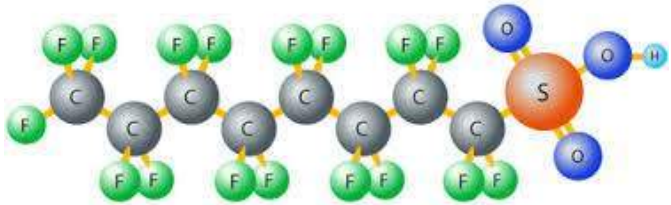
# Northeast Waste Management Officials Association

# PFAS FATE & TRANSPORT

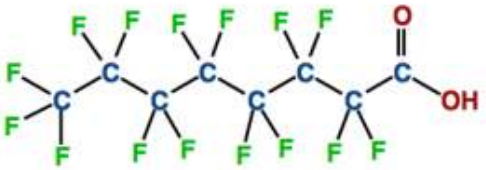



*June 4, 2020*

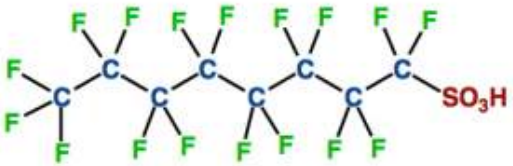
Weston & Sampson

# Important Concepts for PFAS Fate and Transport

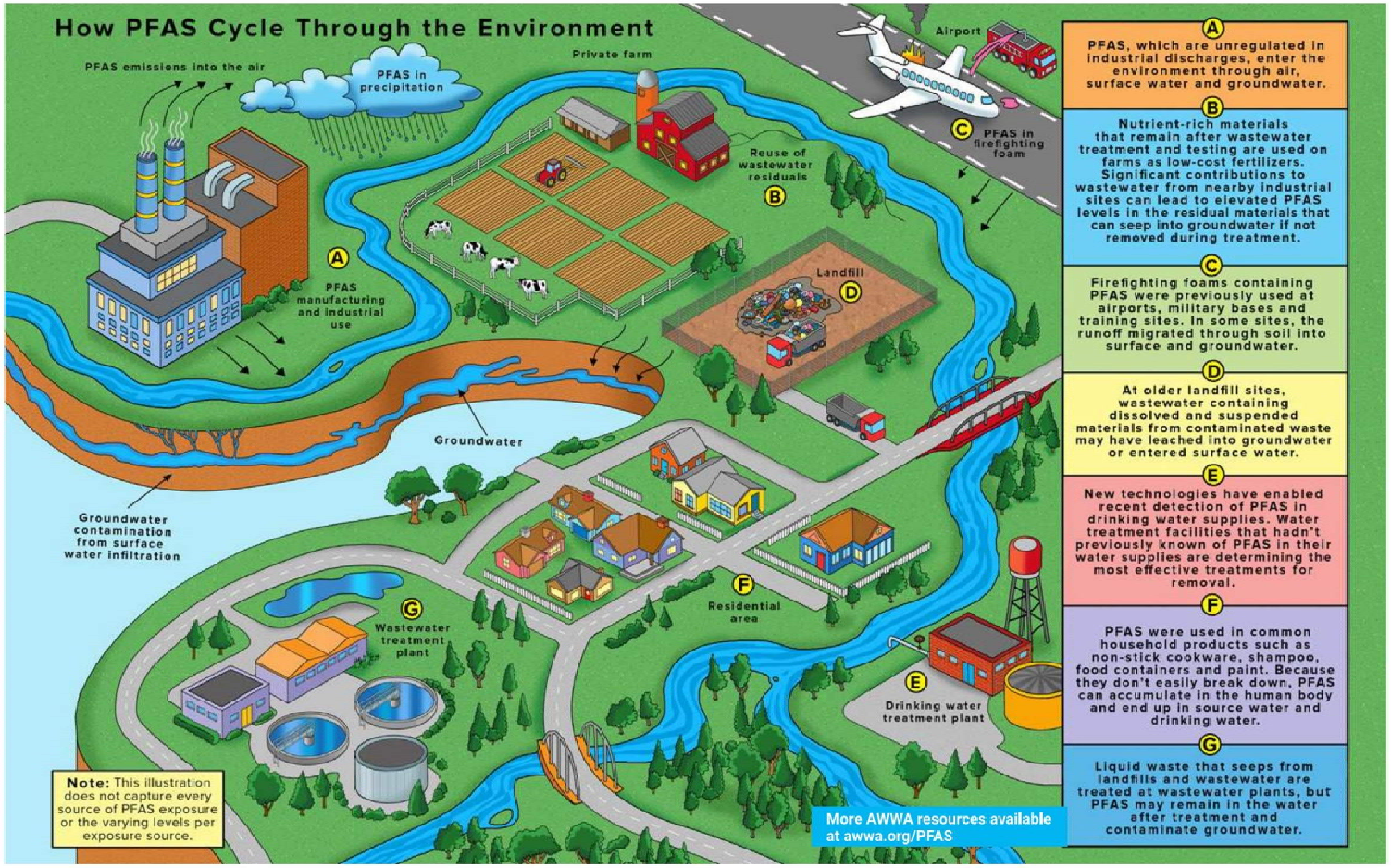
- Release Mechanisms
- Source Material Makeup
- PFAS structural make up impacts reactivity and transport (Heads and Tails)
- Persistence in Environment
- Partitioning of PFAS is complicated
  - Hydrophobic effects
  - Lipophobic effects
  - Interface interactions
  - Multiple ionic species present




**PFOA** - perfluorooctanoic acid

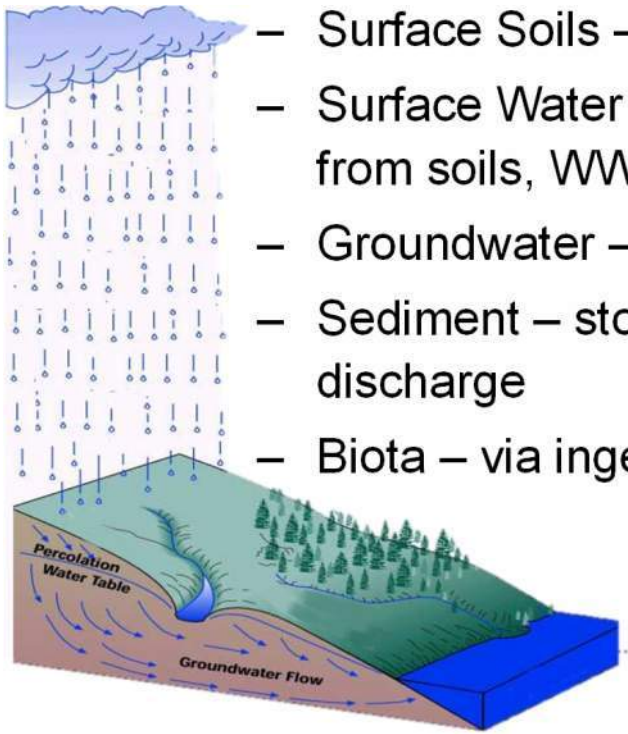



**PFOS** - perfluorooctanesulfonic acid



# Release Mechanisms

- Use/Release of PFAS can result in impacts to:
  - Air– atmospheric transport can result in large impacted areas,
  - Surface Soils – air deposition, AFFF use, infiltration of runoff water
  - Surface Water – via direct discharge, infiltration from soils, runoff from soils, WWTF discharges
  - Groundwater – via infiltration, wastewater disposal and soil
  - Sediment – storm water infiltration, runoff of soils, groundwater discharge
  - Biota – via ingestion of impacted water, plants?, other biota



# Source Type

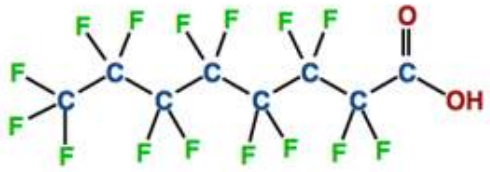
- AFFF Sources
  - AFFF is a mixture of compounds - <5% PFAS
  - There can be many PFAS (short and long) and precursors
  - Hydrocarbons from fire source
  - “Complex Mixture” in source area may effect advection, adsorption, precursor breakdown
- Manufacturing Sources
  - Can have single PFAS source or complex PFAS mixture
  - Additional compounds may be present
- Landfill Leachate
  - “Complex Mixture” in source area may effect advection, adsorption, precursor breakdown
- Wastewater Treatment Facilities
  - Multiple inputs may be present (industries, humans, surface water)
  - Treatment may cause oxidation of precursors
  - Concentration of PFAS in biosolids due to high TOC
  - Biosolids drying, composting, spreading

# Structural Makeup

- Anionic Perfluorinated Alkyl Acids
  - Negatively charged
  - Low vapor pressure
  - Water soluble

PFAAs generally act as surfactants with tail in the air and head in water

Perfluorinated TAIL  Anionic HEAD



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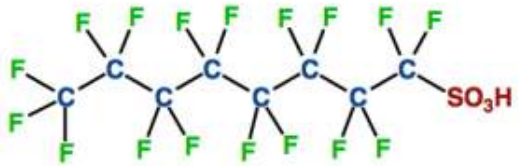

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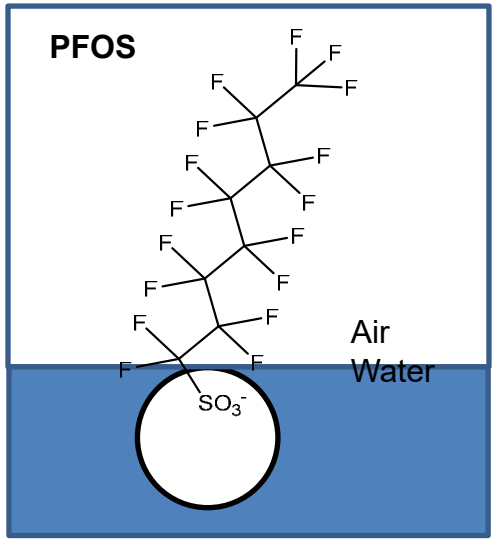


# Structural Makeup

- Anionic Perfluorinated Alkyl Acids
  - PFSAs more strongly sorbed than PFCAs
  - Sorption generally increases with C
  - Short chains can have greater sorption than expected.
  - Retardation factors for anions can be predicted as with other contaminants (generally)

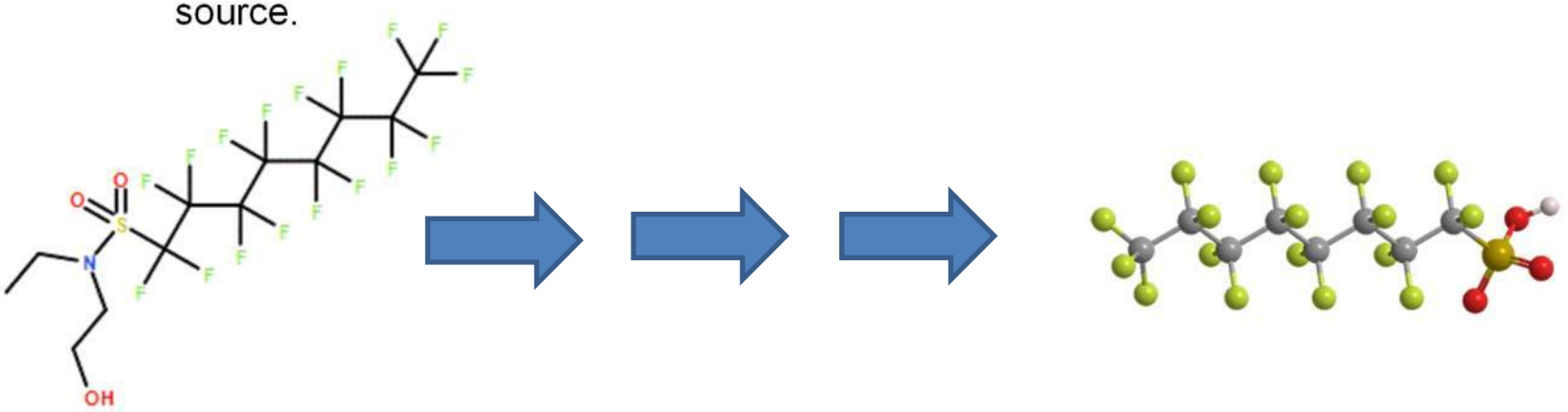
$$R_f = 1 + K_d \frac{\text{Bulk density}}{\text{Porosity}}$$

| Analyte | # Carbon | $K_{oc}$[1] | $R_f$ |
|---|---|---|---|
| PFBA | 4 | 76 | 5 |
| PFPeA | 5 | 23 | 1.4 |
| PFHxA | 6 | 20 | 1.1 |
| PFHpA | 7 | 43 | 3 |
| PFOA | 8 | 78 | 5 |
| PFNA | 9 | 229 | 14 |
| PFDA | 10 | 912 | 57 |
| PFUnA | 11 | 3,600 | 225 |
| PFBS | 4 | 62 | 4 |
| PFHxS | 6 | 112 | 7 |
| PFOS | 8 | 631 | 39 |

[1] Koc data from Guelfo, J.L., Higgins, C.P. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol*. **2013.** 47, 4164–4171.

# Structural Makeup

- Polyfluorinated Substance transport
  - State of charge may dominate retardation
    - Anions > Cations > Zwitterions
  - Short Chains generally migrate faster
  - Cation exchange onto soils may be significant….on par with organic carbon
  - Transformation into Perfluorinated end products may occur with distance from source.




N EtFOSE PFOS

# Precursor Transformation

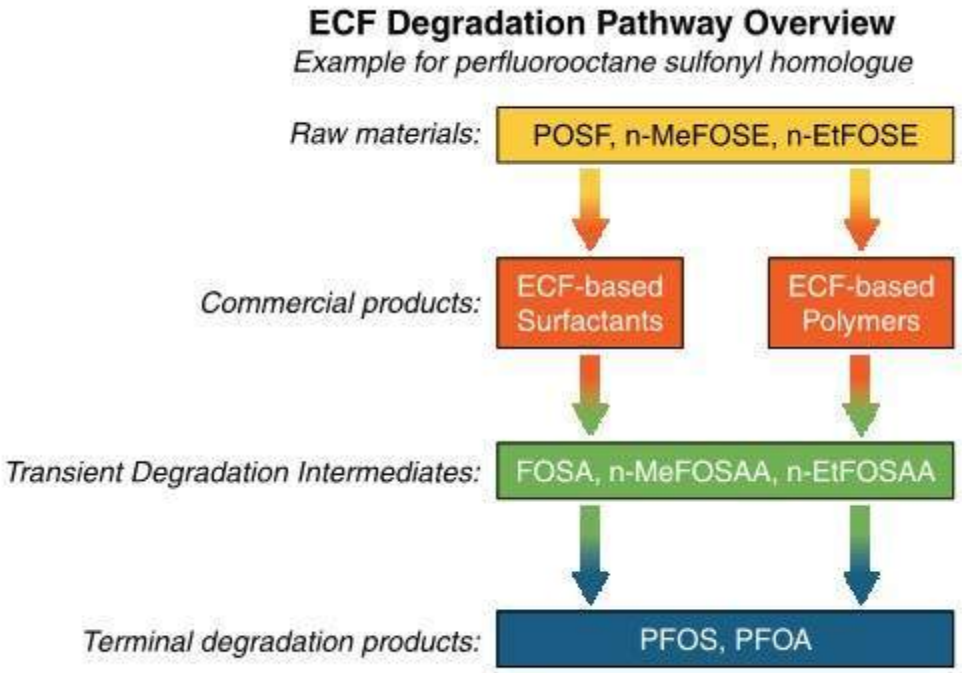



**Figure 2-5. ECF degradation pathway overview (*Example for perfluorooctane sulfonyl homologue*).**

Source: ITRC PFAS Fact Sheet – Fate and Transport 3/16/18

- Branched and linear isomers
- Complex mixture
- Cationic & zwitterionic
- PFSAs (and some PFCAs) as end products

# Precursor Transformation

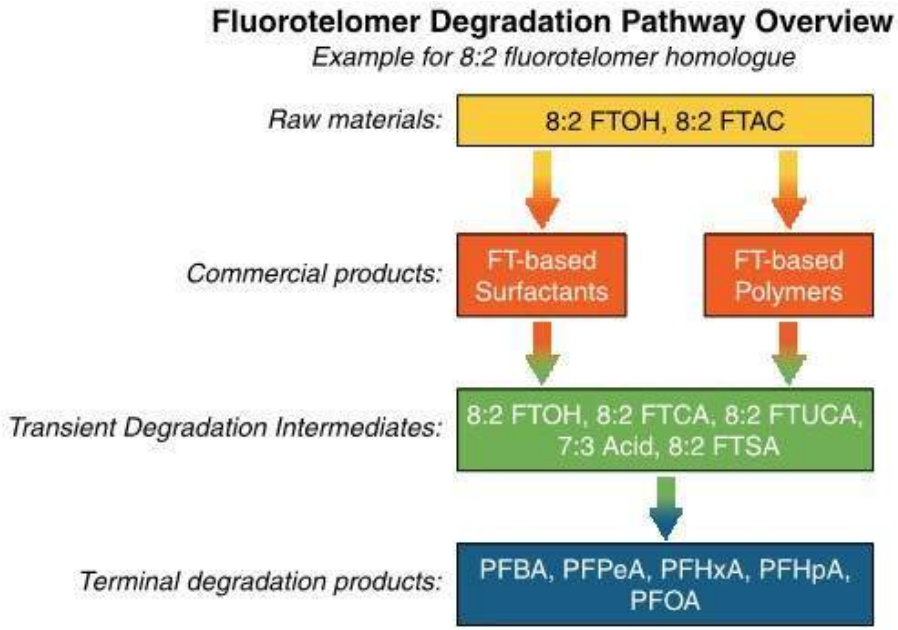



**Figure 2-4. Fluorotelomer degradation pathway overview (*Example for 8:2 fluorotelomer homologue*)**

- Built by 2's
- Fairly "clean" process yielding predictable mixtures
- PFCAs only as end products

Source: ITRC PFAS Fact Sheet – Fate and Transport 3/16/18

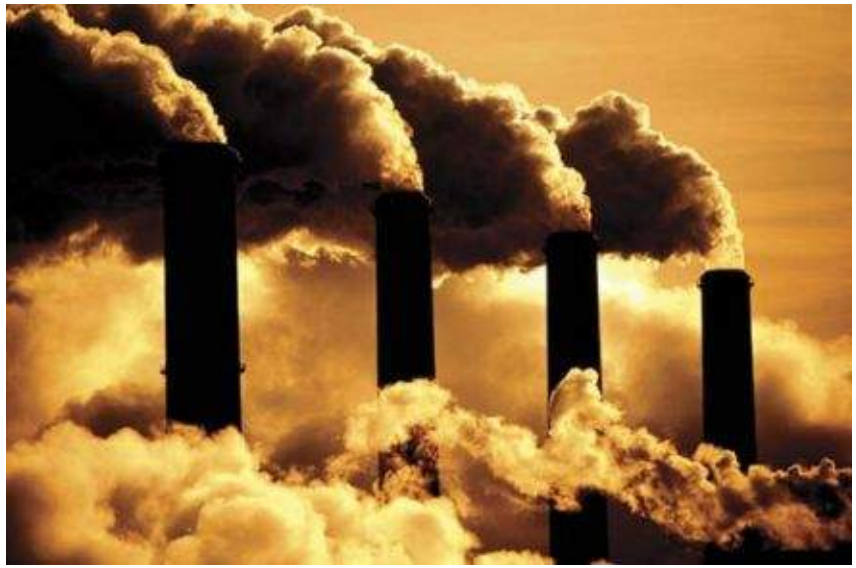
# What is Expected Where?

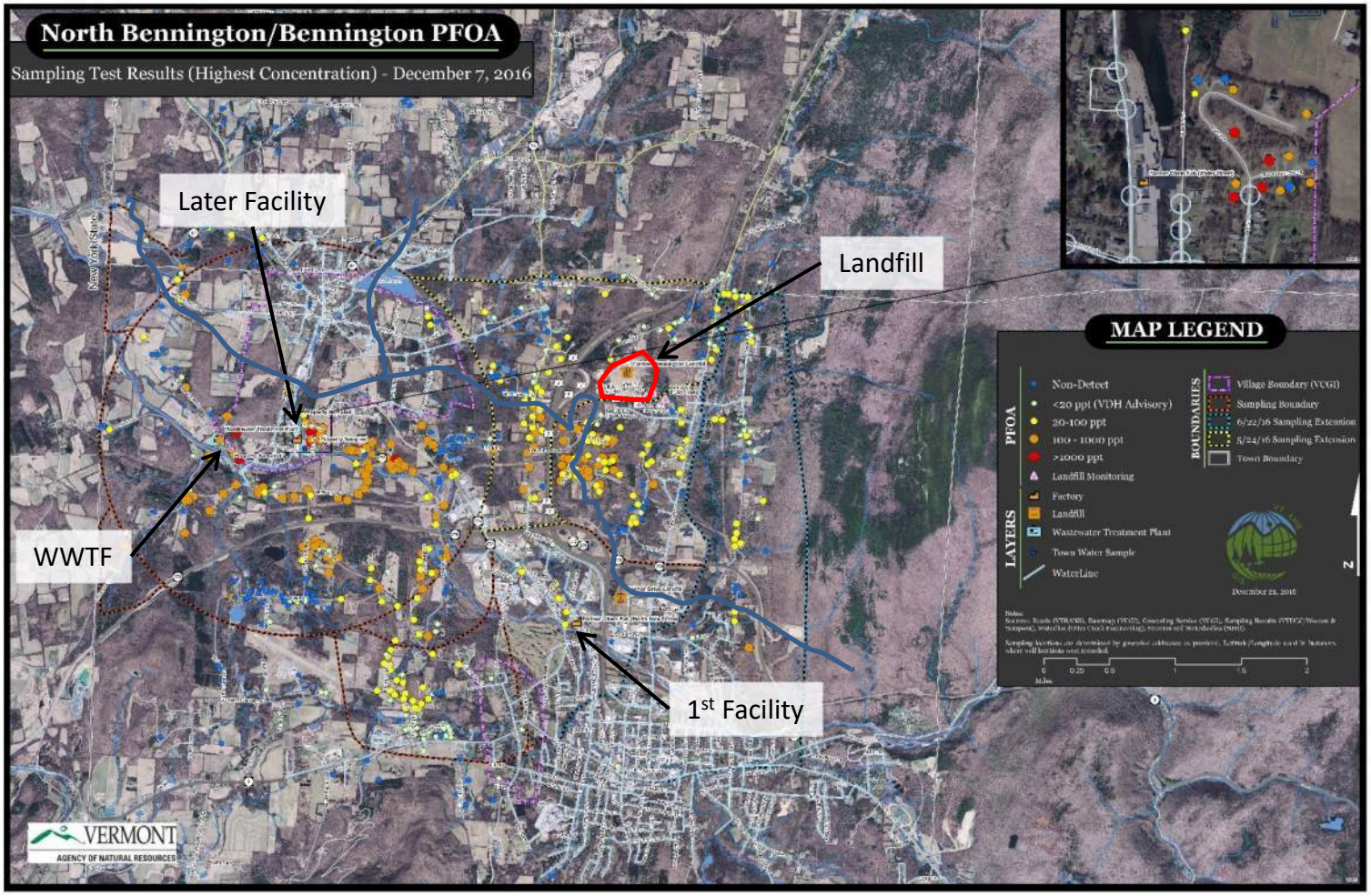
PFAS plumes have varying complexity related to source type, time since release and location relative to the source.

- Source Zone
  - complex chemistry
  - multiple “families” of contaminants
  - competing transport mechanisms
  - “minimal” precursor breakdown (unless remediation has occurred)
- Transition Zone
  - separation of “families” via sorption/retardation/biodegradation
  - precursor transformation seen (more PFAAs with distance?)
  - separation of PFCAs/PFSAs and short chain/long chain via sorption/retardation
- Distal Zone
  - “simpler” chemistry
  - terminal end products dominate

# Transport in Air

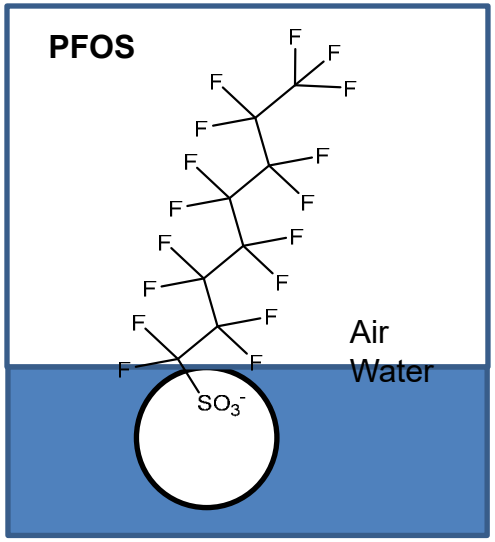
- PFAS can be volatized by drying activities (precursor alcohols)
- “Carried” in water vapor
- “Carried” on or as particulate
- Deposition via wet and dry methods
- Transported in all wind directions, potentially miles




North Bennington/Bennington PFOA
Sampling Test Results (Highest Concentration) - December 7, 2016
Later Facility
Landfill
WWTF
1st Facility
MAP LEGEND
PFOA
Non-Detect
<20 ppt (VDH Advisory)
20-100 ppt
100 - 1000 ppt
>1000 ppt
Landfill Monitoring
LAYERS
Factory
Landfill
Wastewater Treatment Plant
Town Water Sample
WaterLine
BOUNDARIES
Village Boundary (VCGI)
Sampling Boundary
6/22/16 Sampling Extension
8/24/16 Sampling Extension
Town Boundary
VERMONT
AGENCY OF NATURAL RESOURCES

# Transport in Vadose Zone

- Chain length and organic content of soil dependent transport dominant
- However, individual PFAS Koc, ionic state and the presence of other contaminants may have significant impact
- Soil types will define advective transport via infiltration
- Adsorbed PFAS may act as “source” to groundwater for decades
- Air/Water Interface interactions likely results in retardation of migration
- Formation of micelles and interactions with NAPL



# Transport in Groundwater

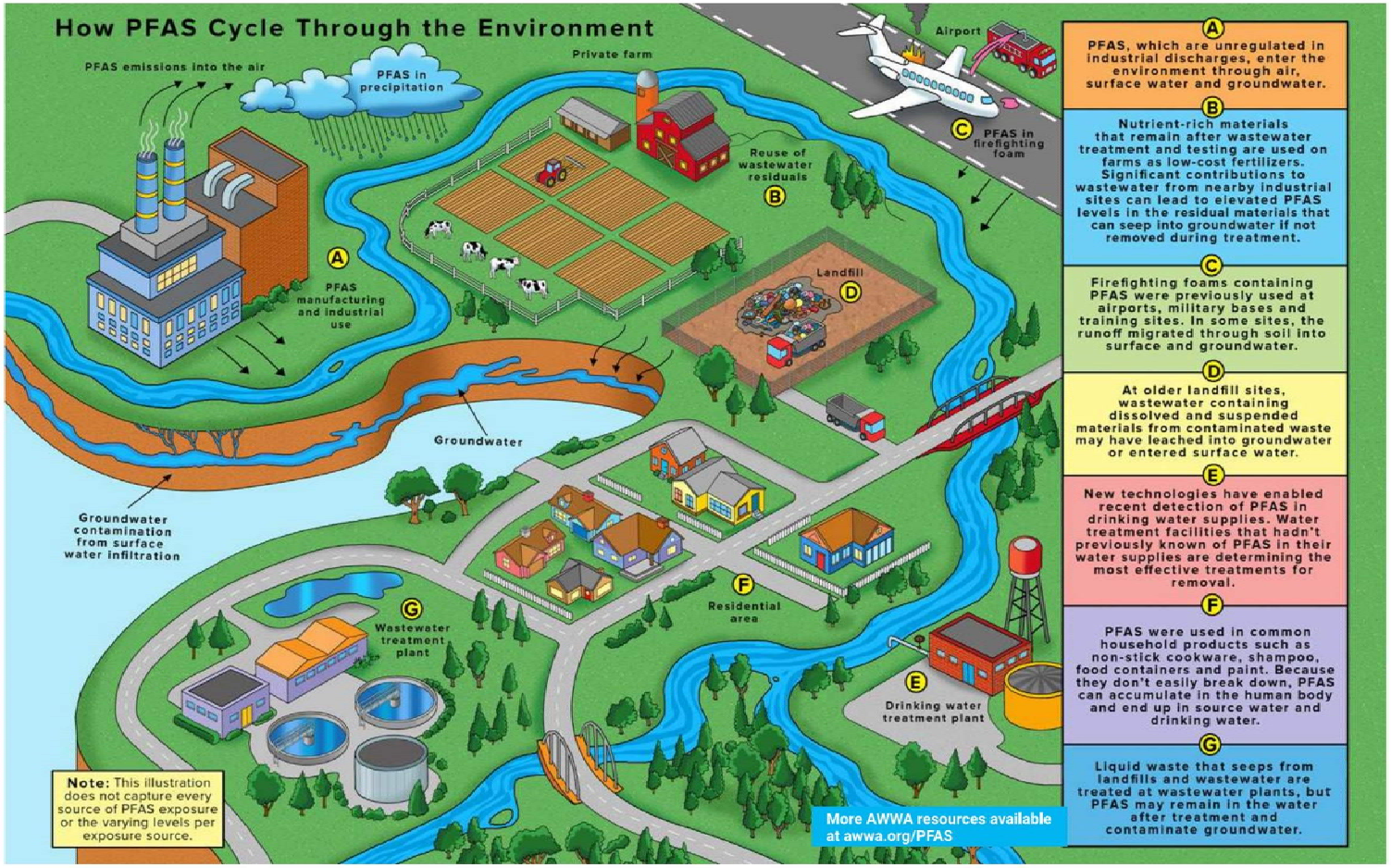
- Chain length and organic content of soil dependent transport dominant
- However, individual PFAS Koc, ionic state and the presence of other contaminants may have significant impact
- Soil types will define advective transport via infiltration
- Air/Water Interface interactions likely results in retardation of migration
- Formation of micelles and interactions with NAPL

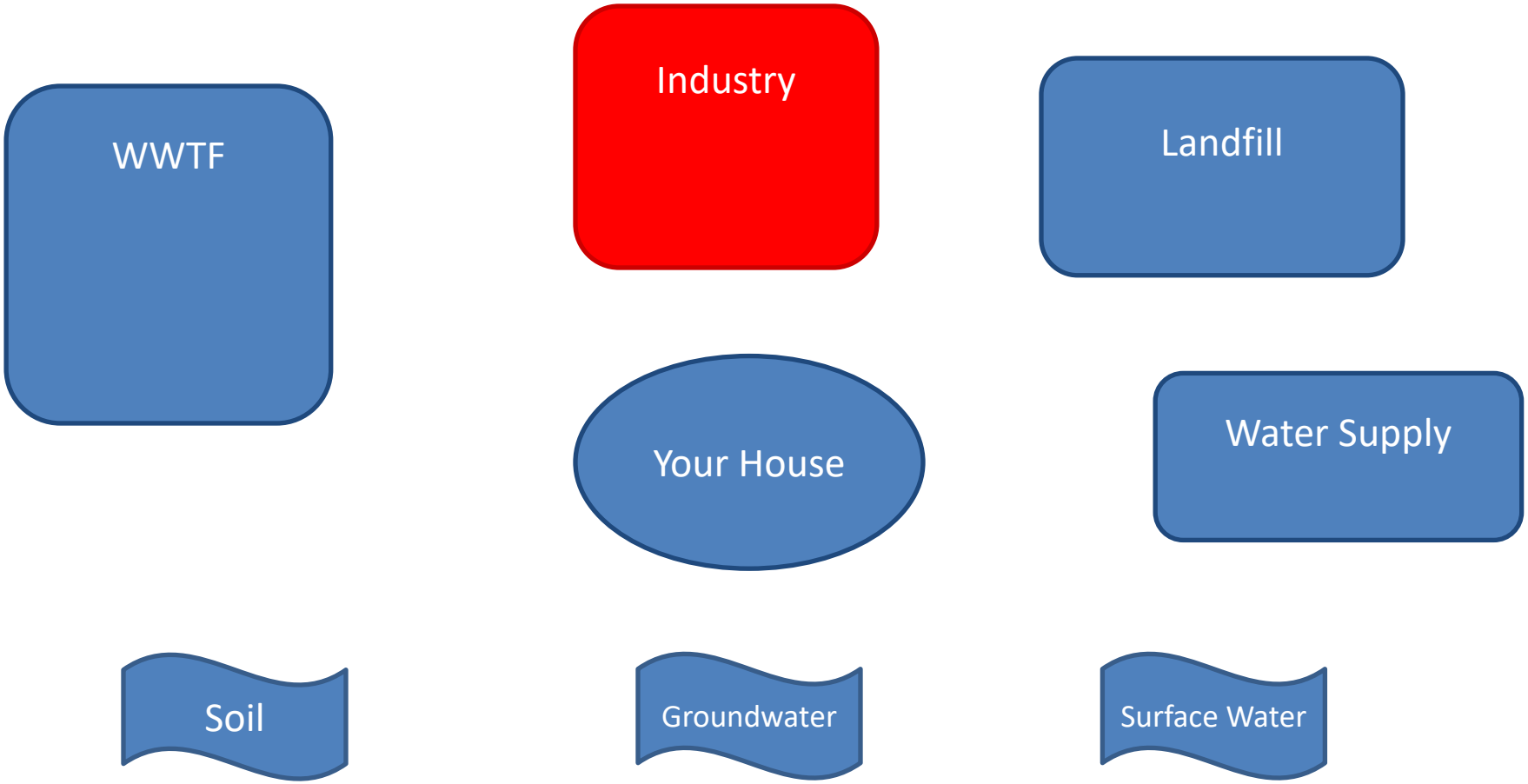
# “RECYCLING”

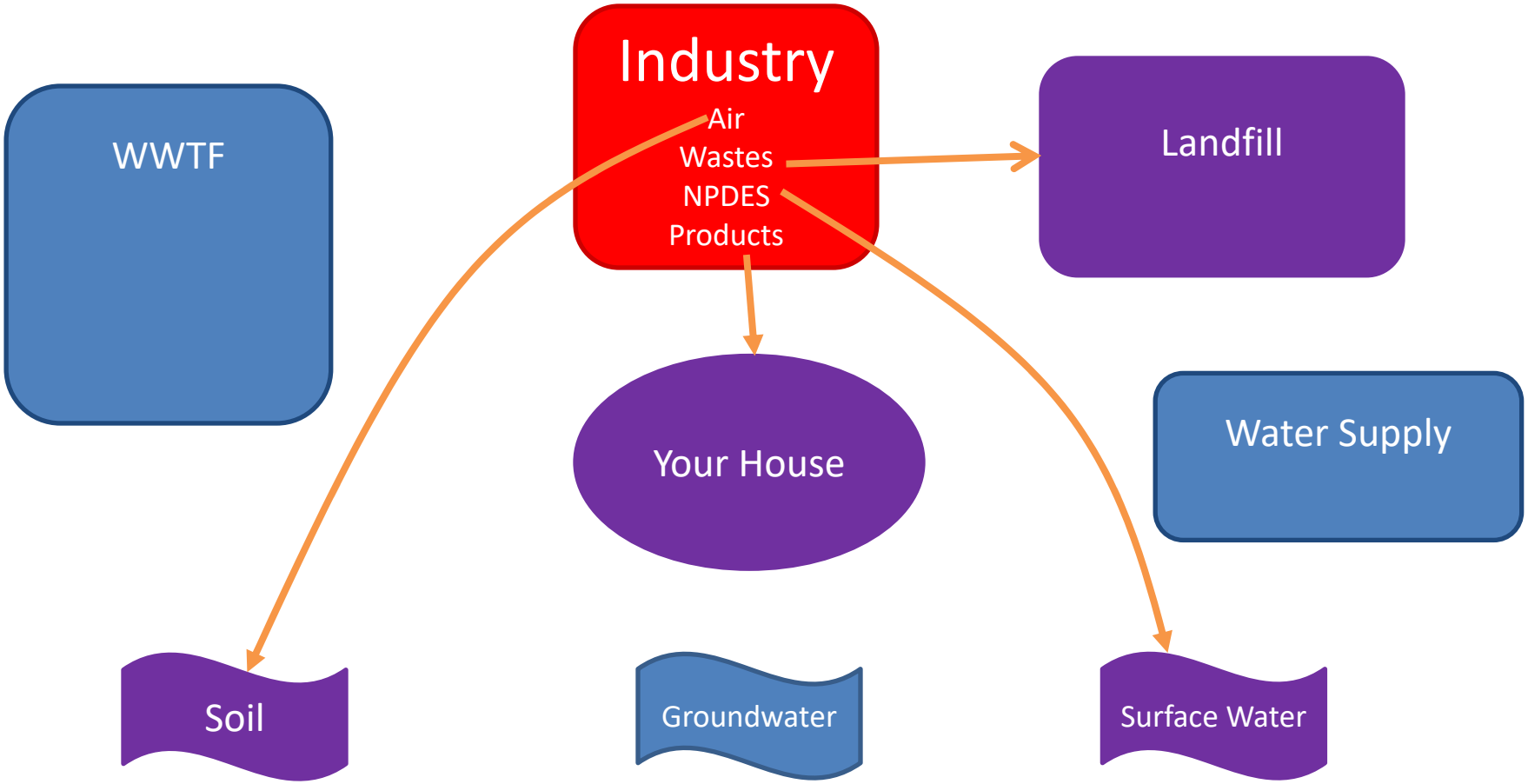
- Terminal…”FOREVER”….no degradation of perfluorinated PFAS
- Soluble, “Mildly” bound to organic carbon, “Mildly” bound ionic soils.
- Nearly Ubiquitous in Environmental Media

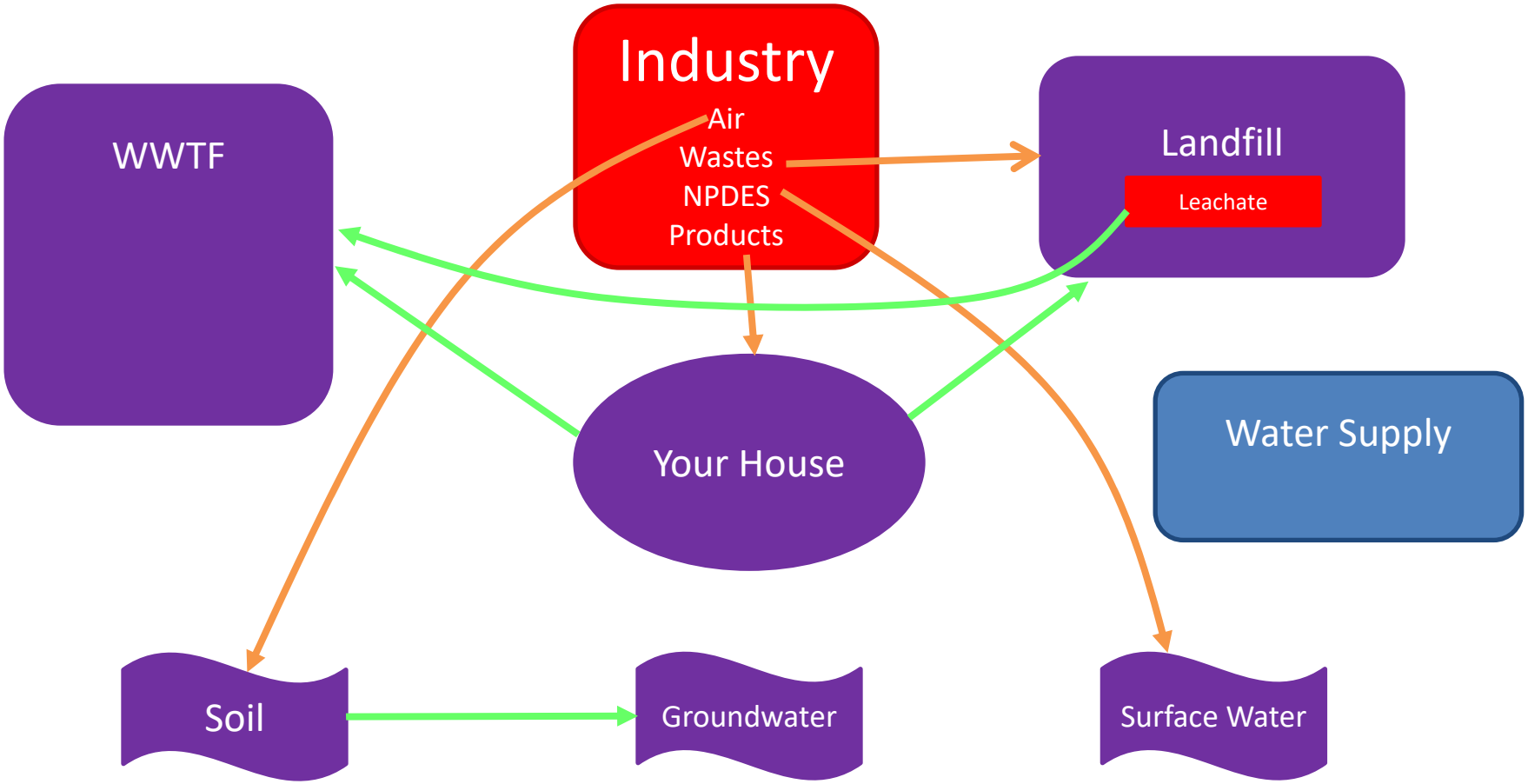
**Conceptual Site Models for Release, Fate and Transport Complicated**




WWTF
Industry
Landfill
Your House
Water Supply
Soil
Groundwater
Surface Water


Industry
Air
Wastes
NPDES
Products
WWTF
Landfill
Your House
Water Supply
Soil
Groundwater
Surface Water


Industry
Air
Wastes
NPDES
Products
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Landfill
Leachate
Your House
Water Supply
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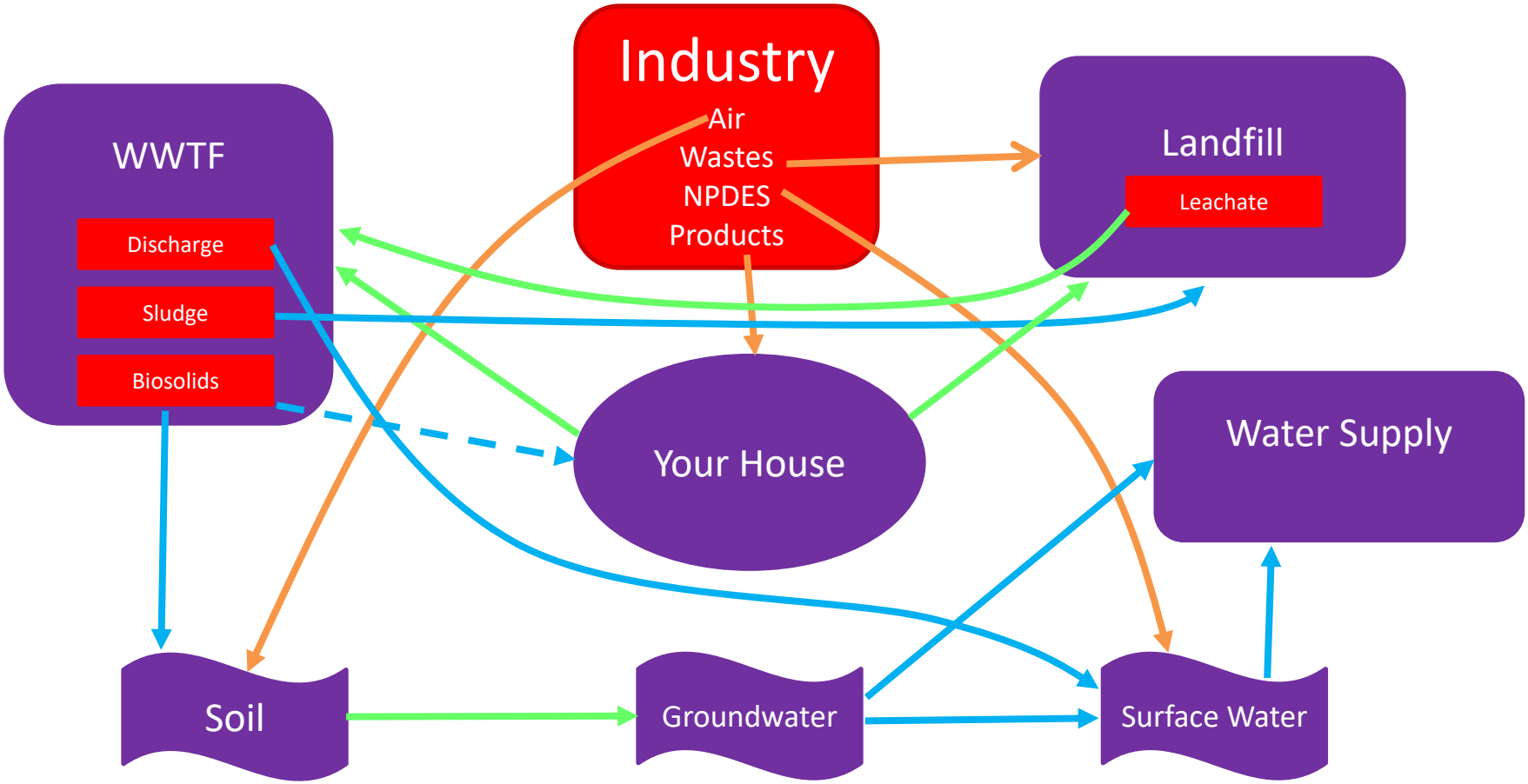
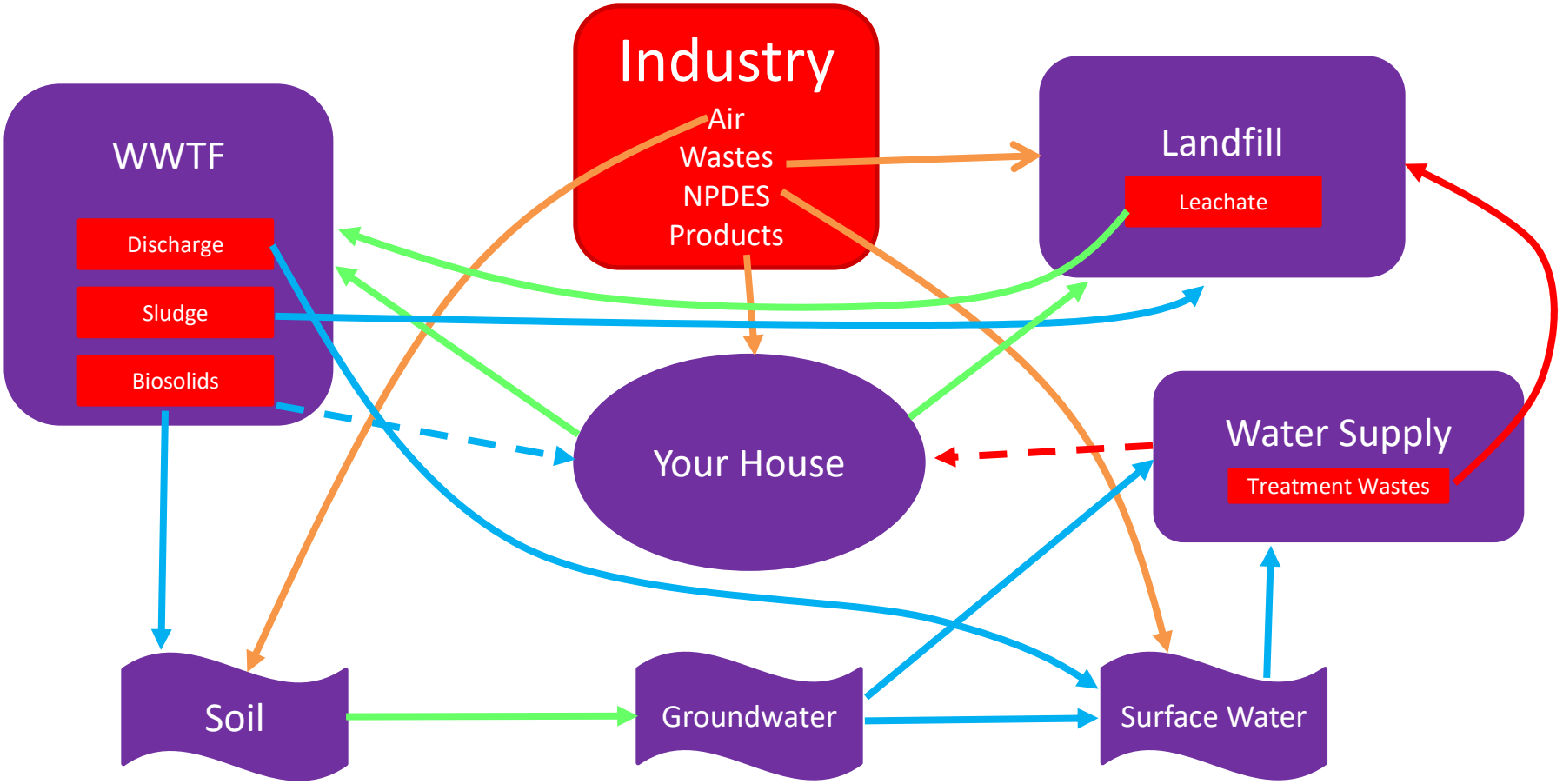
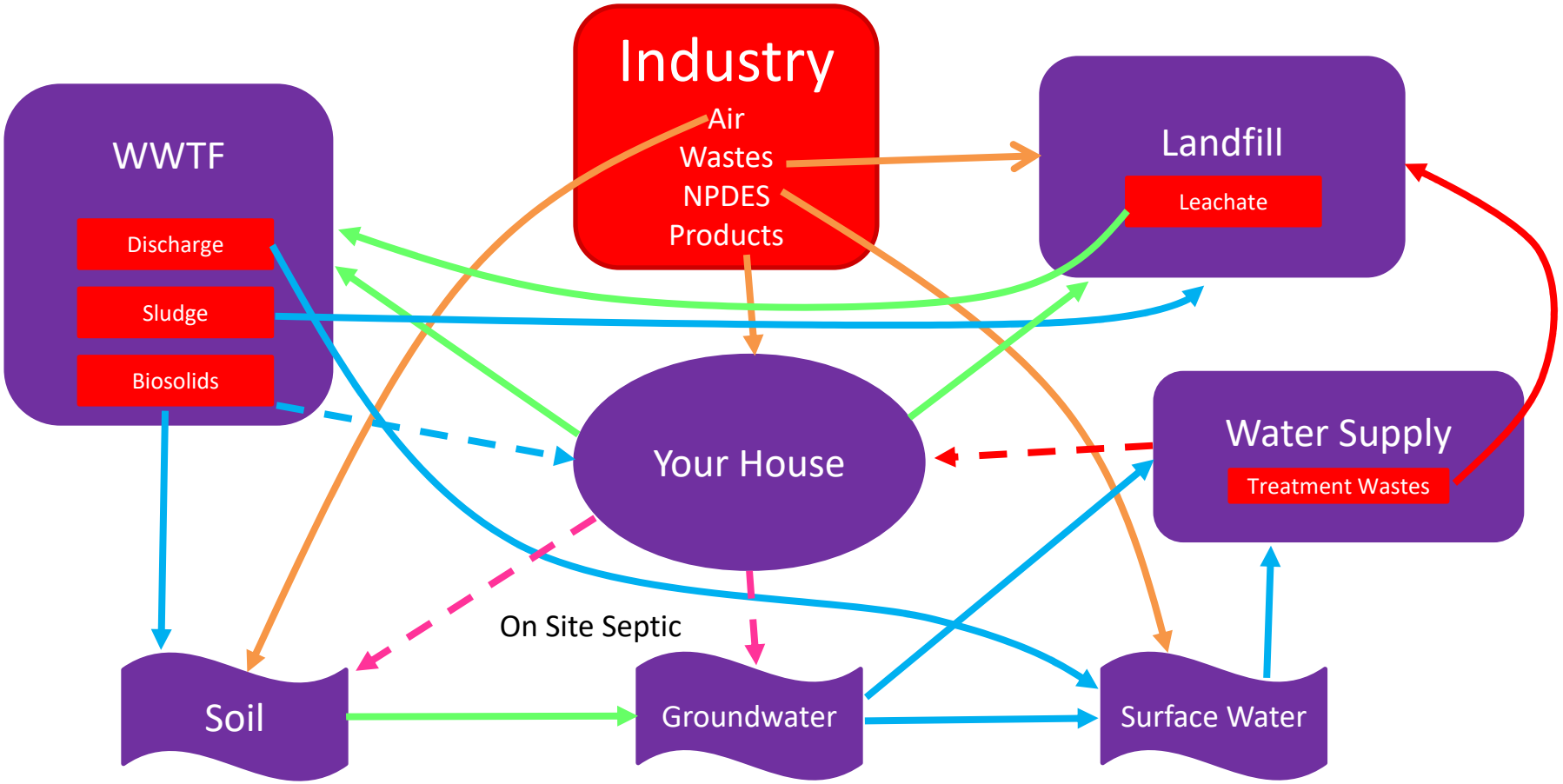

Industry
Air
Wastes
NPDES
Products
WWTF
Discharge
Sludge
Biosolids
Landfill
Leachate
Your House
Water Supply
Soil
Groundwater
Surface Water


Industry
Air
Wastes
NPDES
Products
WWTF
Discharge
Sludge
Biosolids
Landfill
Leachate
Your House
Water Supply
Treatment Wastes
Soil
Groundwater
Surface Water


Industry
Air
Wastes
NPDES
Products
WWTF
Discharge
Sludge
Biosolids
Landfill
Leachate
Water Supply
Treatment Wastes
Your House
On Site Septic
Soil
Groundwater
Surface Water

# Important Concepts for PFAS Fate and Transport

- Source zones may be complex: long-term discharge potential
  - Non PFAS related contaminants can confound understanding of source area
  - Investigation areas may be larger than you're used to
- Perfluorinated PFAS:
  - TERMINAL
  - Mobility is chain-length dependent, affected by OC, pH, inorganic cations, etc.
- Polyfluorinated PFAS (precursors) are varying in their stability
  - Much more variable in terms of transport
  - Oxidizing remedial techniques (ISCO, air sparge, aerobic bioremediation) can transform precursors to TEMRINAL PFAAs
- Surfactant properties may lead to increased concentrations at air/water interface or at water/NAPL interface

# IMPORTANT WEBSITES

NEWMOA
https://www.newmoa.org/

ITRC FACT SHEETS
https://pfas-1.itrcweb.org/fact-sheets/

EPA PFAS Webpage
https://www.epa.gov/pfas

Northeastern University PFAS Project
https://pfasproject.com/

# Questions?

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