Proactive By Design.
Our Company Commitment

Polyfluoroalkyl Substances (PFAS):
Regulations, Research, Risk, Mitigation & Alternatives
Pathways & Mitigation

Presented to:

Massachusetts Chemistry & Technology Alliance

Presented by:

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Introduction

Pathways & Mitigation

1. Fate & Transport

2. Remediation Technologies

What's wrong with these pictures?

- ❖ Fire fighting foams (AFFF);
- ❖ Airborne & particulate contaminant distribution;
- ❖ Soil & Groundwater impacts; (TPH, VOCs, PFAS)
- ❖ Runoff to surface water;
- ❖ Human & Ecological receptors

At least 126 bases report water contaminants linked to cancer, birth defects

- 25 Army base;
- 50 Air Force base;
- 49 Navy or Marine Corps base;
- 2 Defense Logistics Agency site

"DoD tested 2,668 groundwater wells both on and in the surrounding off-base communities and found 60 percent of them tested above the EPA's recommended levels".

DoD has spent $200 million studying and testing, and estimates cleanup costs at $2 billion.

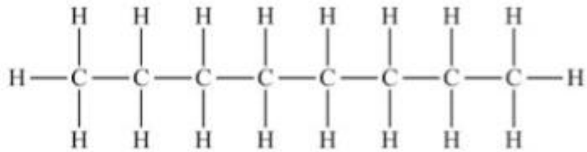
MilitaryTimes, April 27, 2018

Sources

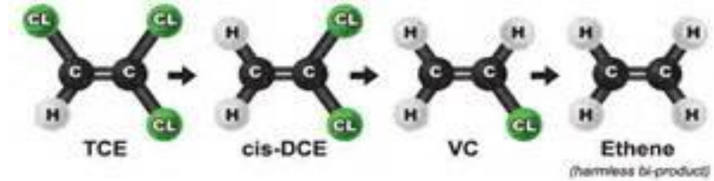
- ***Aqueous film forming foams (firefighting)***
  - *Airports, training centers, military facilities*
- ***Electroplating mist suppressants***
  - *Dust/vapor suppression for chrome plating*
- ***Semiconductor manufacturing***
- ***Aerospace & electronic applications***
- ***Consumer products***
  - *Oil and water resistant finishes on paper, textile, stain resistant carpeting, cookware*
    - *Teflon, Scotch Guard, Stain Master, GORE-TEX*

Chemical Molecule

Octane



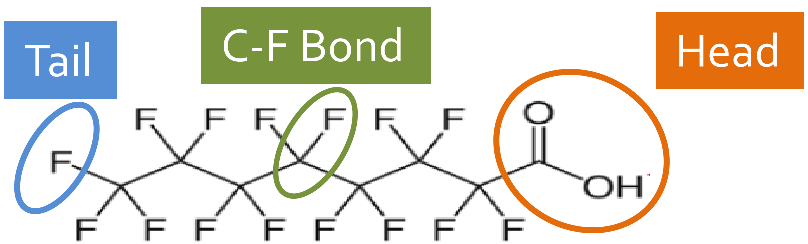
Common Chlorinated Compounds



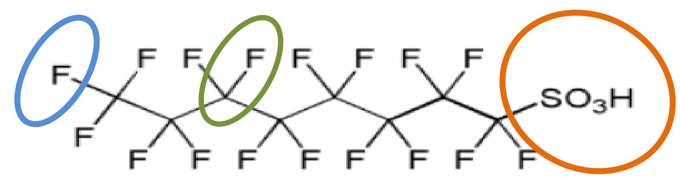
What make PFAS different?

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

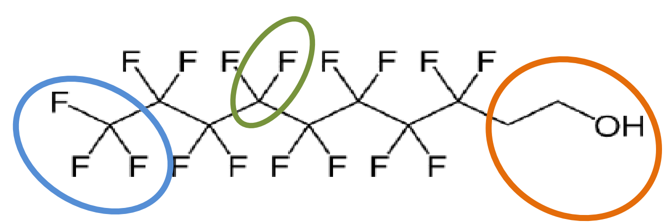
PFOA – Perfluorooctanoic acid



PFOS – Perfluorooctane sulfonic acid



- *Precursor of PFOA*
  - *Fluorotelomer alcohols*



Major Pathway: Fire Training Areas (AFFF)

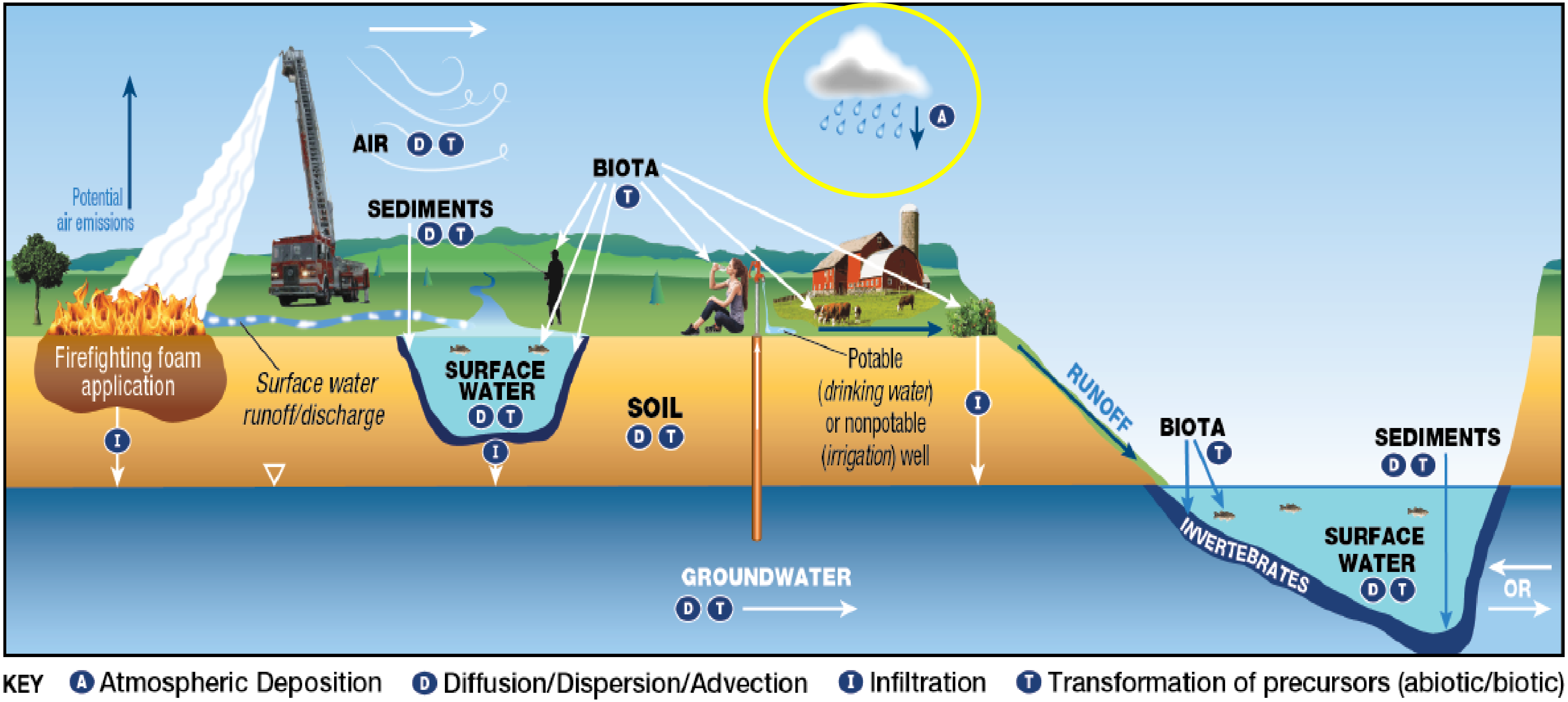


Figure 1. Conceptual site model for fire training areas.

Adapted from figure by L. Trozzolo, TRC.

Major Pathway: Industrial Facilities

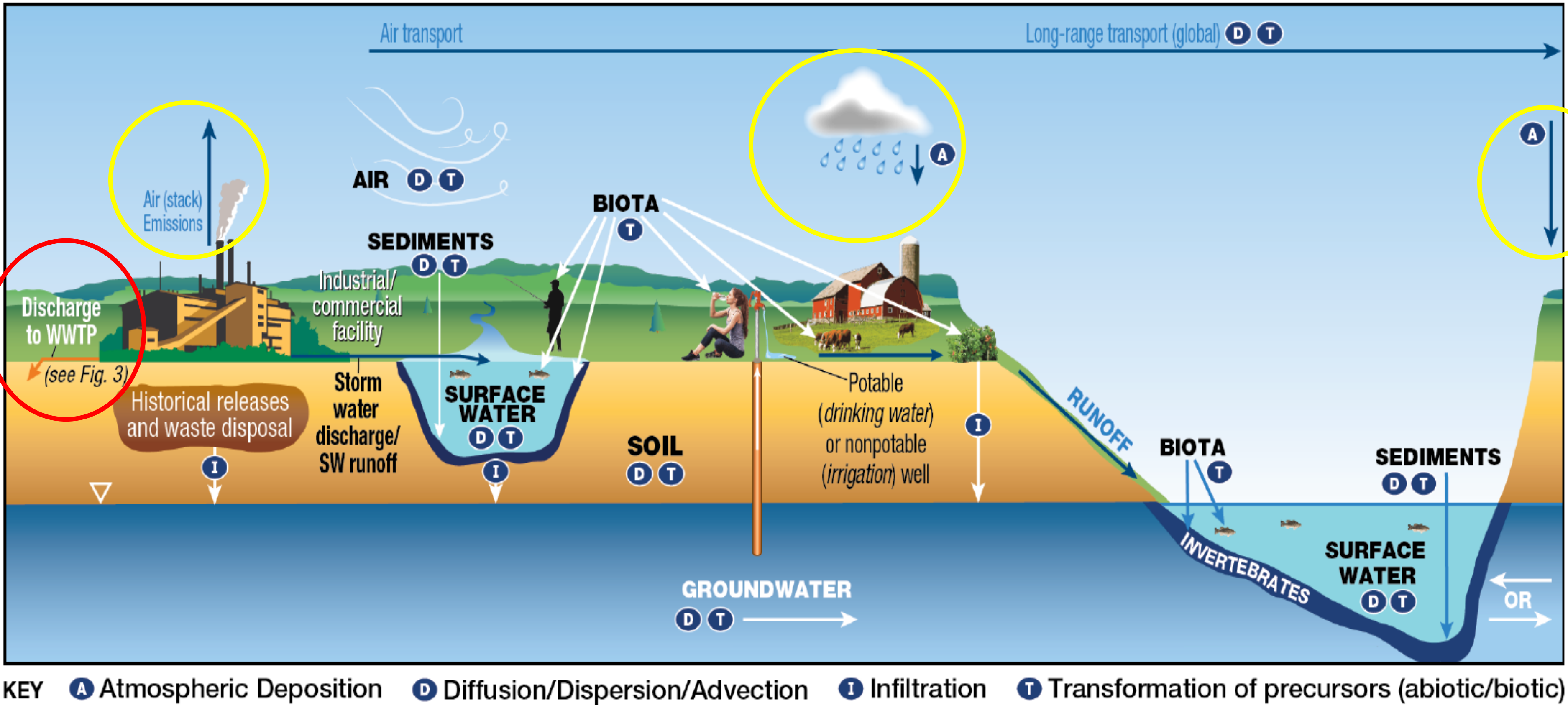
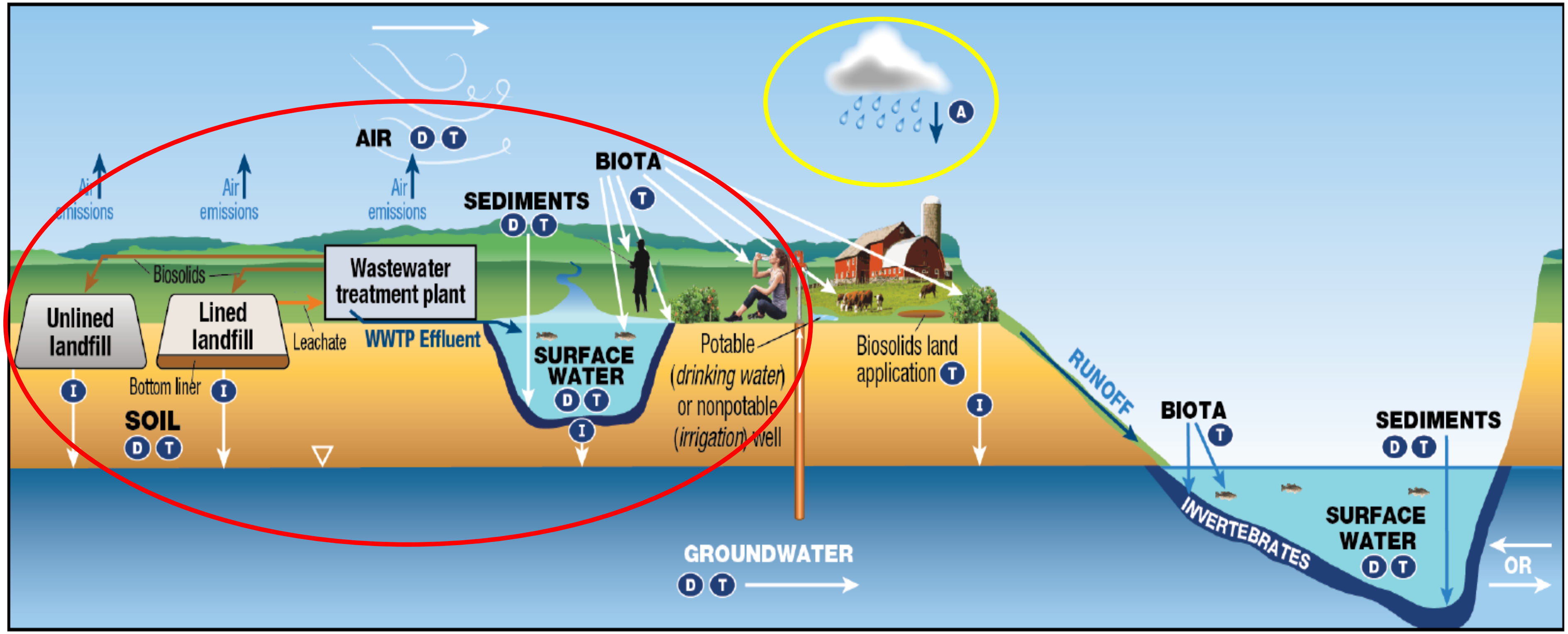


Figure 2. Conceptual site model for industrial sites.

Adapted from figure by L. Trozzolo, TRC.

Major Pathway: Landfills & WWTP

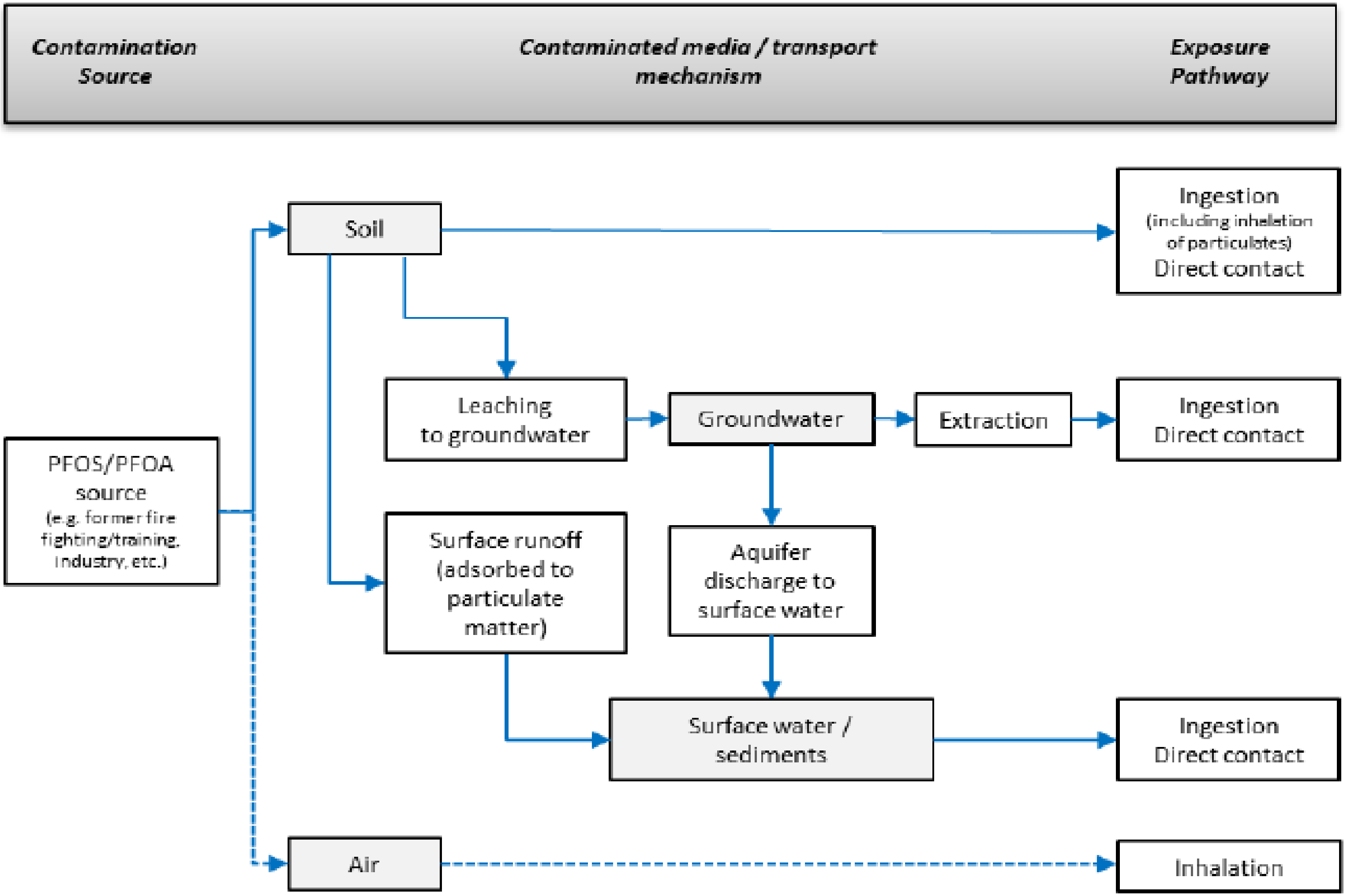


KEY A Atmospheric Deposition D Diffusion/Dispersion/Advection I Infiltration T Transformation of precursors (abiotic/biotic)

Figure 3. Conceptual site model for landfills and WWTPs.

Adapted from figure by L. Trozzolo, TRC.

Fate & Transport - Conceptual Site Model

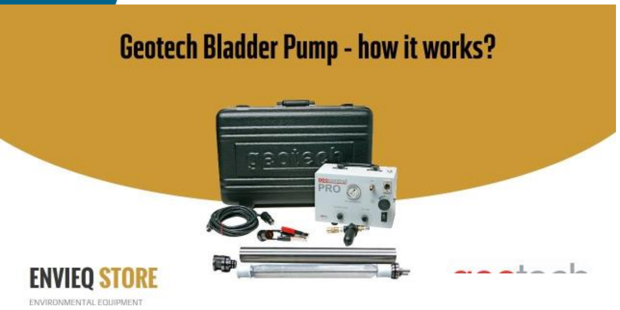


CRCCARE, Technical Report 38, March 2017

WWTP- Example

- Waste Water Treatment Facility
  - PFAS was identified in biomass
  - Biomass was distributed on dairy farm
  - PFAS was detected in cows' milk

Cross Contamination - Sampling Issues



Partitioning

- Partitioning Mechanisms
  - PFAS "tail" is hydrophobic and lipophobic
    - drives associations with organic carbon in soil
  - PFAS "head" are polar and hydrophilic
  - Electrostatic interactions - function of the polar functional group (head)
    - E.g. soil and groundwater often have negative surface charges that can repel negatively charged heads. This can be in conflict with the tail resulting in partitioning interfaces (soil/water, water/air, water/NAPL
- Sorption & Retardation
  - Increases with perfluoroalkyl tail lengths
    - Shorter chains are retarded less than the longer chains
  - PFSAs are sorb more strongly than PFCAs of equal chains
  - Branched isomers have less sorption than linear
  - Decreases in pH, increases in cations = greater sorption & retardation
- Volatility
  - Vapor pressures are low, water solubility is high (very mobile in groundwater)
    - limiting partitioning from water to air
  - Stack emissions = atmospheric and particulate transport

Partitioning

- Advection
  - Advection flow drives PFAS mobility; however does not reduce concentrations along the plume
  - Advection is based upon media properties and not molecular, physical, or chemical interactions
- Dispersion
  - Changes in air and surface water velocities can dispense PFAS in multiple directions
    - Surface water to sediment; air to surface soil
  - Dispersion is limited in groundwater resulting in narrow plumes, wider plume might be influenced by secondary factors
- Diffusion
  - Surface water and air as a result of turbulence
  - Groundwater generally slow compared to advection
  - PFAS can diffuse into lower permeable materials (clay, bedrock, concrete)

Partitioning

- Deposition
  - Accumulation from atmosphere deposition to soil and surface
  - Atmospheric transport can result in measurable concentrations away from the source point
- Leaching
  - Precipitation or irrigation promotes downward dissolution of PFAS from surface soil
    - Soils to groundwater or surface water
  - Surface applications (AFFF and biosolids)
  - Leaching is a function of media (pH, redox, partitioning coefficients) and the PFAS structure (ionic charge, chain length)

Where PFAS can Occur

- Air
- Soil
- Sediment
- Groundwater
- Surface Water
- Biota & bioaccumulation
- Plants
- Invertebrates
- Fish
- Humans

Issues with Precursors

PFAS – not just per...

PFAS (Per- and Poly-)

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

← Precursors

+ others

PFOA - Perfluorooctanoic acid

PFOS - Perfluorooctane sulfonic acid

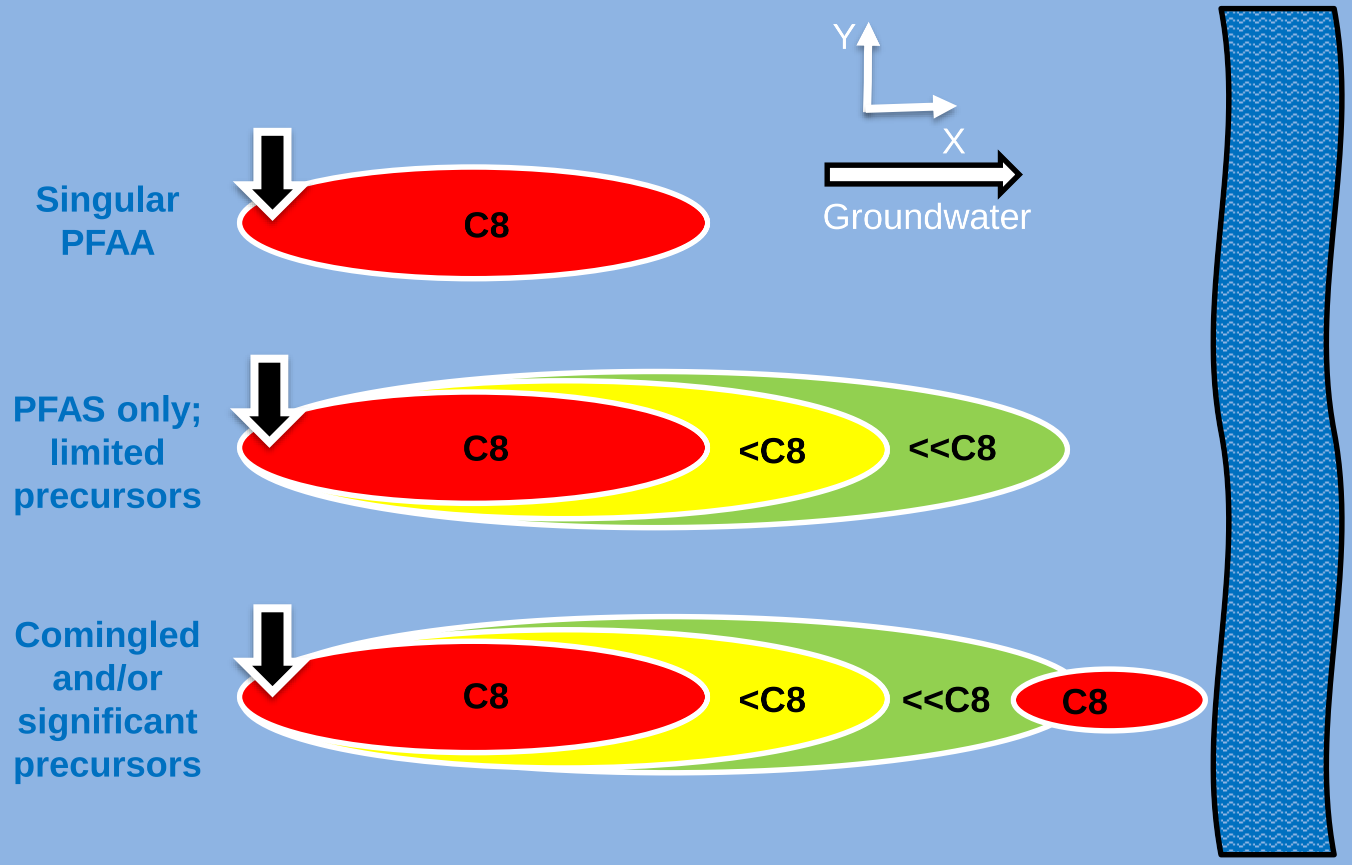
PFHxS - Perfluoro hexane sulfonic acid

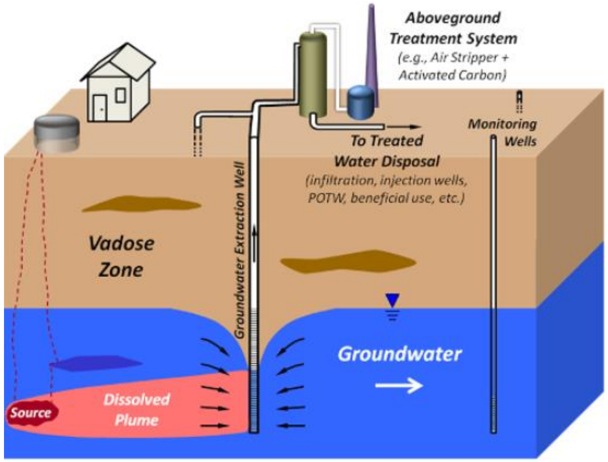
PFNA - Perfluoronoonanoic acid

PFDA - Perfluorodecanoic acid

Greater than 6,000 compounds
40+ different subcategories

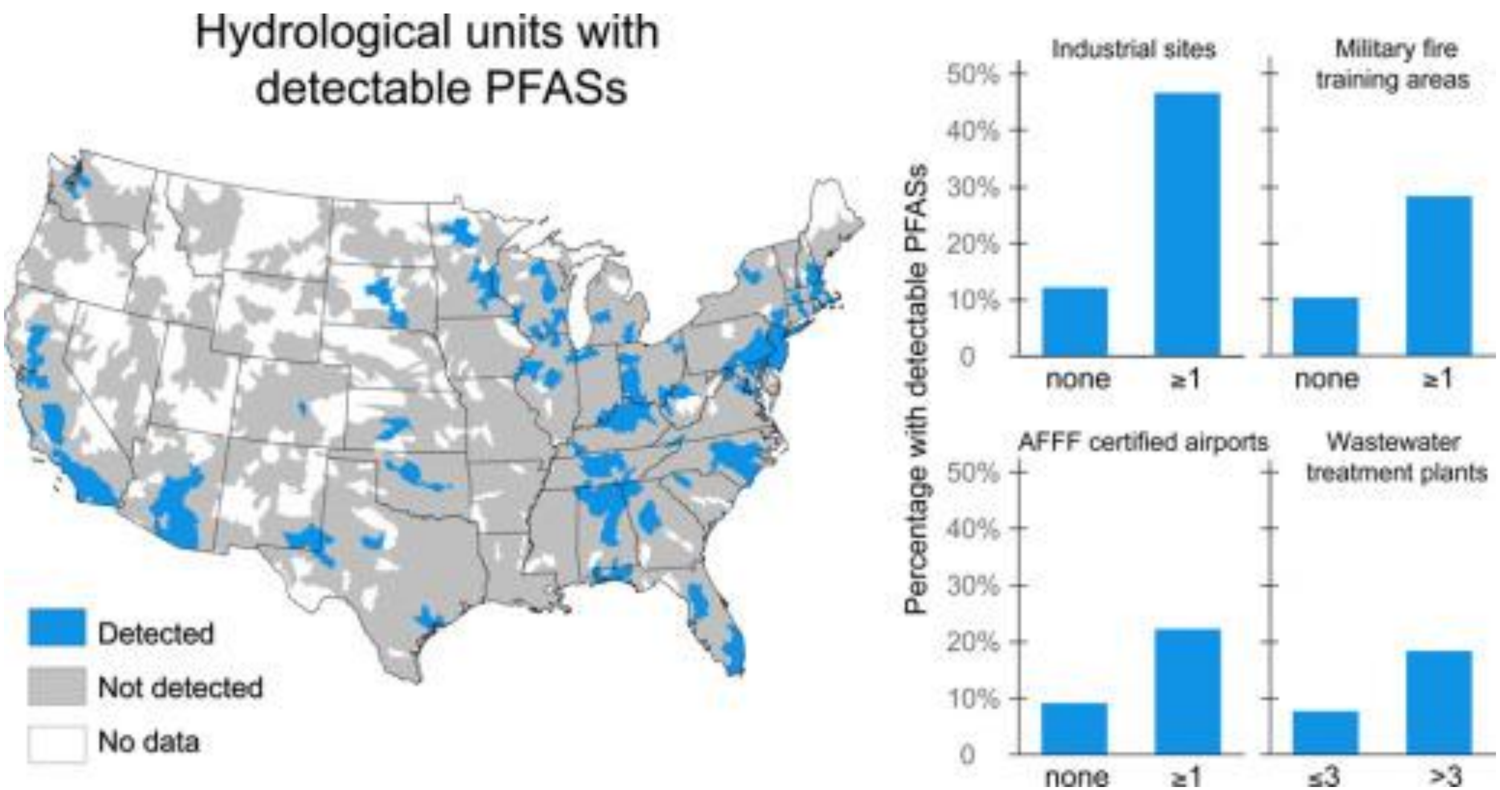
Fate & Transport Scenarios





Remedial Approaches to PFAS

PFAS - Detected



Areas with detectable levels of poly- and perfluoroalkyl substances (PFASs) in the US and their proximity relationship to industrial sites, military fire training sites, airports and wastewater treatment plants. Image by Hu XC et al., Environmental Science & Technology Letters, 2016.

SSEHRI Northeastern University Social Science Environmental Health Research Institute

Soil Remediation Approaches

Soil Excavation

- Transfer of mass to anther location, does not destroy PFAS
  - Example - landfill
- Many PFAS are very soluble, and can create PFAS leachate
- Leachate discharge may require treatment
  - Irrigation reuse
  - Municipal sewers to wastewater treatment plants
- Time for PFAS to degrade may exceed life of landfill
- Expensive and potential long term exposure
- Better when concentrations are low; high volumes;

Soil Remediation Approaches

Soil Capping/Containment (removes exposure pathway)

- Environmentally Isolating Source
- Engineering controls to isolate and prevent spreading
- On-going management of engineering controls
- ELURs

Incineration

- Requires high temperature to destroy (>1,200 °C) Hawley et al., 2012;
- Better when concentrations are high, low volumes;

Soil Remediation Approaches

In-situ soil stabilization/solidification

- Leachability analysis to demonstrate PFAS will not leach
  - Long-term effectiveness of binding agents not well known
- Promising technologies
  - RemBind - Powdered reagent (Activated Carbon, Organic Matter, and Aluminum Hydroxide);
    - bench and pilot scale only (1 – 10% by weight added to soil)
  - MatCARE - Modified clay adsorbent
    - Immobilizes PFOS in soil and groundwater
    - pH, clay content and organic content influence PFOS release from soil

Chemical Oxidation

- Mixing soil with chemical oxidants (not proven)
  - Fate of precursor products must be considered (PFOA, PFOS)
  - May require permitting, if adding additives within 100 feet of stream

Groundwater 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 all home water (NHDES)
  - ❖ RO uses additional water as part of the process

Groundwater Remedial Approaches

Filtration/Sorption

- Activated 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 (i.e., PFOA)
  - Type of GAC important along with micropore size
- Zeolites/clay minerals
- Ion exchange resins
  - May produce concentrated PFOA waste requiring incineration
- Reverse osmosis/nanofiltration
  - Management of waste stream

Institutional Controls

- Restrict use and access

Groundwater Remedial Approaches

Pump and Treat

- ❖ Large volumes of water requiring treatment
- ❖ Mass removal dependent on aquifer formation
- ❖ Discharge to municipal sewer will require additional treatment
- ❖ Consider treatment trains – remove VOC then PFAS
- ❖ Long-term operation and maintenance

Chemical Oxidation

- ❖ Radical chemistry
  - ➢ Fenton reaction, persulfate, UV w/peroxide, O_3-peroxide, ozone
  - ➢ Electo-chemical oxidation
  - ➢ Fate of precursor products must be considered (PFOA, PFOS)
  - ➢ May have unintended consequences
- ❖ Photolysis

Groundwater Remedial Approaches

Chemical Reduction

- Zero valent metals
- Alkaline metals
- Experiments with vitamin B-12

Biodegradation

- PFASs do not biodegrade readily
  - Experiments using fungal and bacterial enzymes

Groundwater Remedial Approaches

Natural Attenuation

- Low cost, sustainable
- Coupled with source mitigation and receptor risk assessment studies
  - Relies on sorption, dilution and dispersion
  - Long-term monitoring

In-Situ Treatment

- No one silver bullet
  - Development of treatment trains (combination of oxidants)
  - Use of carbon injected into formation
  - Development chemical reduction methods

Remedial Technology Take-away

Soil

- "No well-established commercially available treatment technology for PFAS-contaminated soil and sediments." The current treatment is excavation and/or encapsulation.

Groundwater

- Limited remedial technologies – pump & treat
- Treatment goal should be to reduce concentration to reduce human and ecological risks.
- Consider treatment trains

Treatability Studies

CRCCARE, Technical Report 38, March 2017

PFAS Take Away

- PFAS is Ubiquitous
- PFAS science is not mature
- New information is rapidly expanding
- Additional investigation warranted to define pathways
- No remedial silver bullet – treatment trains
- States implementing actions to investigate PFAS compounds
- Evaluation through risk management
- If you suspect PFAS, it is likely present
  - Before sampling, have a plan should it be identified
  - Financial & public relations

Questions

Thank You

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