Shepherd, Pernell Judd, Chaitali Bhaumik
Raleigh Regional Office Staff – Especially Ray Stewart
Raleigh Central Office- Especially:

- Permitting – Heather Sands, Tom Anderson, Nancy Jones, Alex Zarnowski, William Willets
- Technical Services – Gary Saunders, Brent Hall, Steve Hall, Steve Carr Gregg O'Neal, Shannon Vogel
- Planning – Elliot Tardif, Kevin Ours
- Ambient Monitoring - Patrick Butler, Derrick House, James Stroup, Joette Steger, Marcus Meadows, Nathan Miller, Sahid Thomas, Scott Ginn, Steven Walters

Special thanks –
<u>Heather Sands – Permit Engineer</u>
<u>Gary Saunders – Source Testing and Technical Expert</u>

Thank you!

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GenX Litigation Update

Geoff Gisler
Southern Environmental Law Center
April 23, 2019

Litigation Landscape

CapeFear Public Utility Authority

NORTH CAROLINA
Environmental Quality

CAPE FEAR RIVER WATCH

The Process

- Who are the parties?
- What claims?
- Why did they sue?

Cape Fear Public Utility Authority, et al. v. The Chemours Company, et al.

- Plaintiffs: CFPUA, Brunswick County
- Claims:
  - Public nuisance
  - Private nuisance
  - Trespass to real property
  - Trespass to chattels
  - Negligence *per se*
  - Negligence
  - Failure to warn
  - Negligent manufacture
- Relief:
  - Injunctive relief
  - Compensatory damages
  - Punitive damages

Victoria Carey, et al. v. E.I. DuPont de Nemours and Company, et al.

- Plaintiffs: Property owners and everyone exposed to GenX
- Claims:
  - Negligence
  - Gross negligence
  - Public and private nuisance
  - Trespass
  - Unjust enrichment
- Relief:
  - Injunctive relief
  - Compensatory damages
  - Punitive damages

State of North Carolina, Dep't of Environmental Quality v. The Chemours Company

- Plaintiff: N.C. Department of Environmental Quality
- Claims:
  - Violation of state groundwater rules
  - Misrepresentation and violation of NPDES disclosure requirements
  - Unpermitted discharge
- Relief:
  - Control air emissions
  - Control all other sources
  - Prohibit discharge of process wastewater
  - Provide accounting of discharge
  - Cease violations of water and air quality laws

Cape Fear River Watch v. The Chemours Company

- Plaintiff: Cape Fear River Watch
- Claims:
  - Unpermitted discharge
  - Violations of NPDES permit conditions
  - Violation of Toxic Substances Control Act
- Relief:
  - Require 99% air pollution reduction
  - Prevent discharges to surface waters

Consent Order: Pollution Reduction

- Air emissions:
  - Oct. 2018-Oct. 2019: 82% reduction
  - Jan. 2018-Jan. 2019: 92% reduction
  - Jan. 2020: 99% reduction
- Surface water discharge:
  - Process water: no discharge until permitted
  - Non-process water: 80% reduction
  - Old Outfall 002: 99% reduction
- Groundwater:
  - Target: practical quantitation limit
  - Minimum: 75% reduction

Consent Order: Drinking Water

- Well users:
  - Whole house filters
  - Under-sink reverse osmosis filters
- Utilities:
  - Requirement to characterize PFAS in raw water
  - Information
    - Input on plans
    - Notification of upsets

Consent Order: Research

- Analytical methods for known and new PFAS
- Sediment contamination in Cape Fear River
- Fate and transport study
- Toxicity studies

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