Understanding the Fate, Transport, and Mitigation of PFAS in the Environment

Wisconsin Public Utility Institute
UNIVERSITY OF WISCONSIN–MADISON

Presented by:

GZA GeoEnvironmental Inc.

John C. Osborne, P.G.

Principal Hydrogeologist/Senior Vice President

Serving:
Architects/Engineers, Attorneys, Contractors, Developers/Retail, Energy/Utilities, Financial/Insurance, Municipal, State & Federal Government, Industry Institutional

31 Offices with 700 science and engineering staff
www.gza.com

Presentation Content

General Presentation Topics

1. Unique Aspects of the ‘PFAS Problem’
2. Key Chemical properties
3. Behavior in the Environment
4. Vulnerability of Water Supply Impacts
5. Consideration for Investigating for PFAS
6. Sampling Plans and Lab Testing
7. Remediation and Treatment approaches
    - Soil
    - Groundwater
    - Point of use

Where is GZA coming From on PFAS?

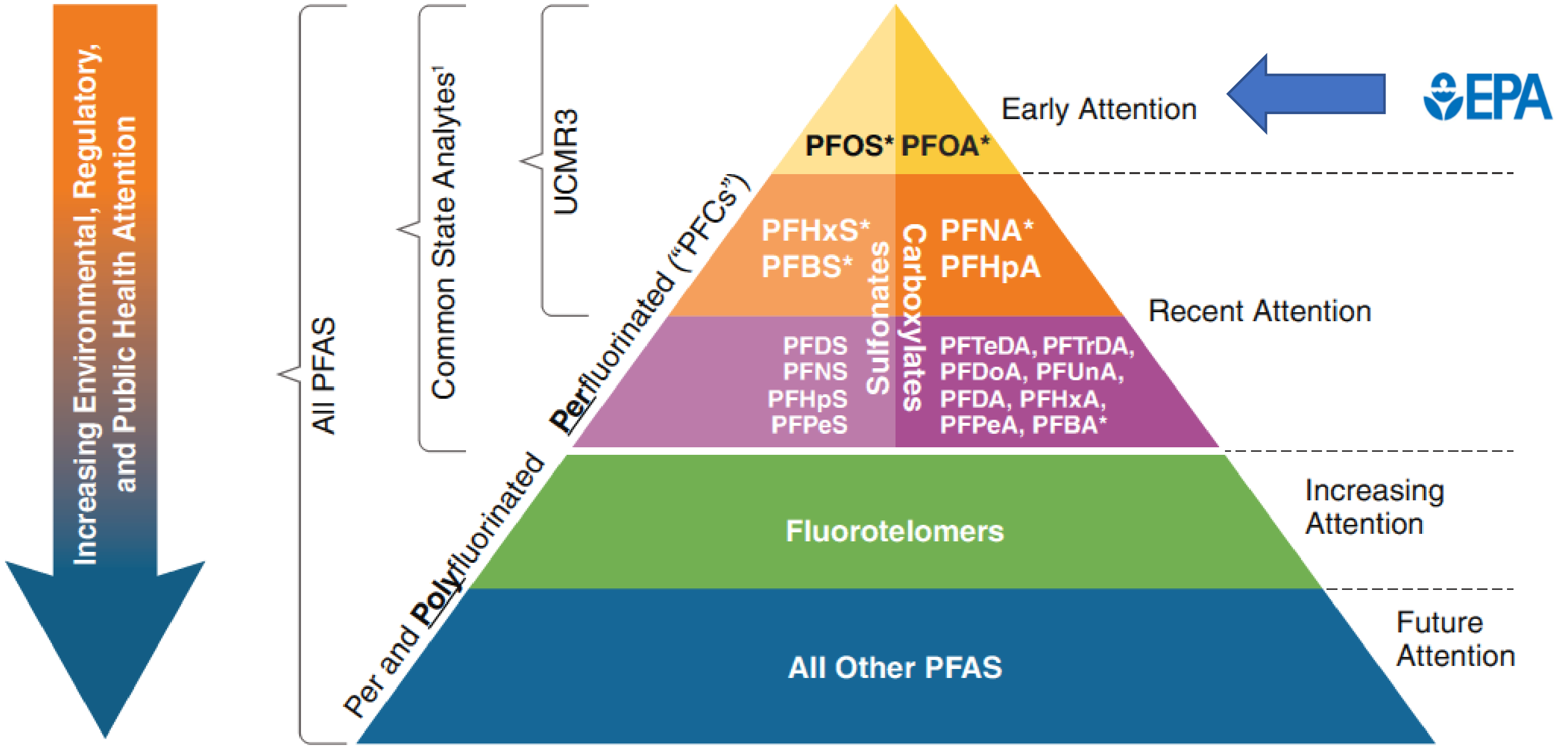
- Working on PFAS projects in 10 States;
- Drafted one of the first USEPA-accepted QAAPs for PFAS multi-media sampling;
- We have trained over 40 field staff on the rigors of PFAS sampling;
- We have sampled 1000s of residential wells for PFAS;
- Installed and maintain over 500 whole-house PFAS treatment systems;
- We are members of the ITRC Task Force on PFAS.

The PFAS Problem – In a nutshell?

1. Large class of over 4,000 synthetically manufactured fluorinated organic compounds
2. Possess a unique combination of properties that offer numerous beneficial applications in industrial and commercial products
3. Same unique properties make them durable in the natural environment
4. Health effects are concerning
5. Until recently, we have not been looking for them

PFASs are used in a variety of consumer and industrial products

PFAS – Produced Through Synthetic Fluorination Chemistry



EPA Health Advisory Level of 70 ppt

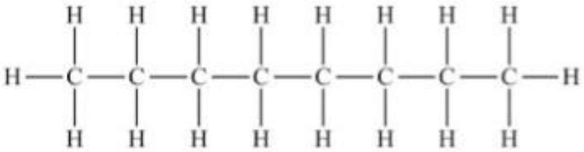
*Common regulatory criteria or health advisories
[1]Sum of informal poll (NJ, NH, MN)

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

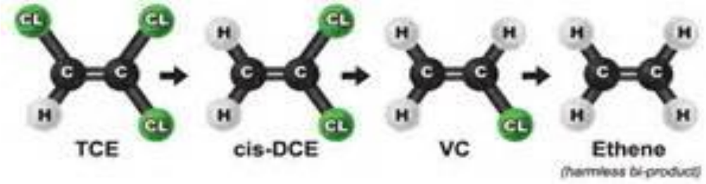
Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment
(Source: J. Hale, Kleinfelder, used with permission)

How is PFAS Different from VOCs

Octane



Common Chlorinated Compounds



What make PFAS different?

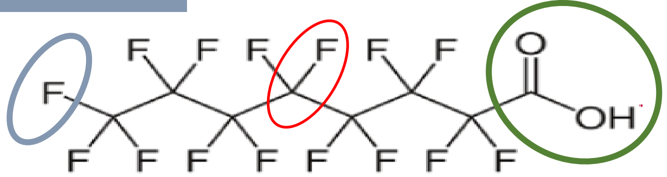
- **C-F bond is one of the strongest bonds**
- **nonfluorinated "head" with a polar functional group (repels)**
- **carbon-fluorine "tail" (dissolves)**

Tail
Hydrophobic/lipophobic

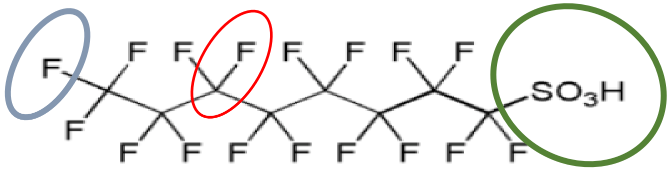
C-F Bond

Head
Hydrophilic

PFOA – Perfluorooctanoic acid

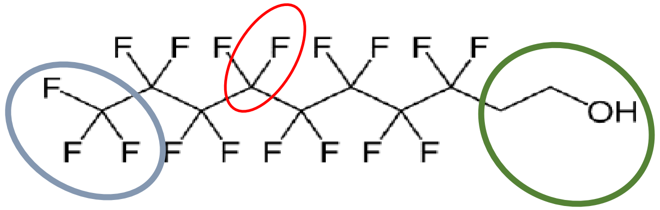


PFOS – Perfluorooctane sulfonic acid

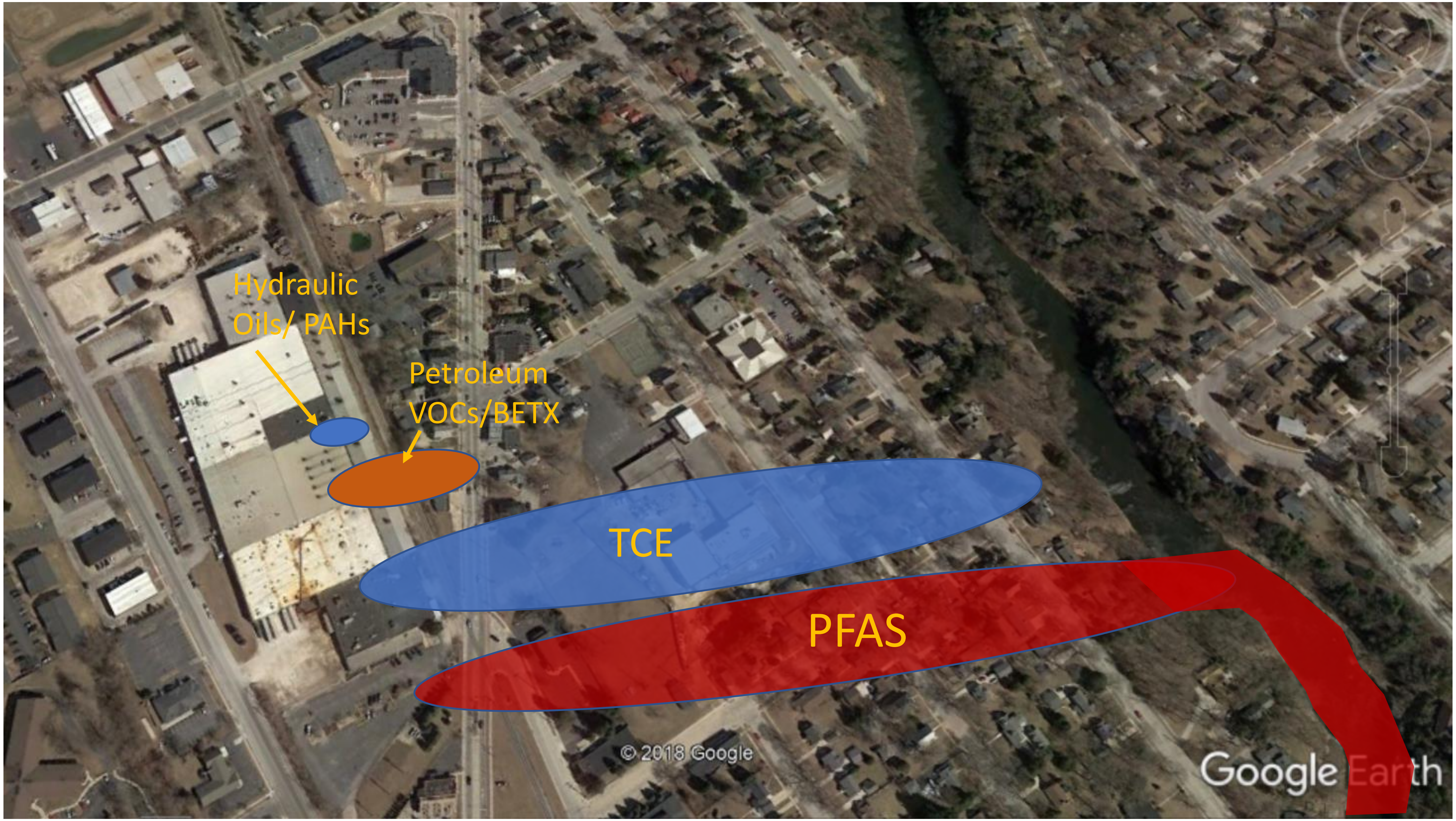


Precursor of PFOA

- ***Fluorotelomer alcohols***



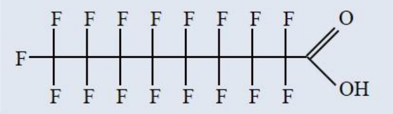
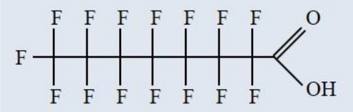
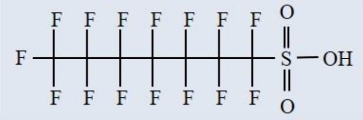
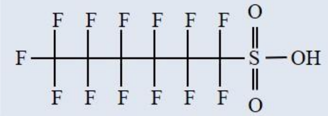
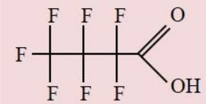
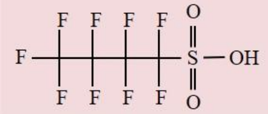
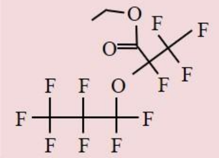
Industrial Site with Relative Plume Dimensions of Common Contaminants



PFAS in the Environment

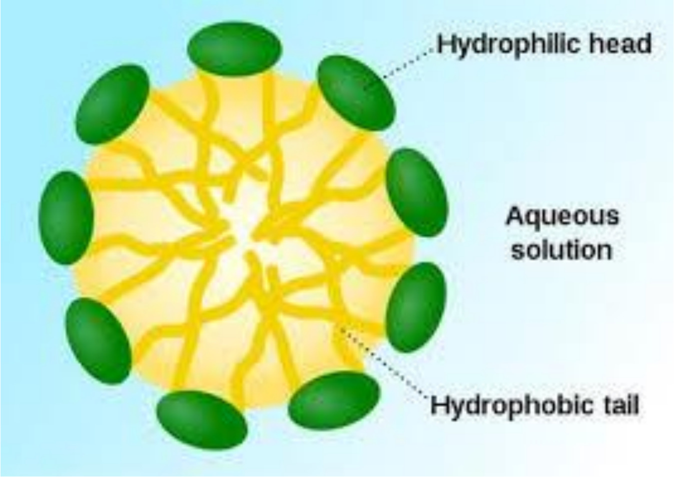
- Highly stable and resistant to degradation mechanisms:
- Relatively Soluble
- Resistant to biological degradation
- The carbon-Fl tail exhibits hydrophobic and lipophobic tendencies
- Like surfactants they have reduced surface tension that enhances infiltration/mobilization
- Prone to sorption through electrostatic forces and organic carbon
- Properties enable bioaccumulation

Figure 1. Description of the most frequent PFAS compounds currently being assessed for specific State action levels and discussed in this paper.

Long Chain	Perfluorononanoic acid (PFNA)	$C_9HF_{17}O_2$	
Long Chain	Perfluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$	
Long Chain	Perfluorooctane sulfonic acid (PFOS)	$C_8F_{17}SO_3H$	
Long Chain	Perfluorohexane sulfonic acid (PFHxS)	$C_6HF_{13}O_3S$	
Short Chain	Perfluorobutanoic acid (PFBA)	$C_4HF_7O_2$	
Short Chain	Perfluorobutane sulfonic acid (PFBS)	$C_4HF_9O_3S$	
Short Chain	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (GenX)	$C_6HF_{11}O_3$	

Partitioning

- Partitioning Mechanisms
  - PFAS “tail” repels water (hydrophobic) and oil/fat repellent (lipophobic)
    - drives associations with organic carbon in soil
  - PFAS “head” are polar and attracted/dissolves in water (hydrophilic)
- Sorption & Retardation
  - Shorter chains are retarded less than the longer chains
  - Longer (C8) chains are sorb more strongly than shorter (<C6) chains
  - Branched isomers have less sorption than linear
- Volatility
  - Low vapor pressures, high water solubility (very mobile in groundwater)
  - Stack emissions = atmospheric and particulate transport
- Advection/dispersion/diffusion
  - PFAS transport flow is controlled by media (soil/water/air), concentration not naturally reduced
  - PFAS groundwater plumes are narrow; whereas, air and surface water have greater dispersion
  - PFAS diffusion in groundwater is slow but greater in air and surface water
- Deposition/Leaching
  - Atmospheric transport can be in miles with deposition to soil/surface water/surfaces
  - PFAS mobilized from soil to groundwater or to surface water (AFFF, Biosolids, precipitation)



Micelle Formation

Precursors - Transformation into PFAS

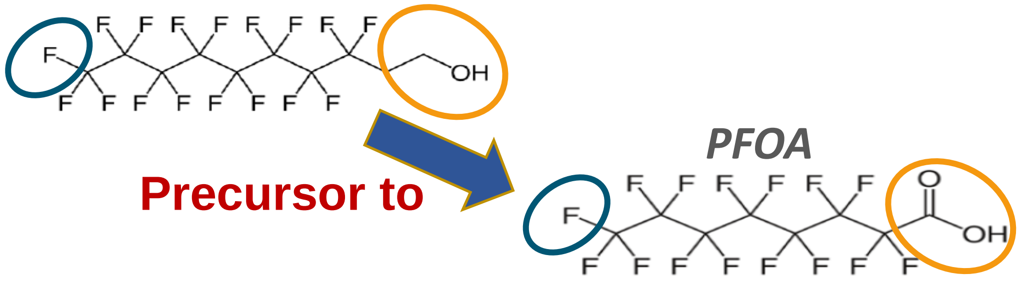
PFAS – not just per...

PFAS (Per- and Poly-)

- **Perfluorinated Substances**
  - PFCAs
  - PFSAs
  - PFPAs
  - Etc.
  - e.g., PFOA
  - e.g., PFOS
- **Polyfluorinated Substances**
  - FTOHs
  - FTSs
  - FSAs
  - Etc.
  - e.g., 8:2 FTOH
  - e.g., 8:2 FTS

Precursors ←

8:2 fluorotelomer Alcohol

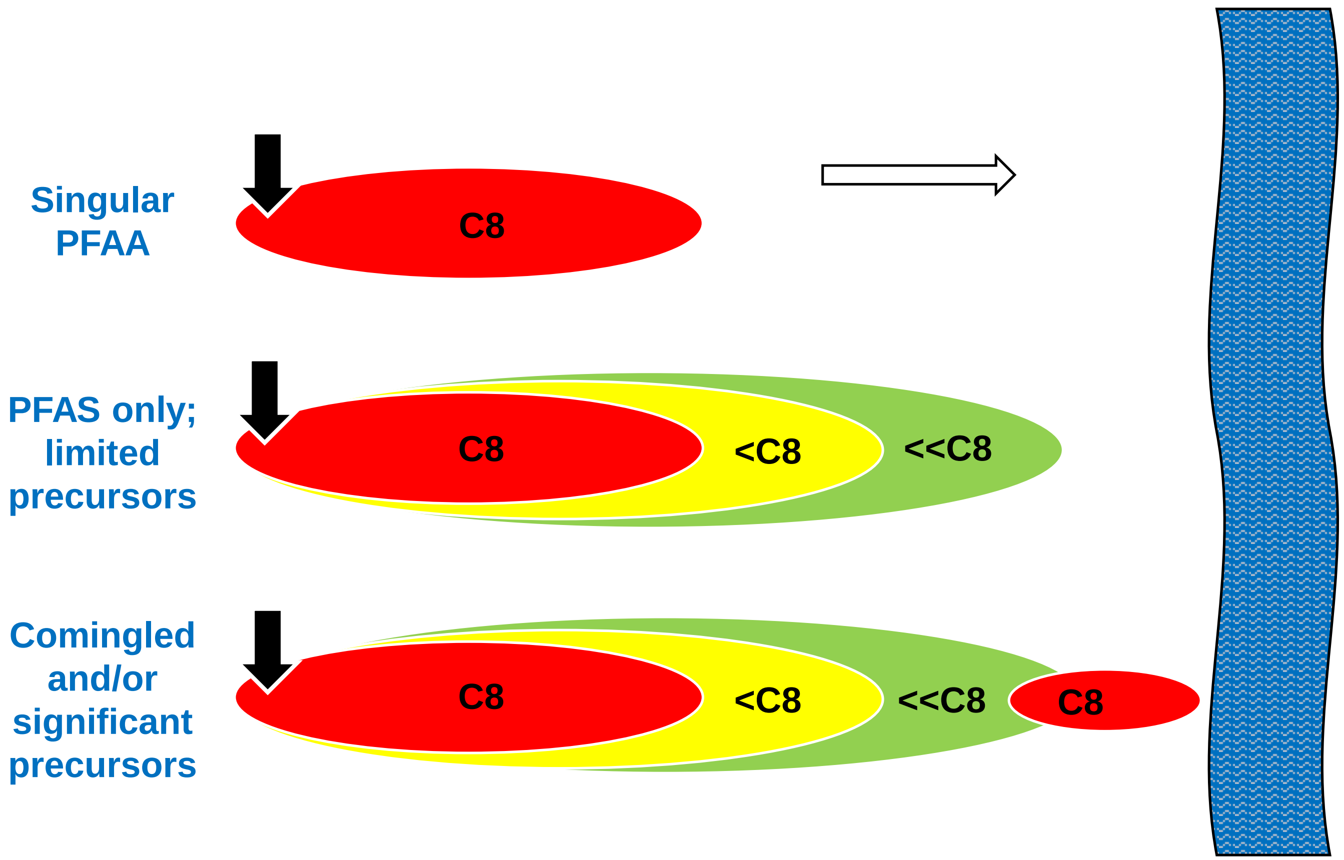


- Both biotic and abiotic transformation of polyfluorinated substances (precursors) to perfluorinated substances of interest (e.g., PFOA)
- Pool of potential precursors (PFAS "Dark Matter") is large and generally unknown

PFOA - Perfluorooctanoic acid
PFOS - Perfluorooctane sulfonic acid
PFHxS - Perfluoro hexane sulfonic acid
PFNA - Perfluorononoanoic acid
PFDA - Perfluorodecanoic acid

Approx. 4,000 compounds 40+ different subcategories

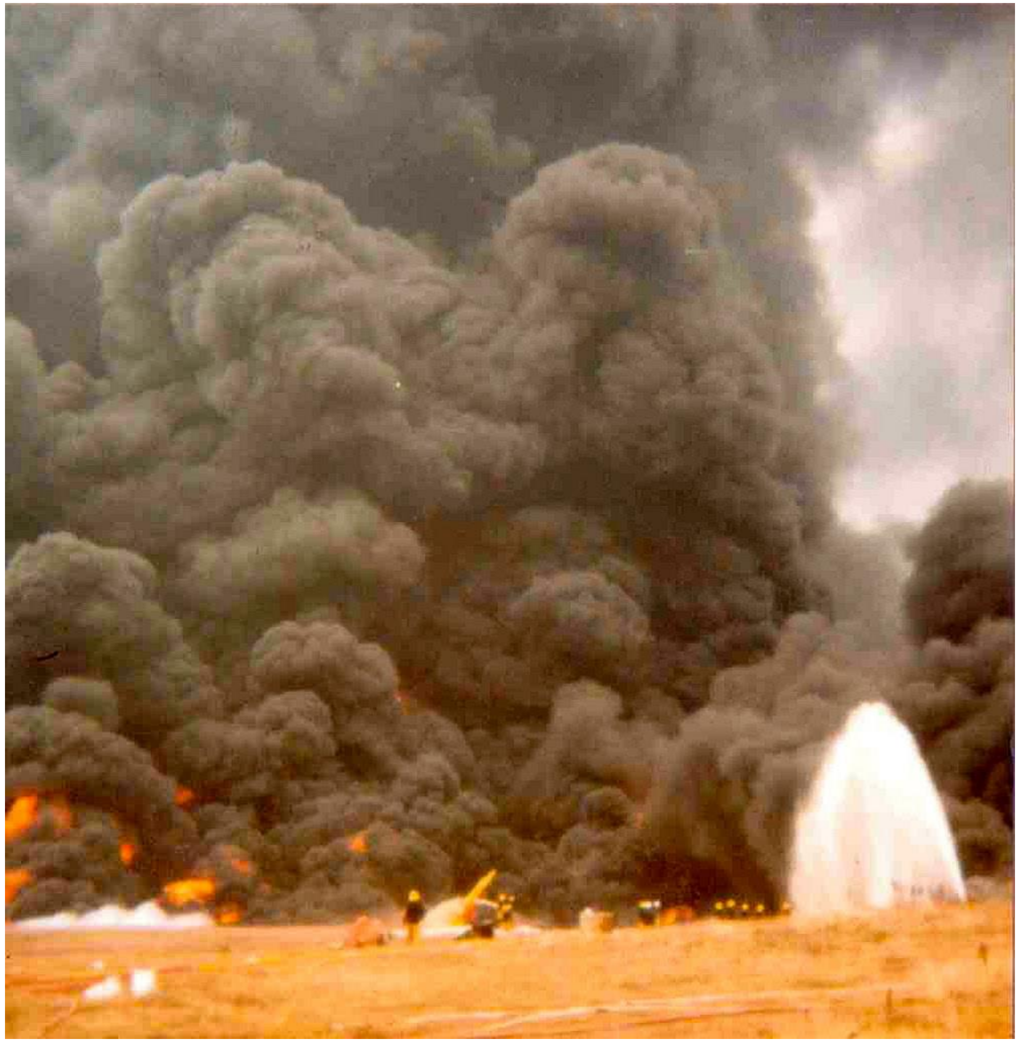
Fate & Transport Scenarios



Acknowledge the Broad Sources of PFAS

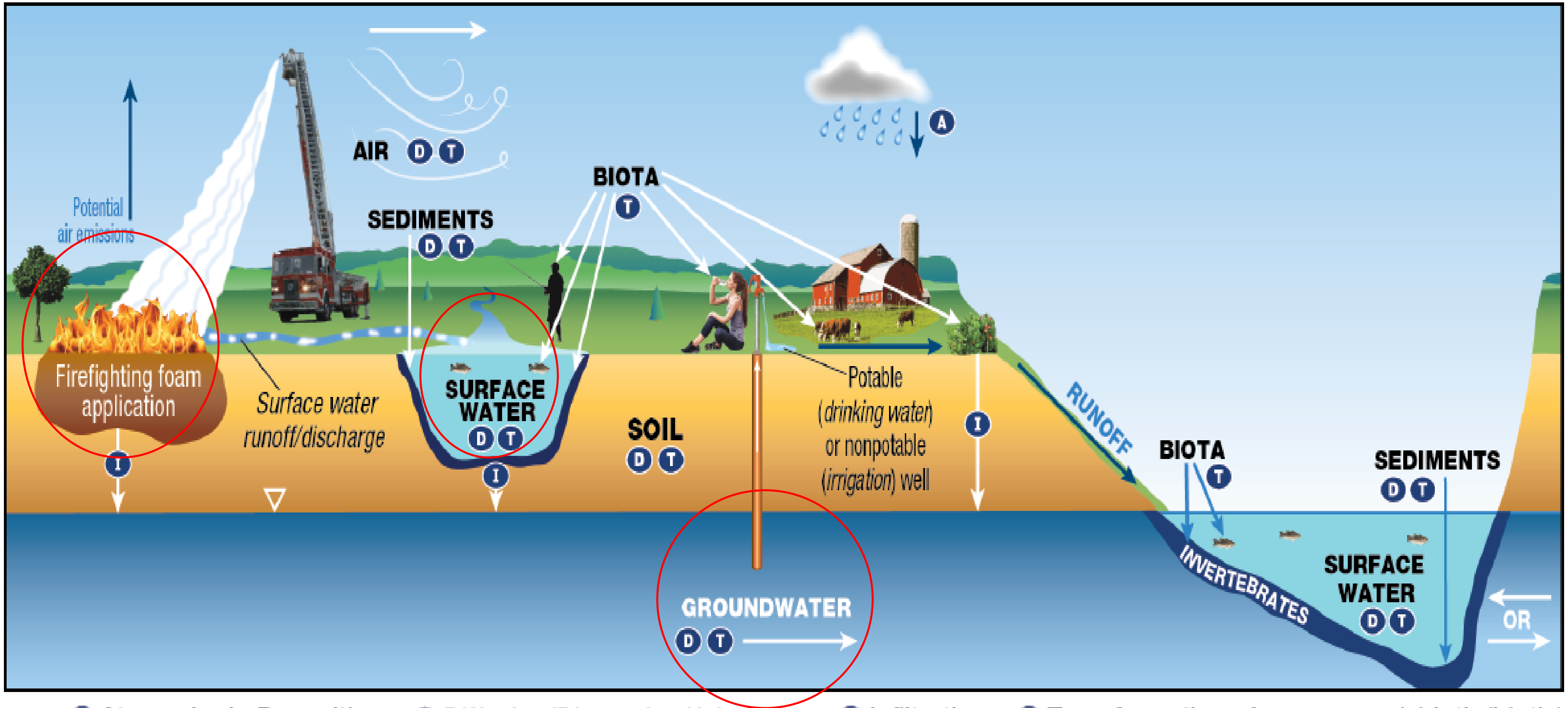
- Fire-fighting foams
  - Airports, training facilities, terminals
- Industrial facilities
  - Electroplating (mist suppressants)
  - Semiconductor manufacturing
  - Aerospace & electronic applications
  - Automobile
- Landfills
  - Leachate
  - Consumer products
- Wastewater treatment plants
  - Effluent discharges
  - Biosolids
- Consumer Products
  - Water Repellents
  - Stain-resistant textiles
  - Teflon cookware
  - Cosmetics

Solving one problem – Creating another



- Fire fighting foams
- Airborne contaminant distribution
- Soil and groundwater impacts
  - TPH, VOCs, PFAS
  - If TCA/TCE – 1,4-dioxane
- Runoff to surface water
- Human and ecological receptors

Fate and Transport at Fire Training Areas (AFFF)



KEY A Atmospheric Deposition D Diffusion/Dispersion/Advection I Infiltration T Transformation of precursors (abiotic/biotic)

Figure 1. Conceptual site model for fire training areas.

Adapted from figure by L. Trozzolo, TRC, used with permission)

Fate and Transport at Industrial Sites

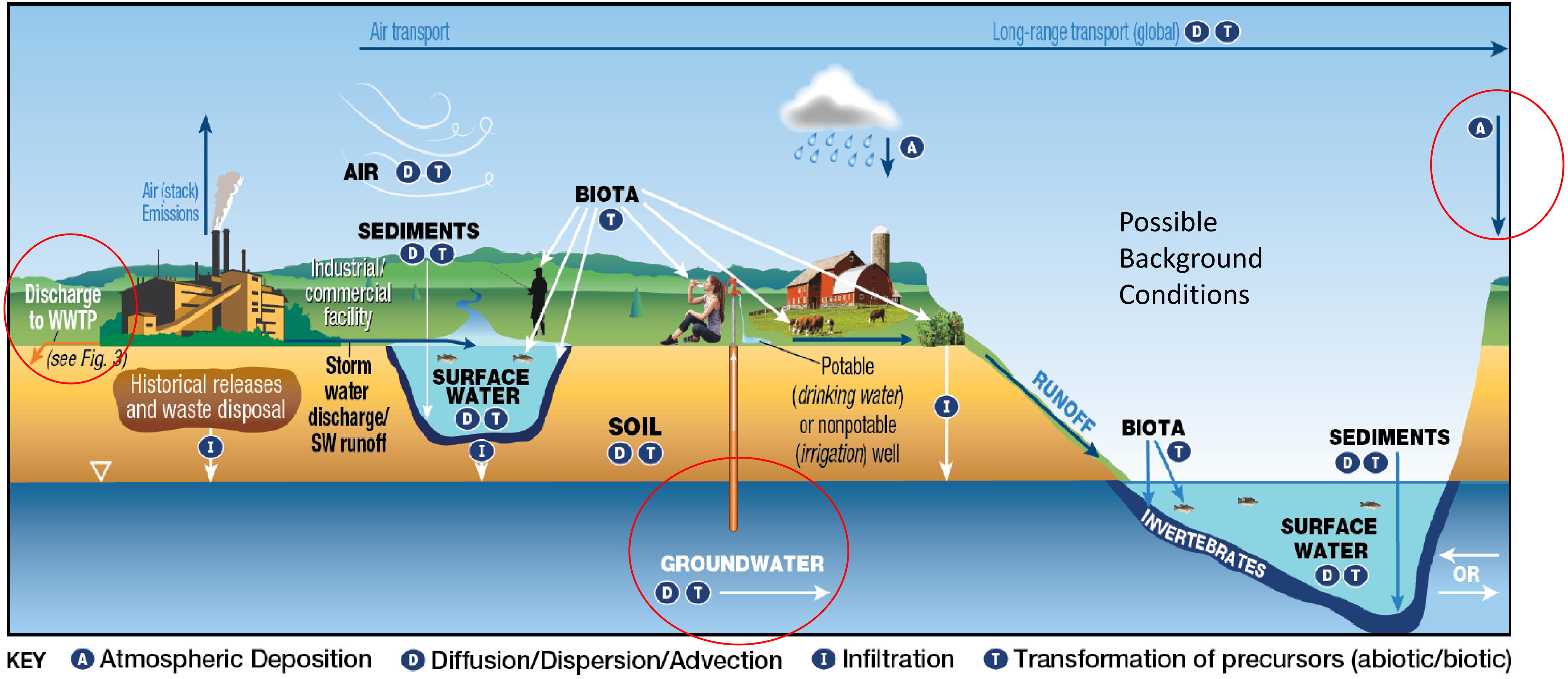


Figure 2. Conceptual site model for industrial sites.

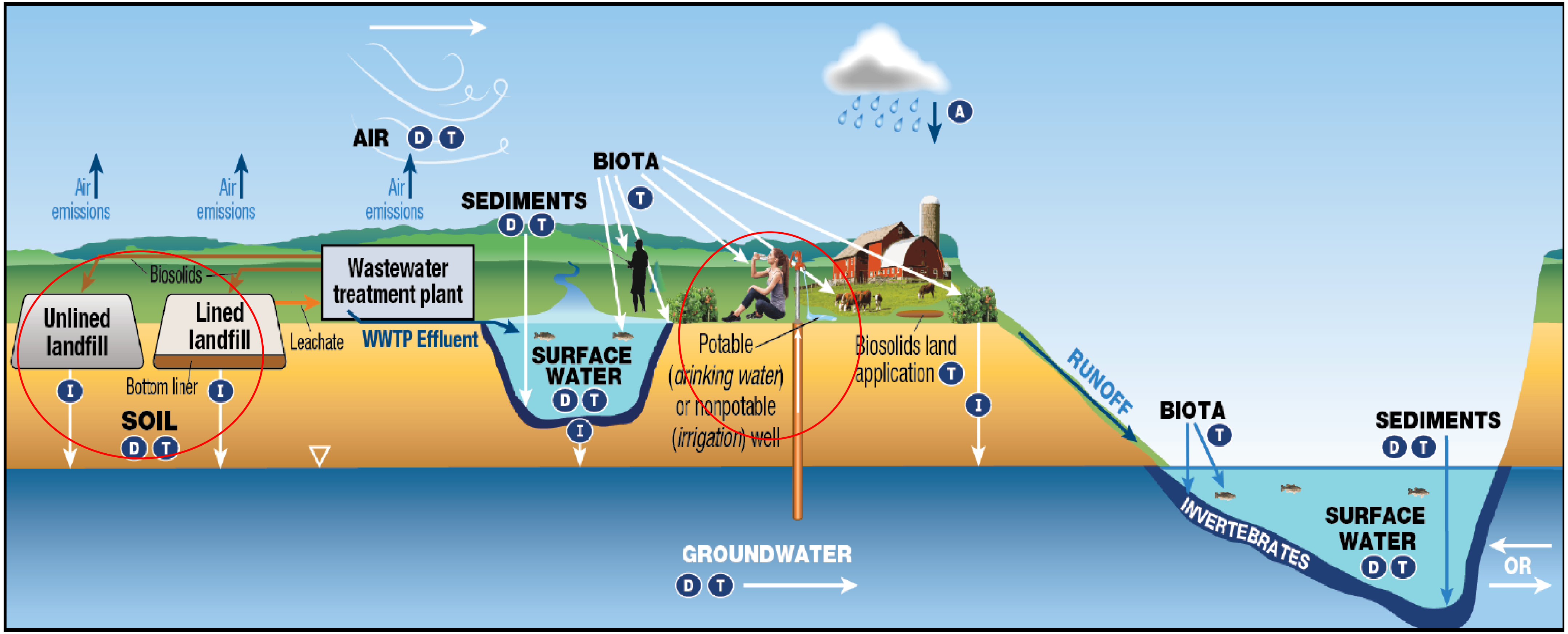
Adapted from figure by L. Trozzolo, TRC, used with permission)

Examples of PFAS Distribution

- PFAS Contaminant identified in WWTP biosolids
- Biosolids landspread on ag fields
- PFAS contamination detected in cows' milk and fields
- Farmer required to destroy milk products

- PFAS impact of shallow groundwater
- Groundwater discharge to natural wetland areas
- Plant uptake as local food source
- Deer found to contain elevated levels
- Hunting moratorium w/in 5 miles of source area

Fate and Transport Related to Landfills & WWTP



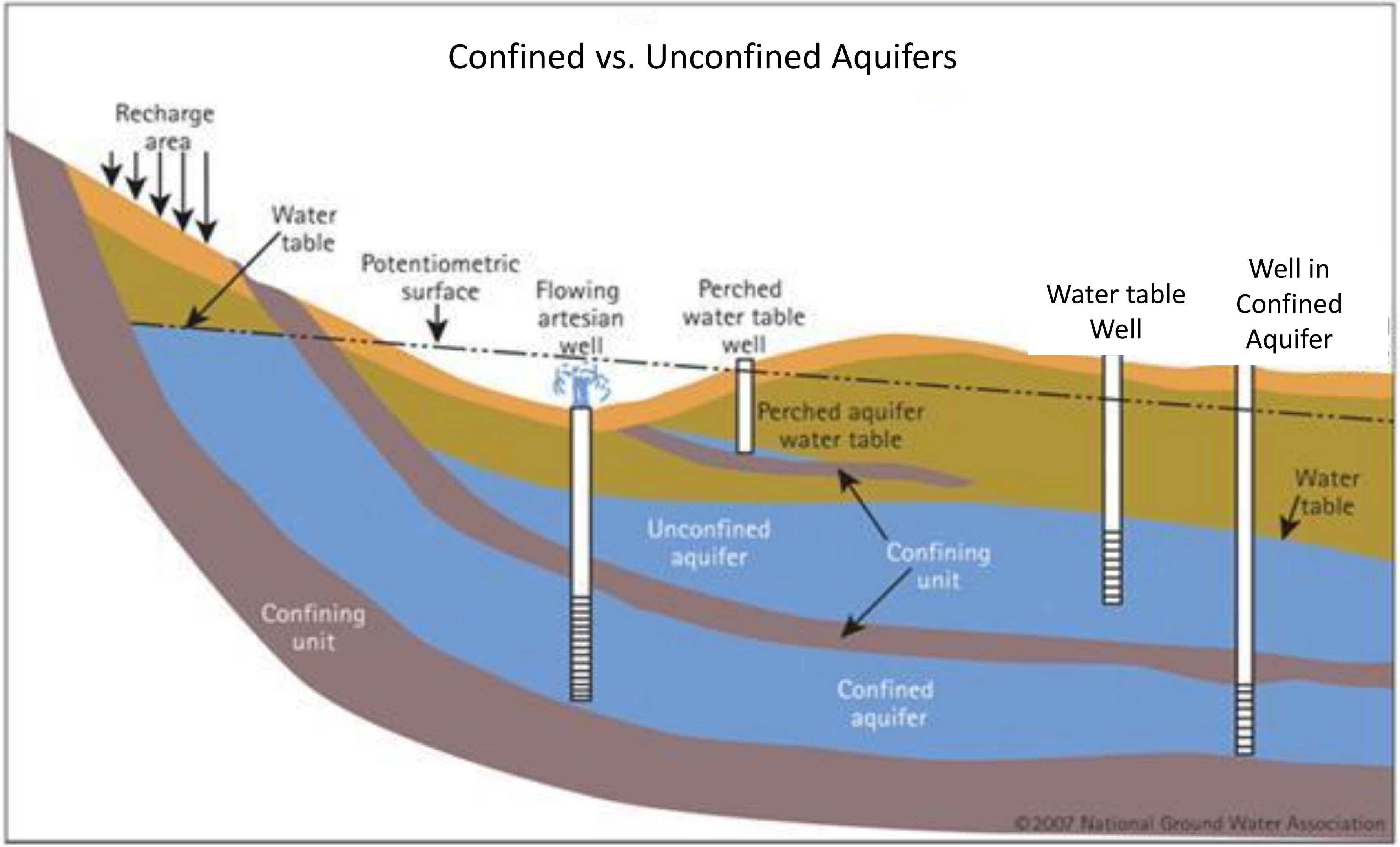
KEY A Atmospheric Deposition D Diffusion/Dispersion/Advection I Infiltration T Transformation of precursors (abiotic/biotic)

Figure 3. Conceptual site model for landfills and WWTPs.

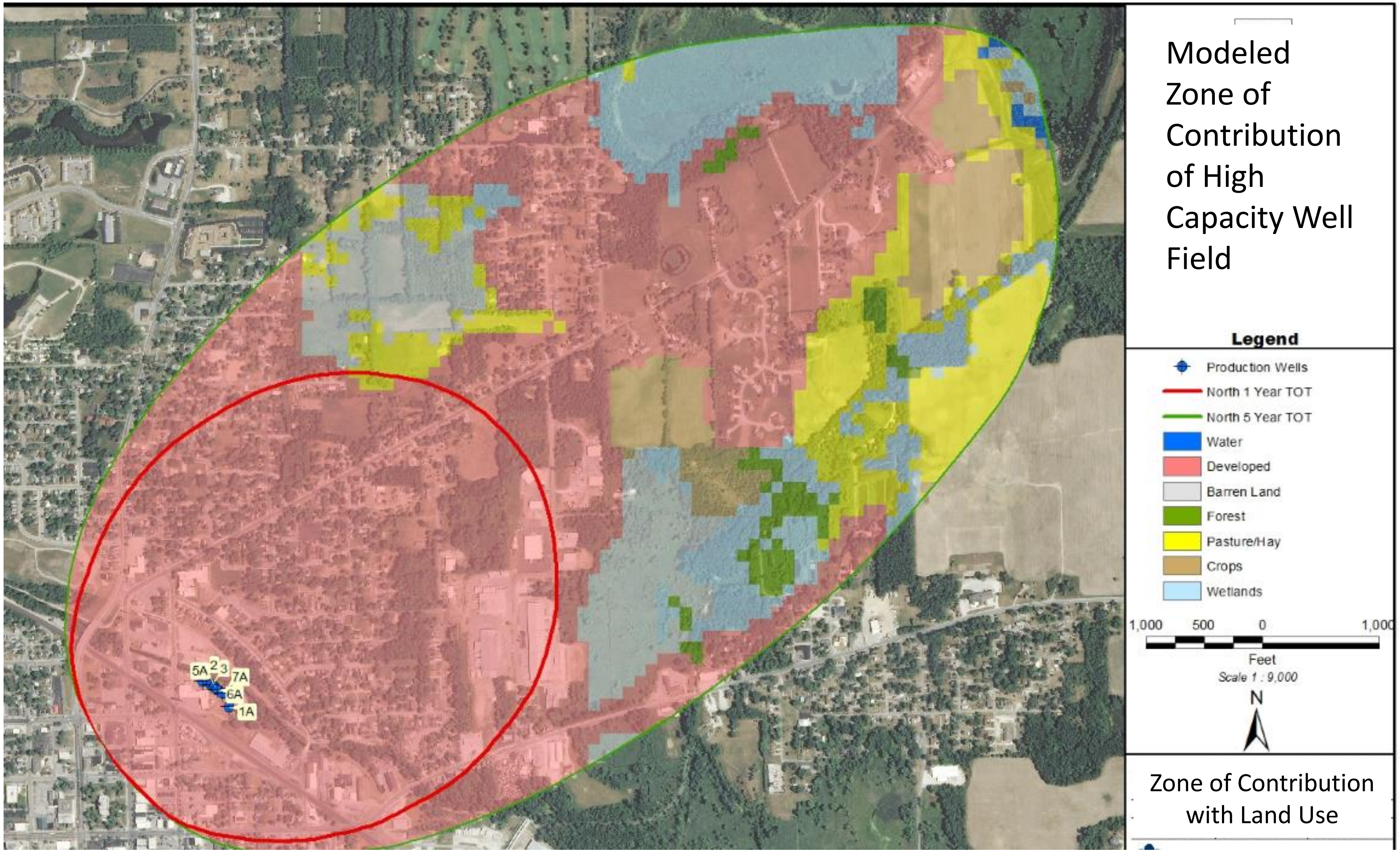
Adapted from figure by L. Trozzolo, TRC, used with permission)

Known for excellence. Built on trust.

Water Supply Susceptibility to PFAS



Modeled Zone of Contribution and Land use



2018 Water Supply Testing for PFAS - Michigan

Drinking Water Supplies Testing Results

Supply Type	Supplies Sampled	Non-Detect	<10ng/L Total PFAS	>10ng/L Total PFAS <70ng/L PFOA+PFOS	>70ng/L PFOA+PFOS
CWS	1112	994	84	35	1
Schools	460	420	21	19	1
Daycares	152	134	10	8	0
Tribal Entities	17	17	0	0	0
Total Supplies	1741	1565	115	62	2
Approx. Population Served	7.7 million	5.8 million	1.4 million	490,000	3,500

Reference: 2018 PFAS Sampling of Drinking Water Supplies in Michigan, Prepared for the Michigan Department of Environment, Great Lakes, and Energy, prepared by AECOM, Inc.
https://www.michigan.gov/documents/pfasresponse/2018_PFAS_Sampling_of_Drinking_Water_Supplies_in_Michigan_663543_7.pdf

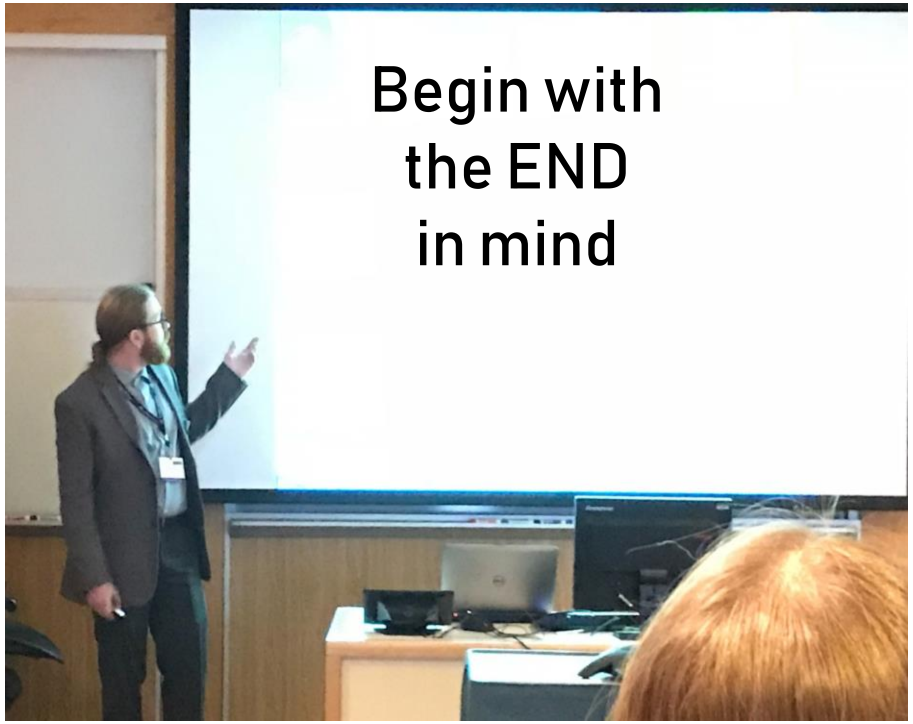
Investigating and Sampling for PFAS

Why Quantifying PFAS Impacts is Uniquely Challenging

1. Extremely Low Levels of Detection
   - 70 ppt USEPA Lifetime HAL
   - Individual States driving the Standard Lower
2. The High Potential for Cross Contamination of Samples From Common Materials
   - Many Industrial and Consumer Products contain PFAS
3. A Lack Numerical Standards for PFAS
   - Every detection has weight
   - We are in a period of Uncertainty
4. Laboratory Variation in the Analytical Testing
5. The Complexity of PFAS as an Uncertain Mixture of Compounds including Precursors
6. Existing Potential for Background PFAS in the Environmental Media

Key Considerations of a PFAS Sampling Plan

1. Clear Definition of Project Objectives
   - How will the data be used?
   - Are we targeting a specific source of PFAS compounds or are we determining presence/absence of any PFASs? Or are we attempting to conduct forensics to pin PFAS to a specific source?
   - Is the media being sampled stagnant and homogenous or subject to temporal or spatial changes in composition?
   - Who will perform the sampling and are they experienced in PFAS sampling?
   - Have you selected an experienced Laboratory and understood its sampling QA/QC requirements;
   - Do the standard Laboratory analytes align with the PFAS sources you are characterizing?
   - Will narrowing the list of analytes better assist Project Objectives than receiving whatever list of PFAS compounds sent to you?
   - Who will have access to the data?
   - What obligations do we have once the data is received?
   - If positive detections are received, do we have a plan to take the appropriate next steps?



Quality Assurance/Quality Control

Investigating PFAS - Sampling Requires Rigorous Adherence to the SOPs

Personal Detox 48 Hours Prior to Sampling

1 – Clothes “laundered”
2 – No fast food consumption

Day of Sampling

1 – No cosmetics or personal care items
2 – No sunscreen or bug repellent
3 – Untreated natural fiber clothing only

Field Equipment Highlights

1 – No waterproof paper
2 – Only ball point pens
3 – Only aluminum clipboard
4 – Absolutely no Teflon in equipment
5 – Only use real ice, no packs or gel-based

Summary Table of Prohibited and Acceptable Items

Prohibited Items	Acceptable items
Field Equipment	
Teflon® containing materials	High-density polyethylene (HDPE) materials
Low density polyethylene (LDPE) materials	Acetate liners
Paper towels containing recycled materials	Silicon tubing
Waterproof field books	Loose paper
Plastic clipboards, binders, or spiral hard cover notebooks	Masonite or aluminum clipboards
Sharpies or markers	Pens
Post-It Notes	Loose paper
Chemical (blue) ice packs	Regular ice
Field Clothing and PPE	
New cotton clothing or synthetic water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex	Well laundered clothing made of natural fibers (preferable cotton)
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex	Boots made with polyurethane and PVC
Tyvek	Cotton clothing
No cosmetics, moisturizers, hand cream, or other related products as pat of personal cleaning/showering routine on the morning of sampling	100% Natural sunblock and insect repellent
Sample Containers	
LPDE or glass containers	HDPE or polypropylene
Teflon-lined caps	Unlined polypropylene caps
Rain Events	
Waterproof or resistant rain gear	Gazebo tent that is only touched or moved prior to and following sampling activities
Equipment Decontamination	
Decon 90	Alconox or Liquinox
Water from an on-site well	Potable water from municipal drinking water supply
Food Considerations	
All food and drink, with exceptions noted on the right	Bottled water and hydration drinks (i.e. Gatorade and Powerade) to be brought and consumed only in the staging area

Sample Collection Protocols

Clean Hands / Dirty Hands

Dirty Hands does all of the equipment hauling, faucets, outside of coolers, note taking,

Clean Hands essentially only touches the sample bottles, labels, and inside coolers.

Gloves are changed between every action, task, or touching of new items.

PFAS Laboratory Methods

Sample Media Type	Laboratory Method
Drinking Water	EPA Method 537
Soil and Ground Water	Modified EPA Method 537
Surface water and Sediments	Modified EPA Method 537
Note: EPA has only approved method 537 for drinking water. Individual laboratories have modified the 537 method for other media. Currently, EPA is working on additional Methods.	

Laboratory Method	
Standard Method EPA Method 537	Uses LC/MS/MS technology and isotropic dilution
TOP Analysis (Total Oxidizable Precursors)	Samples are treated with hydroxyl radical oxidation activated agent with overnight heating converting the masked precursors to their equivalent detectable PFAS compounds. TOP and Standard method combined provide a more complete PFAS assessment

Source of Contamination	Number of Parameters
Coating Sites	NY/NE requesting 12 to 14 compounds
Hazardous Waste Sites	NH requesting 9 to 20 compounds
Drinking water in NH	16 to 27 compounds
DOD/Fire Training	16 to 23 compounds

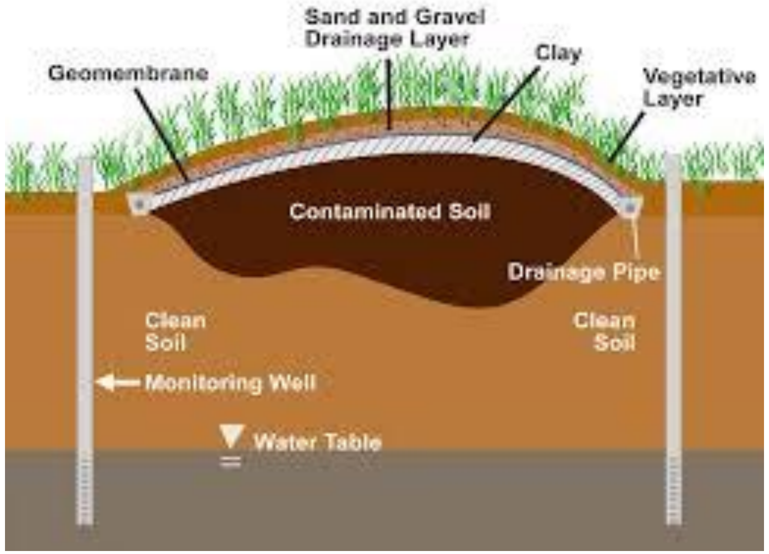
Soil Excavation & Disposal at Landfill

- Transfers PFAS to anther location, does not destroy PFASs
  - Effective at removing source from the property
  - Potential long-term exposure/liabilities
- PFAS are very soluble - resulting in PFAS leachate
  - – Degradation of PFAS may be greater than the life of landfill
  - – Leachate discharge from landfill may be directed to WWTP
    - Potentially another long-term liability

Soil Remediation Strategies (cont.)

Soil Capping/Containment (removes exposure pathway)

- Environmentally Isolates PFAS Source
  - Prevents direct exposure and reduces leaching from soil to groundwater
  - Does not reduce long-term exposure or liability
  - May limit property redevelopment
- Engineering controls required
- On-going management of engineering controls
- Environmental Land Use Restriction
- Long-term groundwater monitoring



CLU-IN

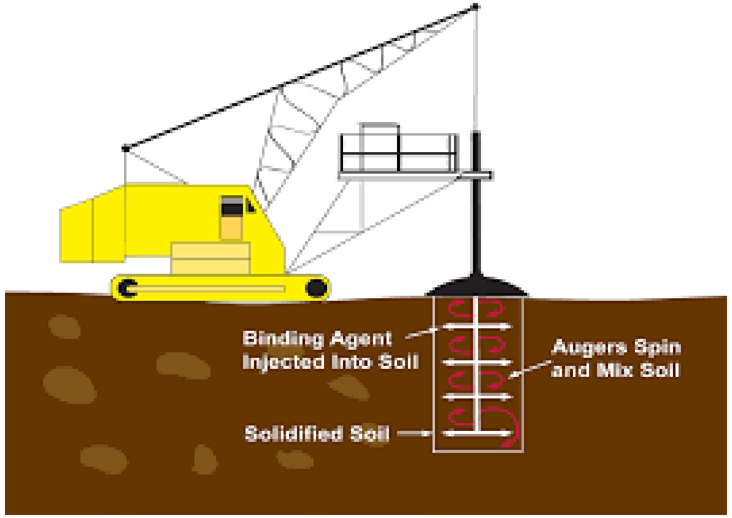
Incineration – Thermal Treatment

- Requires high temperature to destroy (>1,200 ^{o}C) Hawley et al., 2012
- Facilities are providing Certification of Destructions

Soil Remediation Strategies (not proven)

In-situ soil sorption/stabilization

- Amendments added to soil to reduce/remove the mobility of PFAS from soil to groundwater
  - Binding agents may include GAC, non-carbon sorbents (organoclays, iron oxide minerals)
  - Activate carbon (Rembind™, matCARE™, MYCELX, Biochar)
- Leachability analysis will be required demonstrating stabilization
  - Long-term effectiveness of binding agents not well known
- This technology has been effective for other types of contaminants



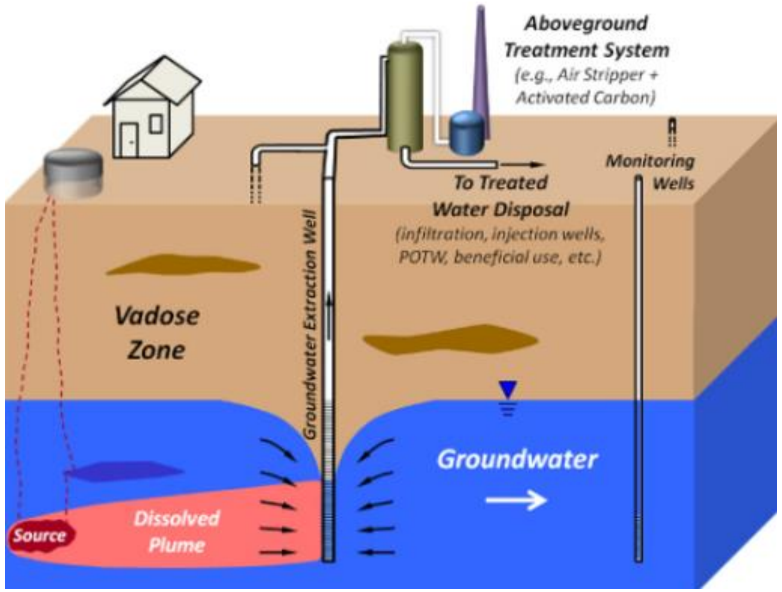
Chemical Oxidation

- Mixing soil with chemical oxidants (not proven)
  - Fate of precursors must be considered

Groundwater Remediation Approaches

Pump and Treat/Plume Capture/Hydraulic Control

- Large volumes of water requiring treatment/Re-injection/Discharge
- Mass removal dependent on aquifer characteristics
- Discharge to municipal sewer may be limited
- Consider treatment trains – remove VOC then PFASs
- Long-term operation and maintenance
  - Treatment GAC & ion exchange resins



Chemical Oxidation (not proven)

- Radical chemistry
  - Fenton reaction, persulfate, UV w/peroxide, O_3-peroxide, ozone
  - Electro-chemical oxidation
  - Fate of precursor products must be considered (PFOA, PFOS, fluoride)

Other Considerations

- Transformation of precursors
- In situ technologies being tested
- Important to conduct treatability Studies

Groundwater Remediation Approaches (Cont'd)

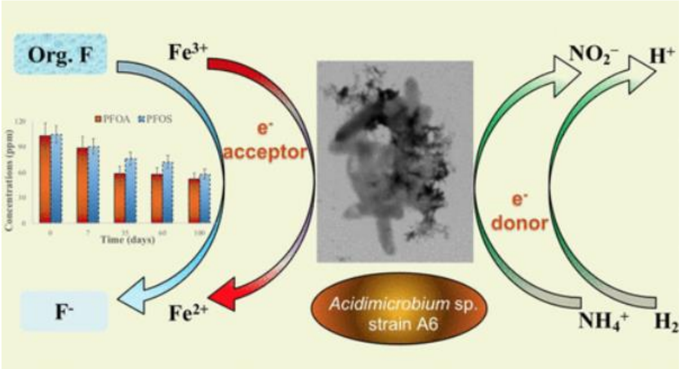
Treatment Options – Sorption/Filtration

- Activate carbon (Rembind™, matCARE™, MYCELX, Biochar)
  - Carbon absorption has lower costs and can be regenerated at high temperatures
  - GAC may be better on PFOS than other PFAS
    - Longer chained compounds
  - Type of GAC important along with micropore size
- Ion exchange resins
  - May produce concentrated PFOA waste requiring incineration
- Reverse osmosis/nanofiltration
  - Management of waste stream

In Situ Biological Degradation

- New Findings - *Environmental Science & Technology*
- *Acidimicrobium* sp. strain A6 — oxidizes ammonium to nitrite while reducing ferric iron, were conducted in the presence of PFOA or PFOS:
  - 60% Reduction of PFOA and PFOS in 100 days (starting w/ up to 100 mg/l)

Ion exchange resin

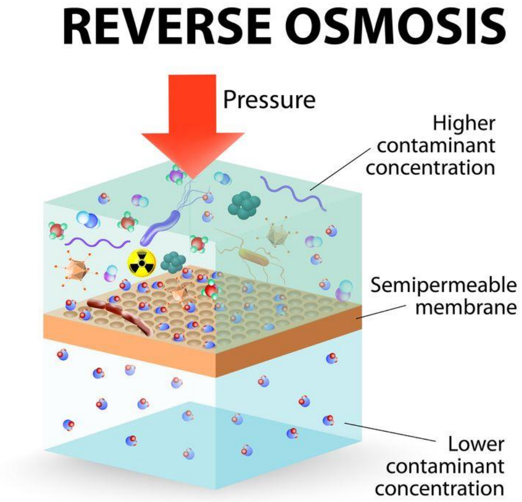


Huang and Jaffe, 2019, Environmental Sci. Technol.

Water Supply Remedial Approaches

Point-of-entry treatment (POET)

- Granular Activated Carbon (GAC)
  - Pre and post 5-micron filters
  - Will not remove arsenic or other compounds
- Effective on long-chain PFAS
  - Need to evaluate change-out of GAC based upon short-chain PFAS
- Other contaminants (VOC) will compete with GAC sorption



Point-of-Use (POU)

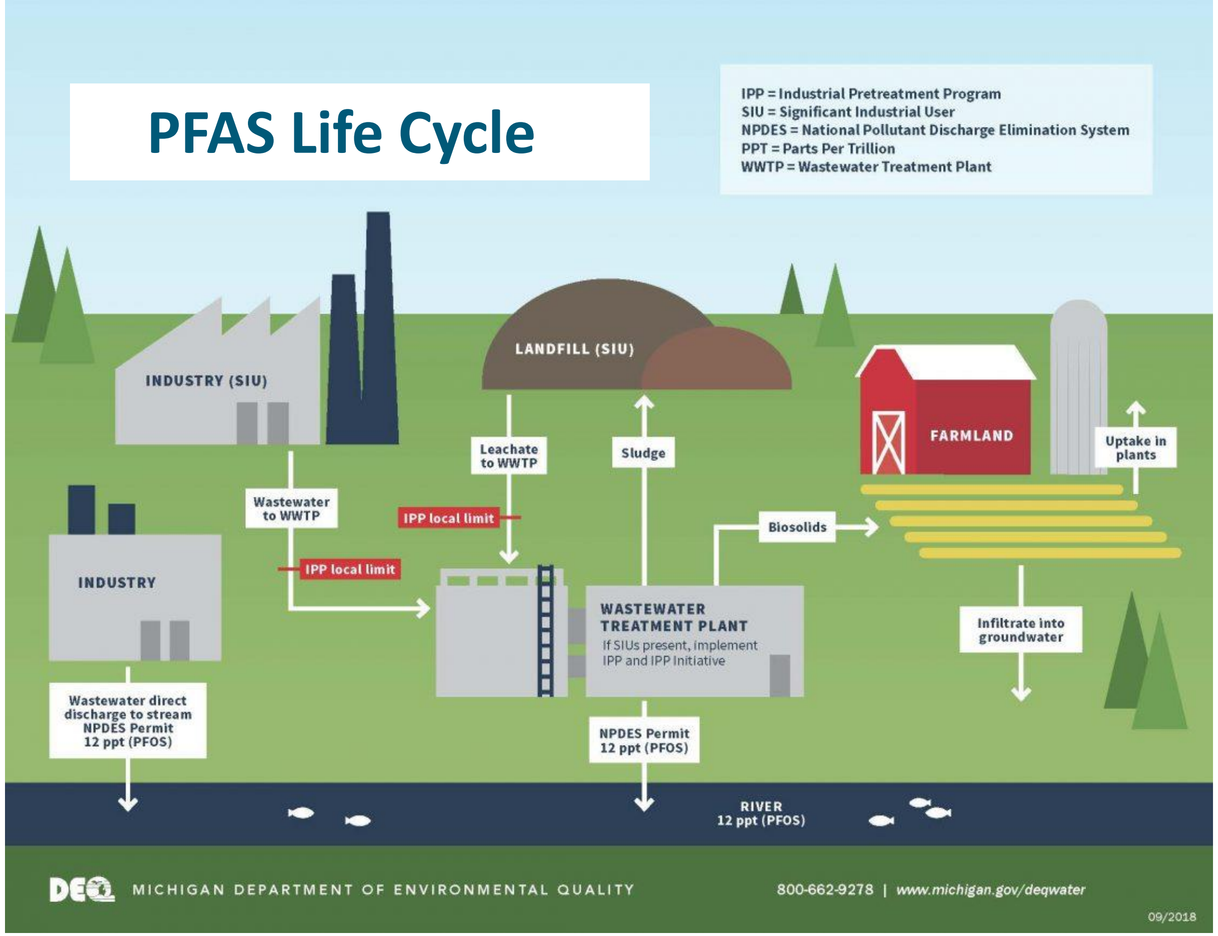
- Granular activated carbon (GAC) or reverse osmosis (RO)
  - RO better at tap location, GAC better for home water (NHDES)
  - RO uses additional water as part of the process

Water Supplies

- GAC and ion exchange resins as treatment trains

Key Takeaways on PFAS

1. Complex class of durable and persistent compounds;
2. Mobile in water systems;
3. Not volatilized or biodegraded;
4. Tend to bioaccumulate;
5. Uncertain toxicology;
6. Undefined regulatory environment;
7. Sampling for PFAS takes great care and attention to prevent x-contamination;
8. Have a defined purpose and plan behind each sampling effort;
9. Have been in our environment for several decades introduced through :
   - Primary and secondary manufacturing;
   - Industrial and residential wastewater;
   - Industrial air emissions;
   - Regulated and unregulated landfills
   - Wastewater biosolids land spreading;
   - Surface runoff;
   - Groundwater migration and discharge;
10. Remedial technologies for soil and groundwater rather limited and new ideas are emerging.



PFAS may not be detectable everywhere you look,
but where it was used or placed it has the potential to be widely distributed

Questions

Thank You

Wisconsin Public Utility Institute
UNIVERSITY OF WISCONSIN–MADISON

John C. Osborne, P.G.
Principal Hydrogeologist
john.osborne@gza.com
GZA GeoEnvironmental, Inc.

REFERENCES

- Michigan Department of Environment, Great Lakes and Energy
- U.S. Environmental Protection Agency (EPA) – clu-in.org
- U.S. Department of Defense, with EPA & DoE – www.serdp-estcp.org
- Air Force Center for Engineering and the Environment –
- www.usaf.com/orgs/environmental.htm
- Naval Facilities Engineering Command – www.navfac.navy.mil
- National Ground Water Association – www.ngwa.org
- Interstate Technology and Regulatory Council – www.itrcweb.org
- Shan Huang and Peter R. Jaffe, 2019, Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by *Acidimicrobium sp*. Strain A6, Environ. Sci. Technol., 2019, 53,19,11410-11419;