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Guidance Document

13 Fact Sheets

External Tables

PFAS Introductory Training

- Clu-In Archive: https://www.clu-in.org/conf/itrc/PFAS-Introductory/

Other video resources

- Available through links on: https://pfas-1.itrcweb.org
- Quick Explainer Videos
- Longer PFAS Training Modules
- Archived Roundtable Sessions

PFAS: Beyond the Basics Training

Fate and Transport
Site Characterization
Source Identification & Forensics

Today's PFAS Trainers

Robert Burgess
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ITRC PFAS Team: “Beyond the Basics” Training

SAMPLING & ANALYSIS, SW ANALYSIS, AIR OCCURRENCE
February 25 2025
1:00-3:00 PM ET

HUMAN HEALTH EFFECTS, ECOLOGICAL TOXICITY, REGULATIONS
March 25 2025
1:00-3:00 PM ET

SOURCE ID, SITE CHARACTERIZATION, FATE & TRANSPORT
April 24 2025
1:00-3:00 PM ET

BIOSOLIDS, SOIL LEACHING, & MOBILITY
May 20 2025
1:00-3:00 PM ET

TREATMENT TECHNOLOGIES
June 3 2025
1:00-3:00 PM ET

PFAS
“Beyond the Basics”
TRAINING

2025

Learning Objectives

Fate and Transport

- Small-scale processes
- Movement in and between environmental media
- Differential transport of PFAS species (environmental fractionation)
- Precursor transformation

Site Characterization

- Concerns for different source types
- Hydrogeological setting
- Sampling and Analysis
- Data interpretation and visualization

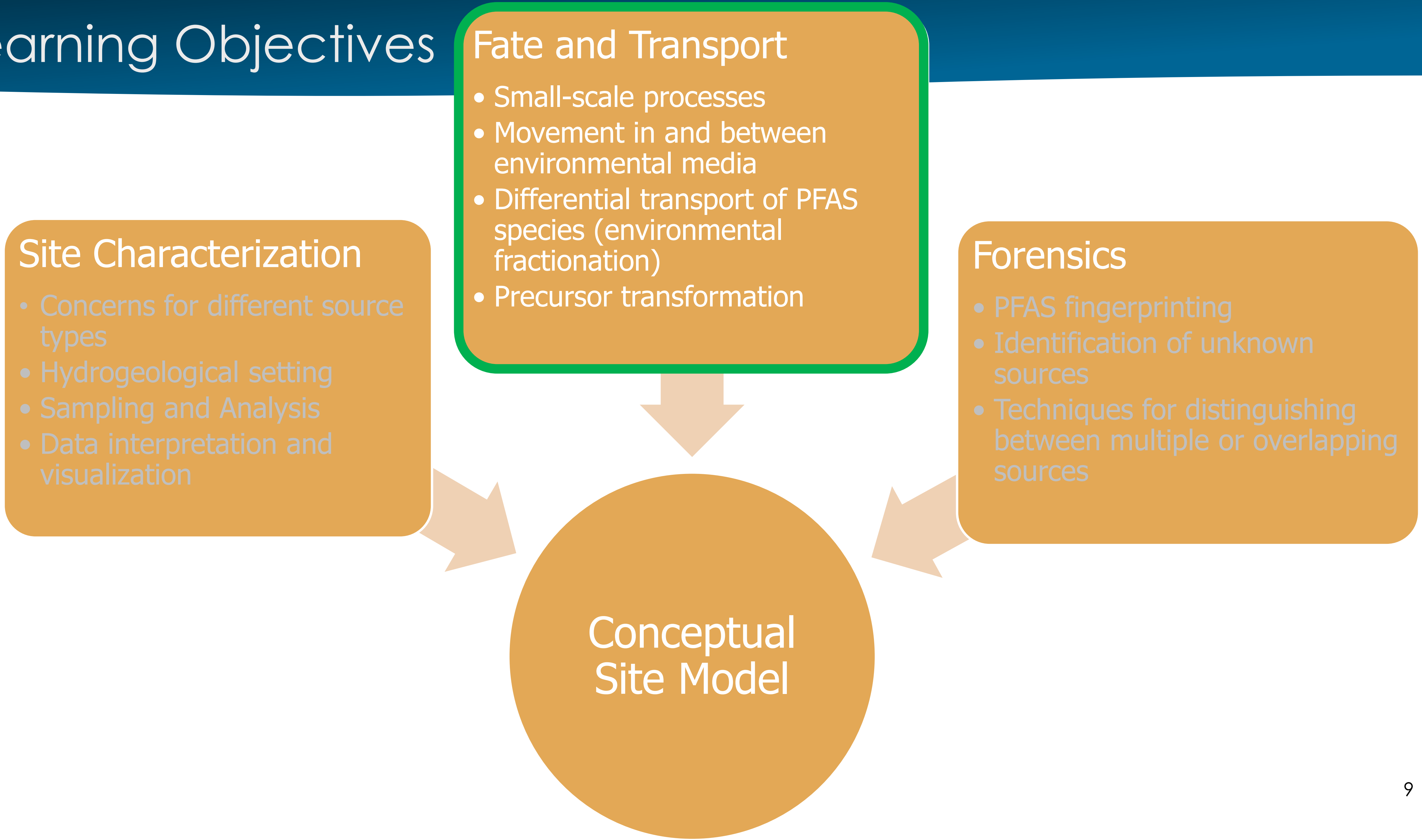
Forensics

- PFAS fingerprinting
- Identification of unknown sources
- Techniques for distinguishing between multiple or overlapping sources

Conceptual Site Model

Fate and Transport Considerations

Learning Objectives



Fate and Transport

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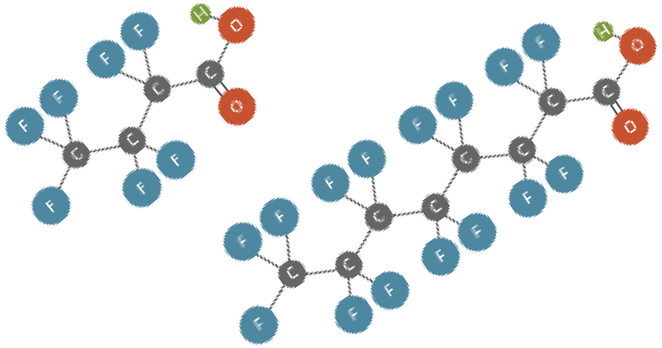
Conceptual Site Model

F&T: What is Fate and Transport?

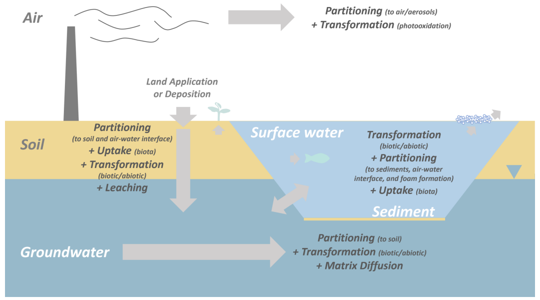
PFAS Characteristics

PFAS
Fate & Transport

Site Characteristics



- *Per*fluorinated vs. *poly*fluorinated
- *Fluorinated tail:* chain length
- *Non-fluorinated head:* functional group and charge state



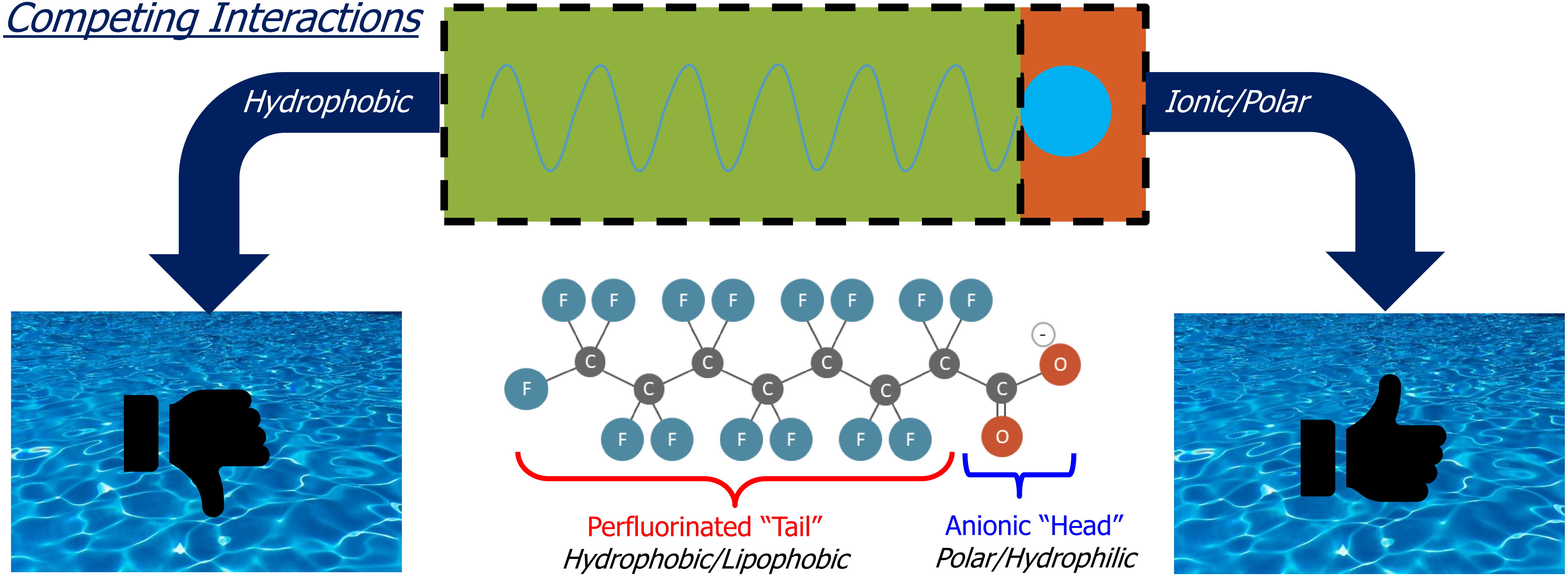
- Nature of Release
- Soil properties
- Groundwater depth/velocity
- Groundwater geochemistry
- Prevailing atmospheric conditions
- Co-contaminants

PFAS figures source: M. Olson, Trihydro. Used with permission.

PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

PFAA Compound Properties

Competing Interactions



Hydrophobic

Ionic/Polar

Perfluorinated "Tail"
Hydrophobic/Lipophobic

Anionic "Head"
Polar/Hydrophilic

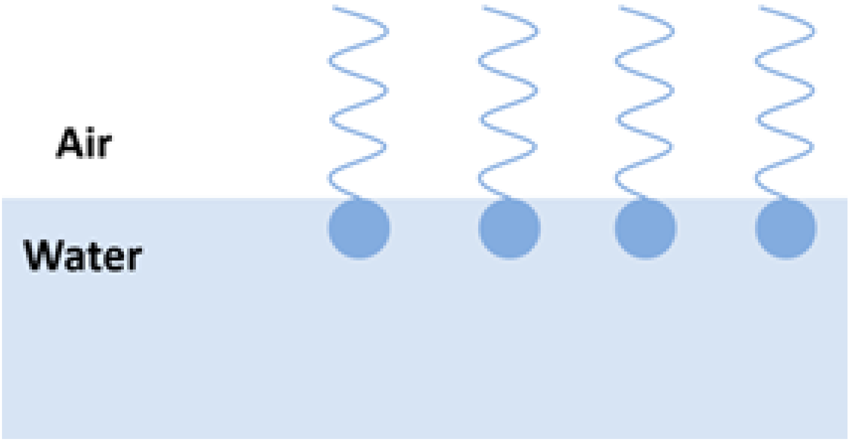
PFAS figure source: M. Olson, Trihydro. Used with permission.

PFAA Molecules Assemble at the Interface

Energetically favorable

Reduces the surface tension at the interface

PFAAs have a greater affinity than traditional surfactants

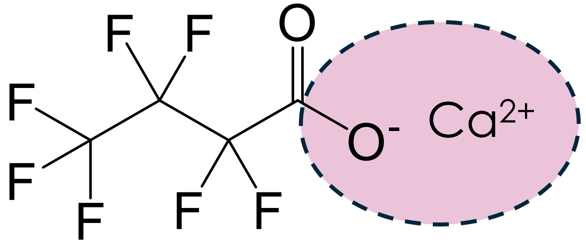


PFAS-1, Figure 4-1. Source: D. Adamson, GSI. Used with permission.

Microscale Partitioning

Electrostatic Interactions

- pH (changing pH changes surface charges)
- Presence of polyvalent cations (Ca2+ Mg2+)
- Clay (positive surface charge)



PFBA

Hydrophobic Interactions

- Organic carbon sorption consideration
  - ↑Chain length ↑Sorption to organic carbon
  - PFSA sorb more strongly than PFCA to organic carbon

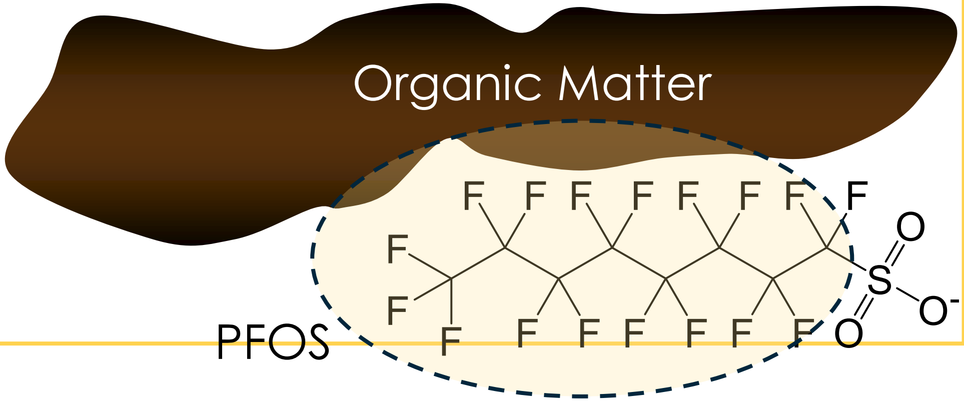
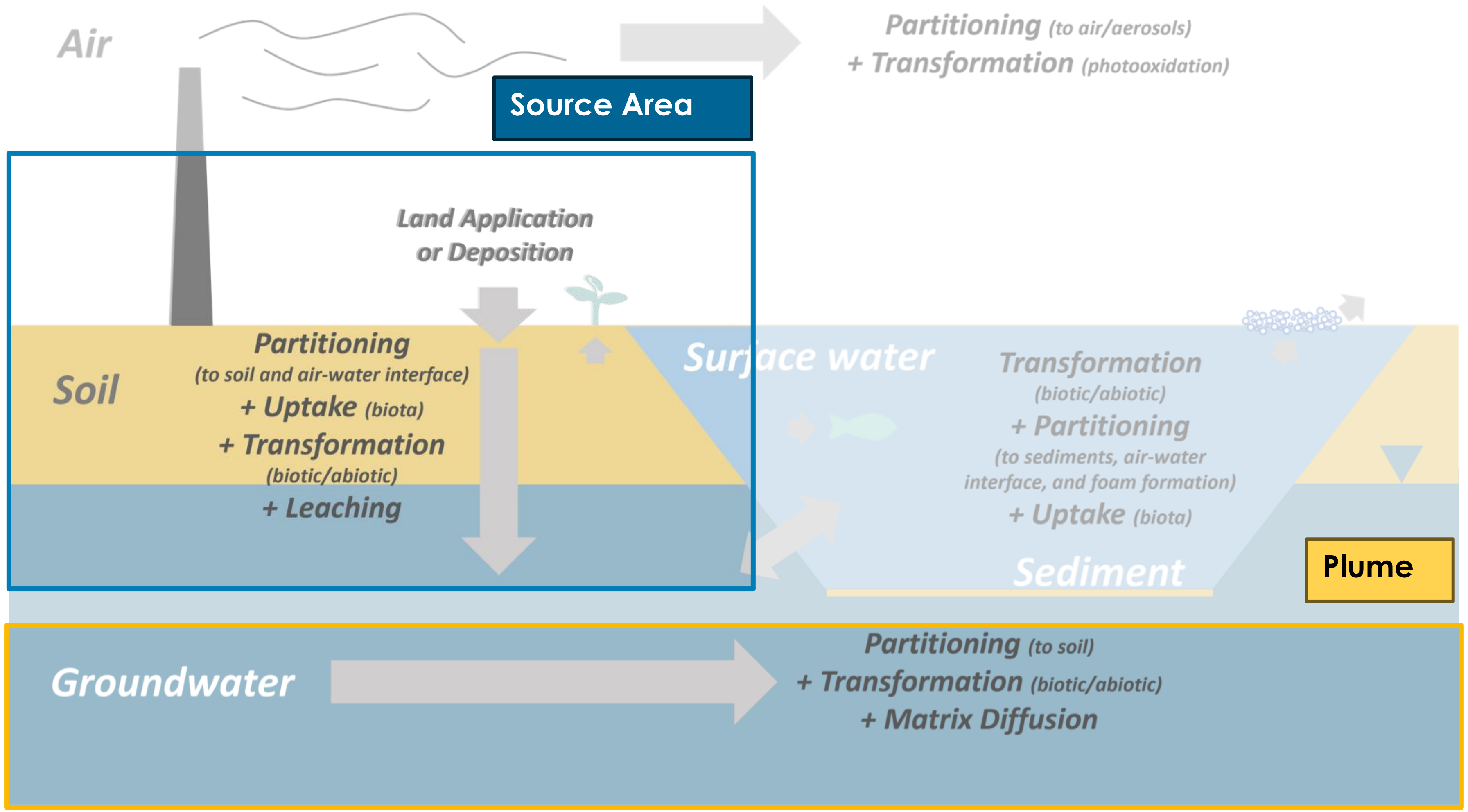


Figure source: Christopher Olivares, UC Irvine. Used with permission.

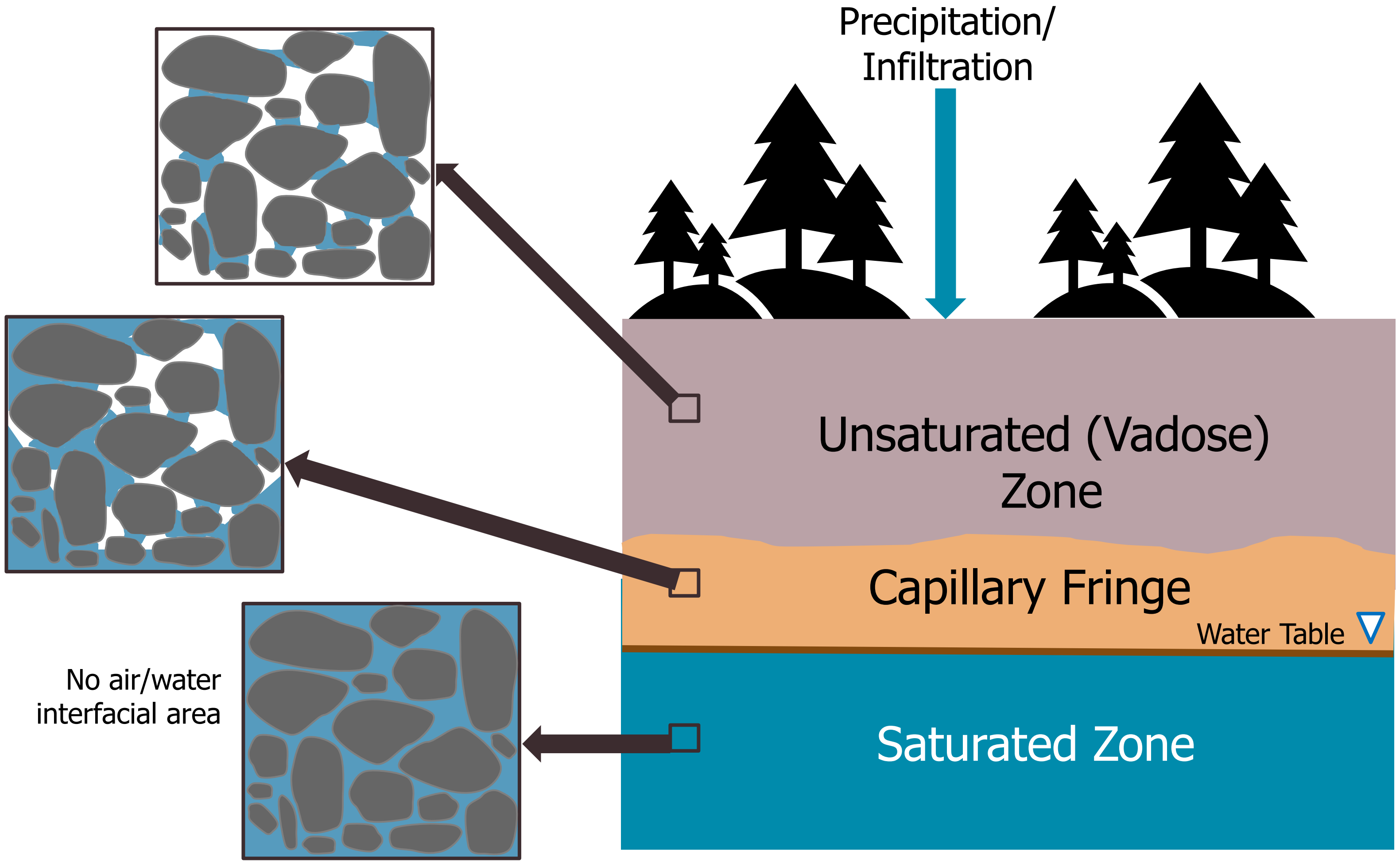
Microscale Partitioning: Interfacial Behavior

The relative importance of phase partitioning changes between the source area and the plume.



PFAS-1, Section 5.2, Phase Partitioning. PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

PFAA Partitioning Depends on Amount of Interfacial Area



- Degree of water saturation affects the amount of interfacial area (nonlinear)
- Larger interfacial area enhances PFAA retention
- Factors affection A-W interfacial area:
  - Soil type
  - Grain size
  - Heterogeneity
  - Organic Content

PFAS-1, Section 5.2, Phase Partitioning

Microscale Factors Influencing Solid Phase Sorption

Hydrophobic Partitioning	• Longer chain PFAAs > shorter-chain PFAAs • PFSAs > PFCAs • Organic carbon dependent
Electrostatic Interactions	• Dependent on pH and ionic strength • Cationic/zwitterionic PFAAs may strongly sorb
Concentration dependent (nonlinear)	• Sorption sites can become saturated
Sorption properties change with precursor transformation	• Aerobic vadose zone→ increased transformation • Changing sorption capacity over space and time

PFAS-1, Section 5.2.3, Partitioning to Solid Phases

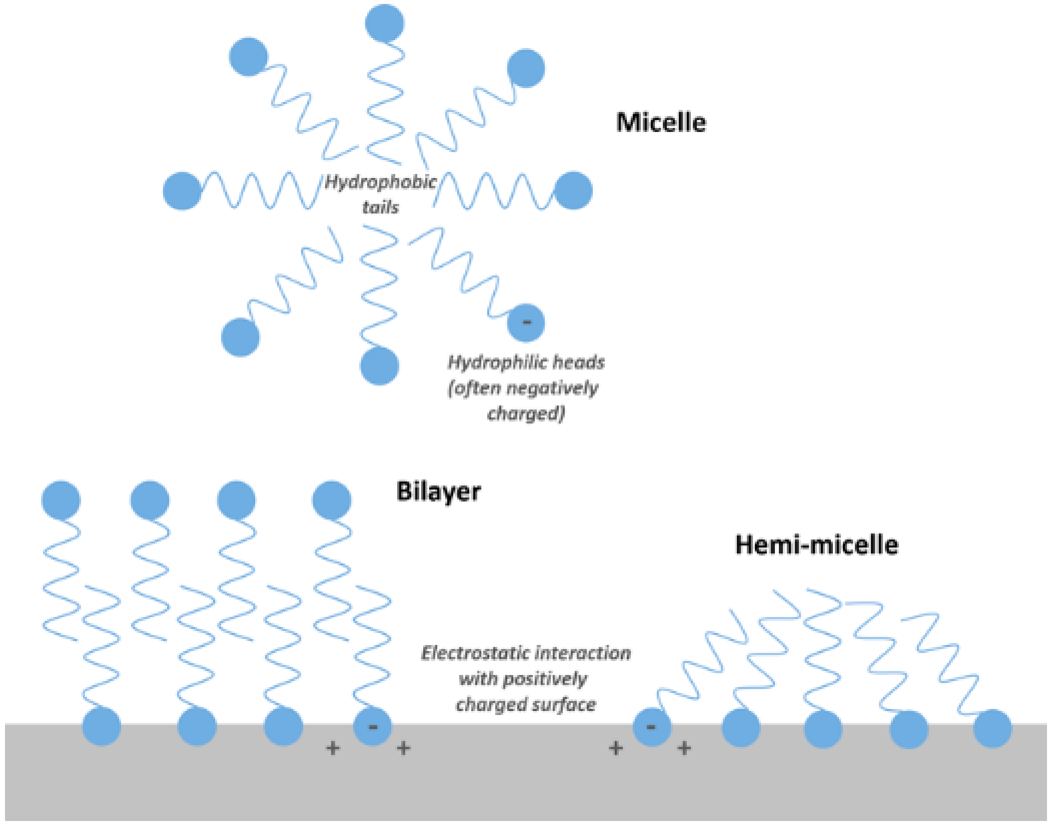
Microscale Partitioning Summary

	PFAS Characteristics	Site Characteristics
Enhanced Sorption	▪ Longer chain ▪ Linear isomers ▪ Sulfonates ▪ Cationic & Zwitterionic	▪ Lower soil pH ▪ Presence of polyvalent cations ▪ Organic carbon ▪ Salinity → increased sorption to AW interface
Reduced Sorption	▪ Short chain ▪ Branched isomers ▪ Carboxylates ▪ Anionic	▪ High clay content→ reduced AW interfacial area ▪ Remediation impacts: Increased soil pH (ISCO), introduction of polyvalent cations

PFAS-1, Section 5.2, Phase Partitioning

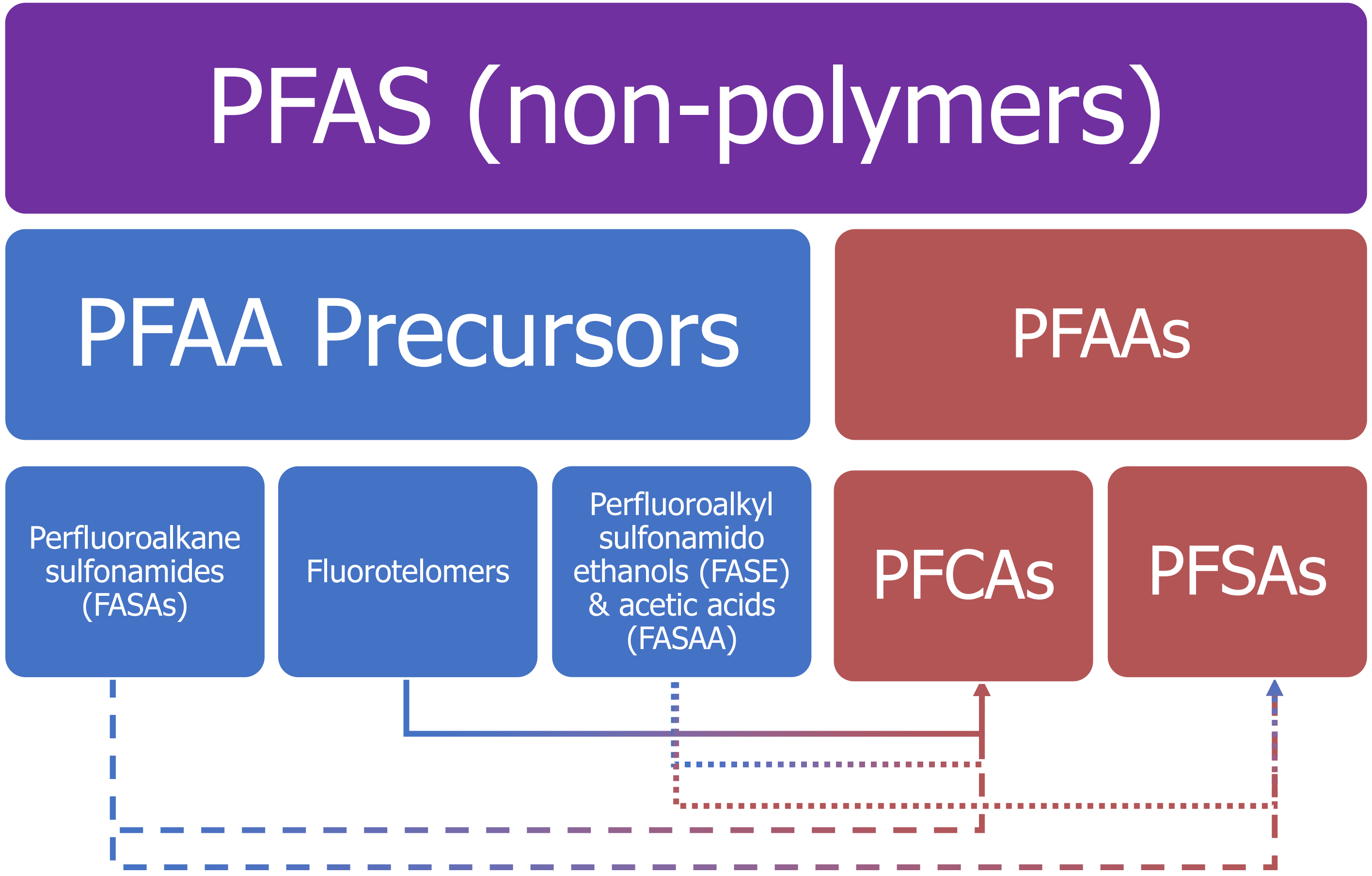
Supramolecular Aggregations

- At high concentrations, certain PFAS can aggregate due to surfactant properties
  - Forms micelles, hemi-micelles, and bilayers
- May not be directly analogous to traditional micelle formation – more research needed.
- May be more complicated in environmental settings
  - Aggregations can occur well below CMC
  - Interaction with charged or hydrophobic surfaces can affect sorption
- More research is needed to understand how this affects fate and transport



PFAS-1, Figure 5-2. Source: D. Adamson, GSI. Used with permission.

F&T: PFAA Precursors (environmental conditions)



PFAS (non-polymers)

PFAA Precursors

PFAAs

Perfluoroalkane sulfonamides (FASAs)

Fluorotelomers

Perfluoroalkyl sulfonamido ethanols (FASE) & acetic acids (FASAA)

PFCAs

PFSAs

- Majority of PFAS are polyfluorinated compounds
- Polyfluorinated compounds (precursors) can be oxidized to PFAAs (PFCAs, PFSAs)
- Total amount of PFAAs expected to increase over time because of **transformation**

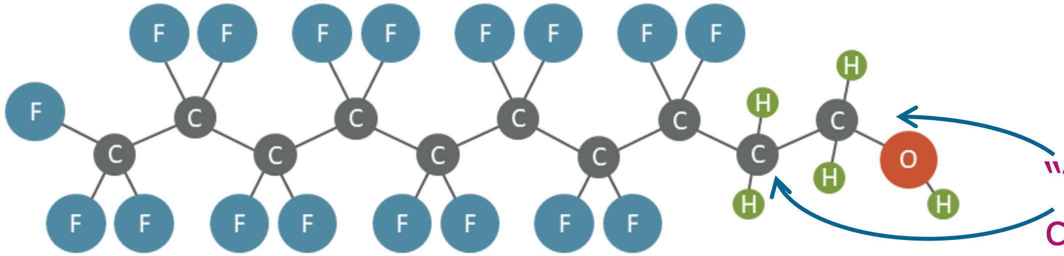
As we learn more about transformation pathways, we may be able to use that information for site characterization – to determine sources, age, history…

See PFAS-1, Section 2.2 for more detailed information regarding nomenclature & the PFAS family tree.

F&T: Transformation of Precursors to PFAAs

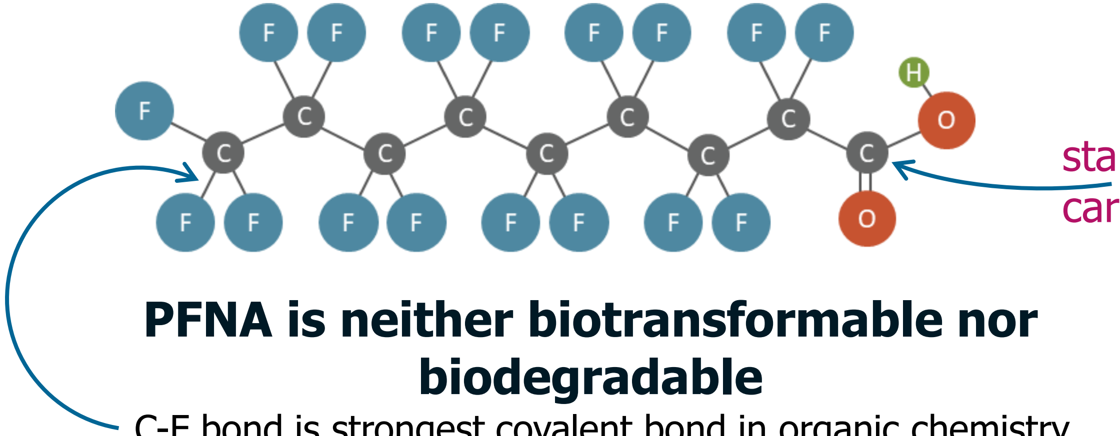
8:2-fluorotelomer alcohol (8:2-FTOH) is biotransformable, <u>not biodegradable</u>

Poly



"transformable" carbons

PFAA



stable carbon

PFNA is neither biotransformable nor biodegradable

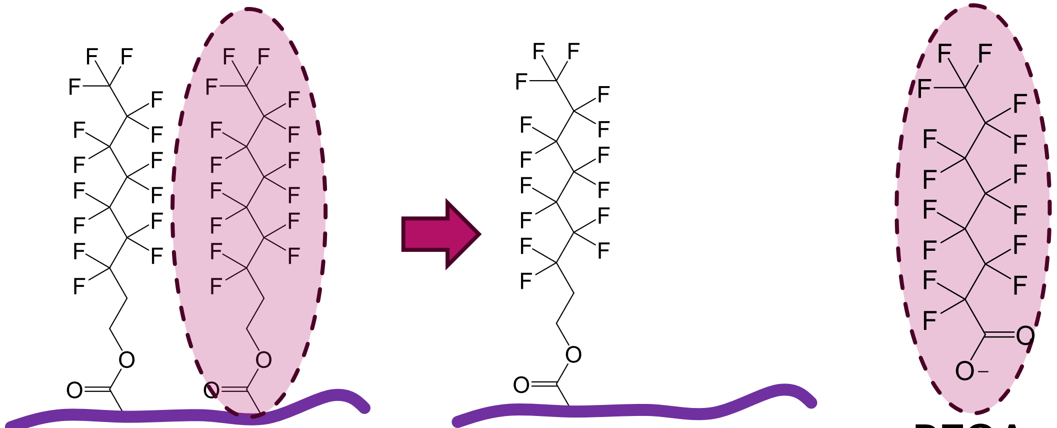
C-F bond is strongest covalent bond in organic chemistry

PFAS-1, Section 5.4.4.2 Aerobic Biological Pathways.

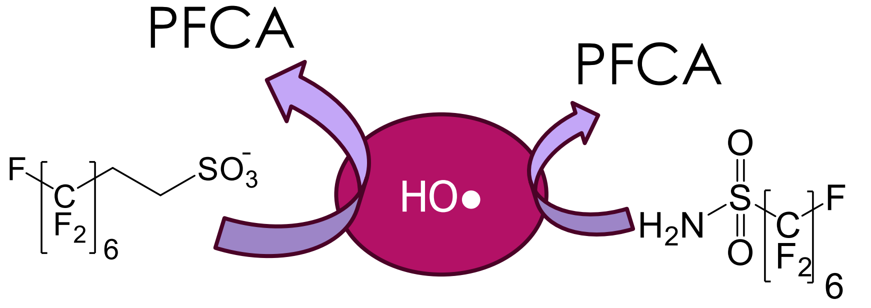
PFAS figures source: M. Olson, Trihydro. Used with permission.

Abiotic transformations (Oxidation reactions)

- Hydrolysis of fluoropolymers can form PFOA
- Hydroxyl radicals formed in natural systems oxidize precursors
- Fluorotelomers oxidize faster than sulfonamides
- PFAAs are not always formed (not complete oxidation)
- Indirect photolysis in the atmosphere (ex. FtOH → PFCAs)



Polymer hydrolysis



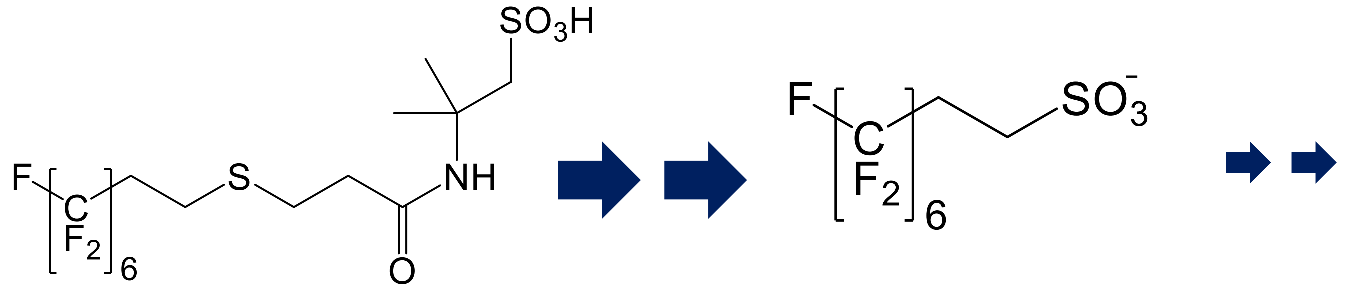
Fluorotelomer
(faster reactions)

Sulfonamides
(Slower reactions)

PFAS-1, Section 5.4.4.1Abiotic Pathways and Section 5.4.3 Atmospheric Transformations.
Figure source: Christopher Olivares, UC Irvine. Used with permission.

Aerobic Biotransformation (Oxidation)

Fluorotelomer (**only** forms PFCAs as terminal products)

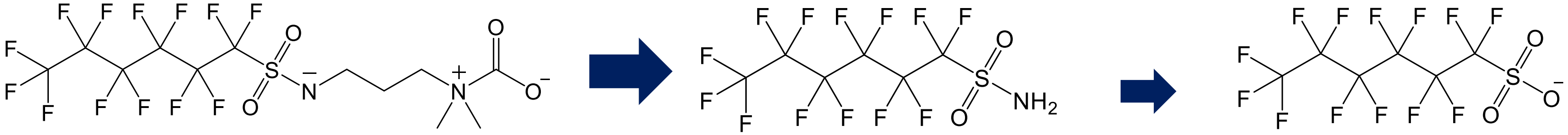


6:2 FtTAoS
(Fluorotelomer)

6:2 FtS

PFBA
PFPeA
PFHxA
PFOA

Sulfonamides (slower rates than Fluorotelomers, **mainly** form PFSAs)



Ampr-FHxSA
(Sulfonamide)

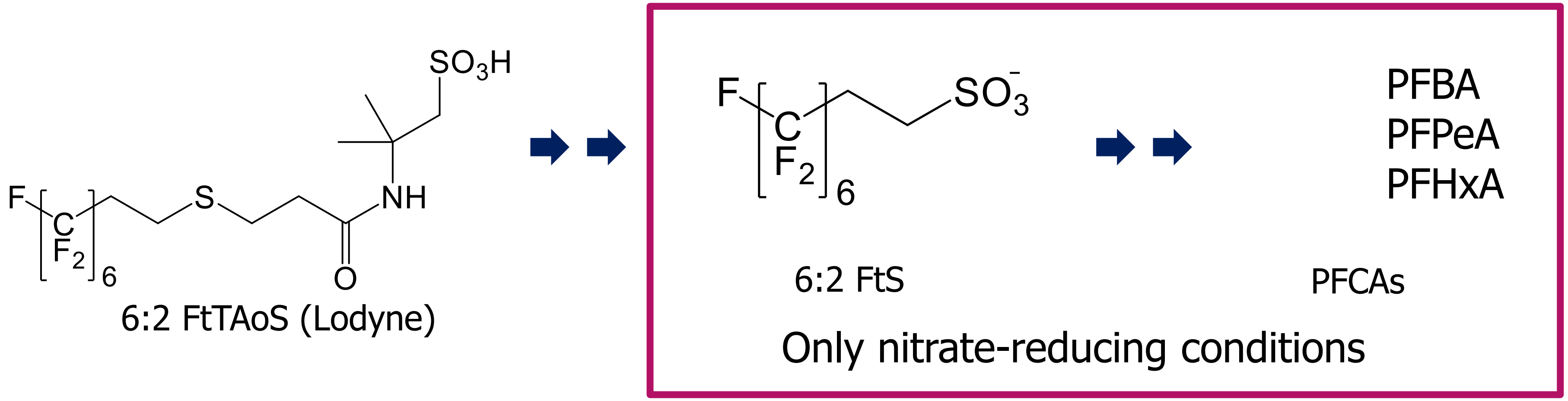
FHxSA

PFHxS

PFAS-1, Section 5.4.4.2 Aerobic Biological Pathways.
Figure source: Christopher Olivares, UC Irvine. Used with permission.

Anaerobic biotransformation

Fluorotelomer



6:2 FtTAoS (Lodyne)

6:2 FtS

PFBA
PFPeA
PFHxA

PFCAs

Only nitrate-reducing conditions

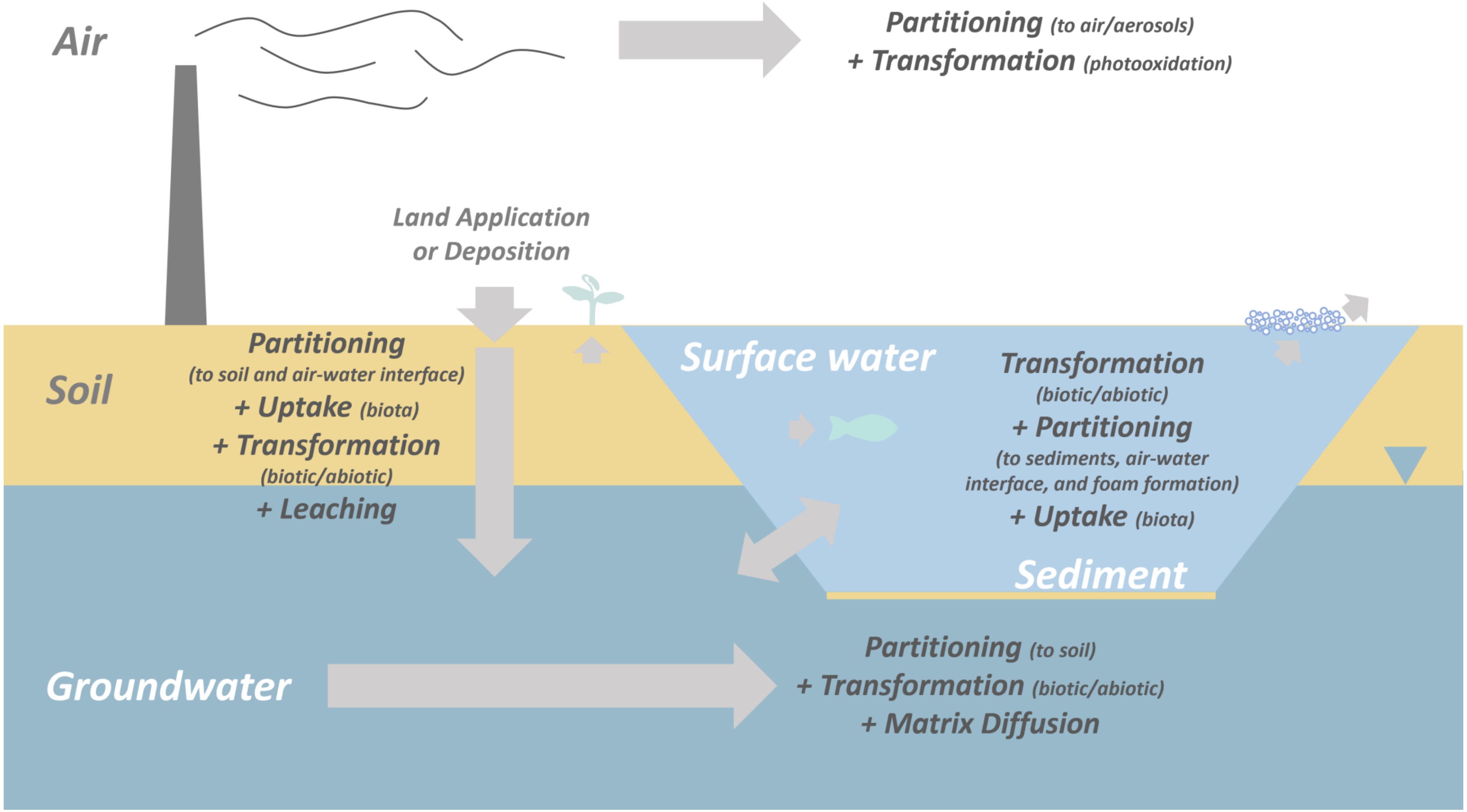
Fluorotelomer acids + other PFAS formed under more reducing anaerobic conditions

Feammox (*Acidimicrobium sp.* Strain A6)

- Anaerobic ammonium oxidation coupled to iron reduction
- Reported defluorination of PFOA, PFOS with release of fluoride

PFAS-1, Section 5.4.4.3 Anaerobic Biological Pathways.
Figure source: Christopher Olivares, UC Irvine. Used with permission.

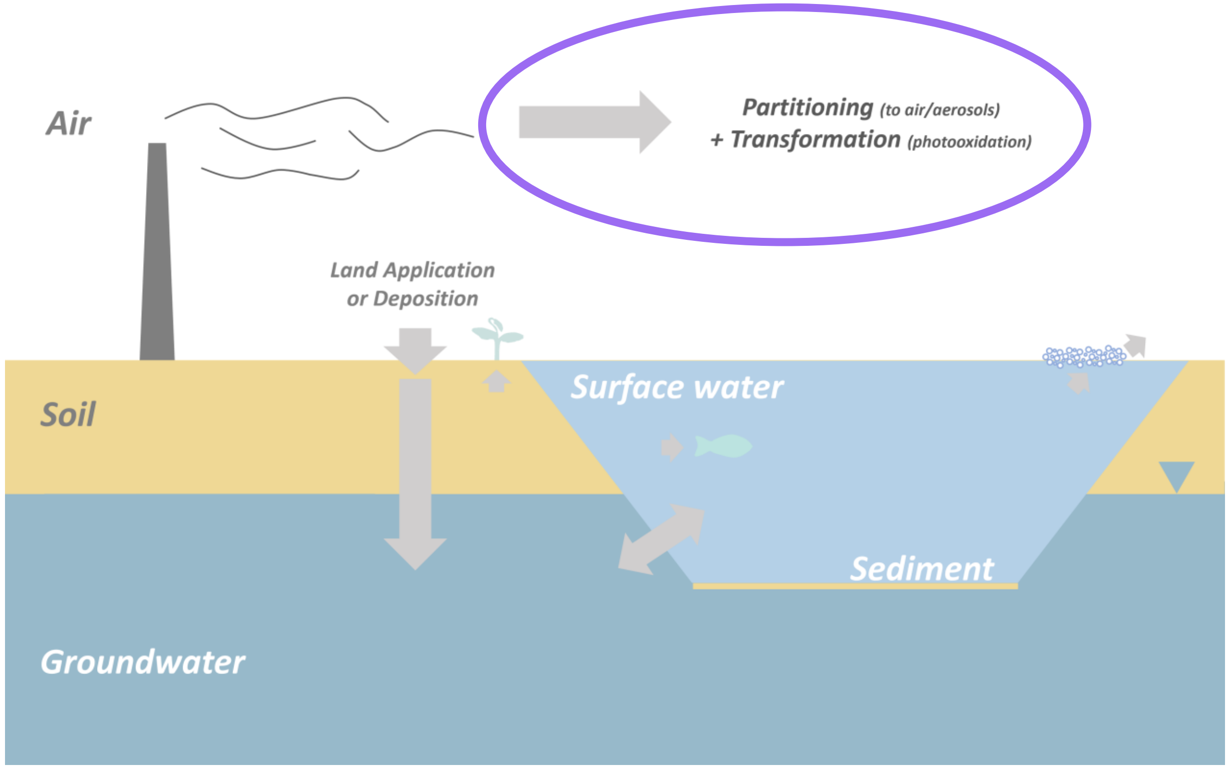
Macroscale Fate and Transport



PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Macroscale Transport: Air

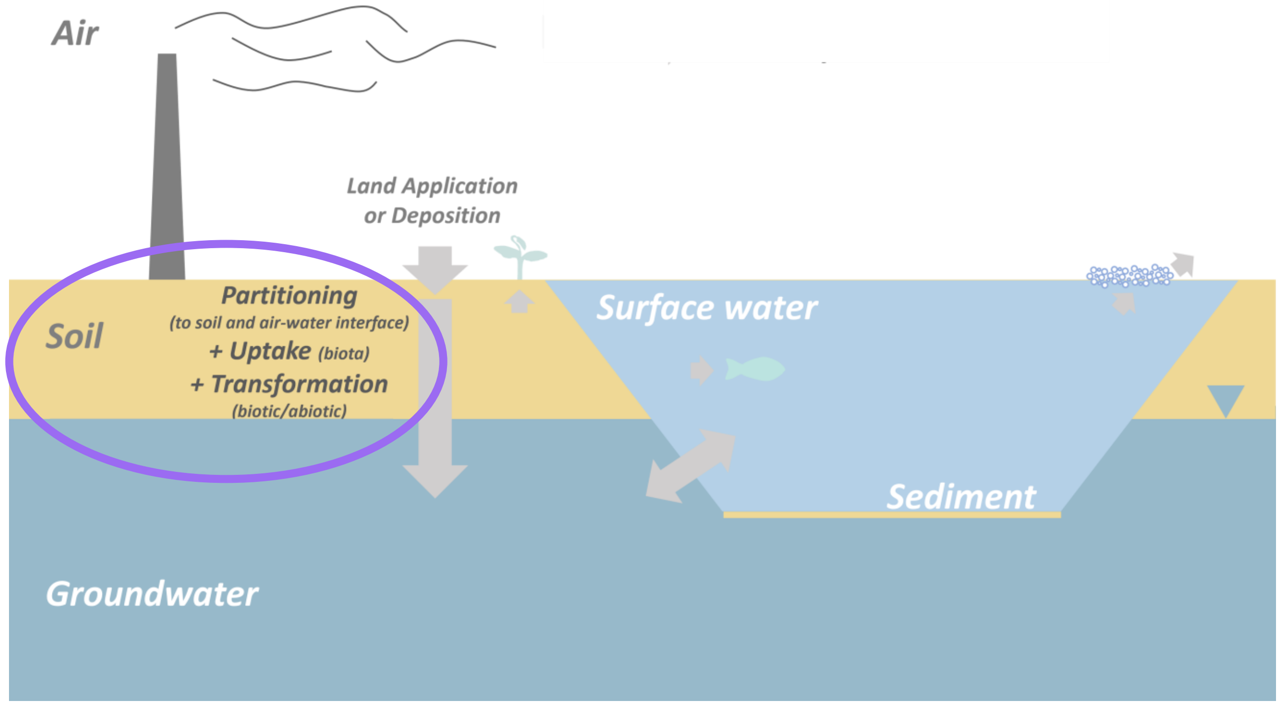
- PFAS sources to air
  - Industrial facilities producing or using PFAS
  - Areas where fluorine foams are used/released
  - Waste management facilities (landfills, WWTPs, biosolids production)
- Fluorotelomer alcohols (FTOHs) and some other PFAS are volatile
- Stack emissions can include volatile PFAS and PFAS attached to particulate matter
- Atmospheric deposition (wet or dry) may result in PFAS contamination several miles from industrial emission sources
- Long-range transport processes and effects are similar to atmospheric transport of other recalcitrant contaminants



PFAS-1, Section 5.2.4, Partitioning to Air and Section 5.3.2 PFAS Transport in Air
PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS.
Source: D. Adamson, GSI. used with permission.

Macroscale Transport: Vadose Zone

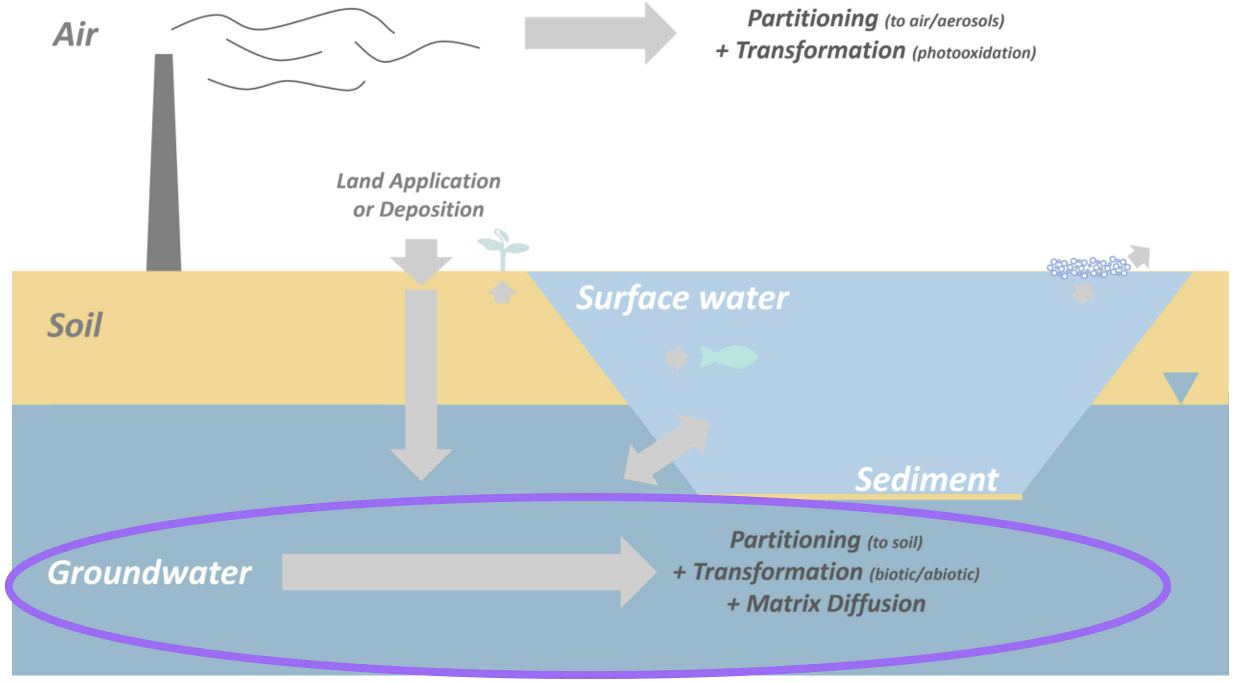
- PFAS source areas: vadose-zone retention may be significant
  - Cationic/zwitterionic precursors may strongly sorb
  - Long-chain PFAA sorption
    - Depends on soil chemistry
  - PFAAs accumulate at air/water interfaces (may retard transport)
- Most PFAS have low volatility (little to no partitioning to vapor phase)
- Leaching may provide long-term source to groundwater



PFAS-1, Figure 5-1, Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Macroscale Transport: Groundwater

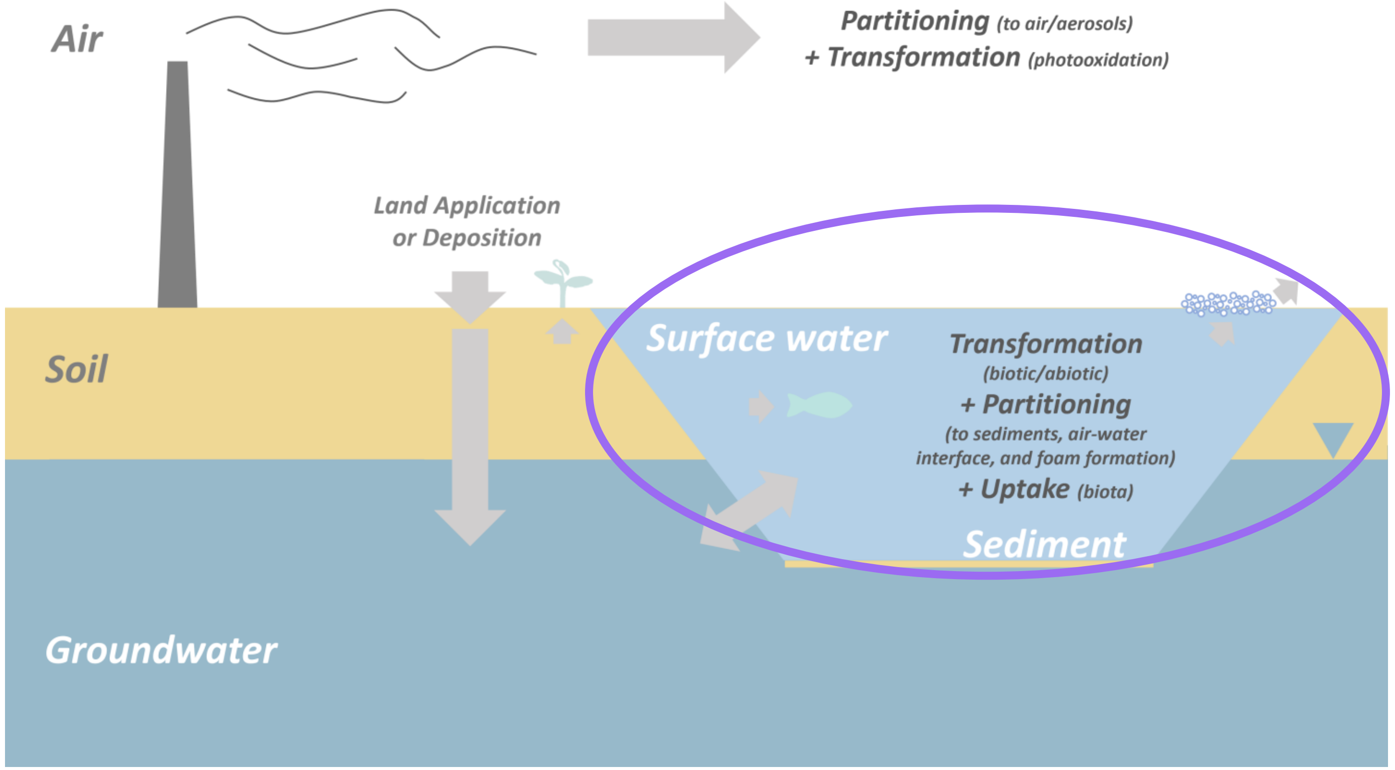
- Readily transported once in groundwater
  - Same processes affecting sorption in vadose zone, but now with groundwater chemistry interactions
  - Dependent on chain length and functional group
  - K_{OC} important, but not sufficient to explain partitioning behavior
- Potential impacts of remedial activities targeting co-contaminants
  - Introduction of oxygen (e.g. air sparge, DO injection) can drive precursor transformation
  - Introduction of cations (e.g., ISCO) can lead to enhanced sorption/retardation of PFAA transport.



PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Macroscale Transport: Surface Water

- Type of water body is important
  - Fast moving, suspended sediments
  - Slow moving, deposition
- Uptake to biota (incl. fish)
- Stratification in water column
- Dissolved PFAS in SW can move downstream, back into GW
- PFAAs aggregate at surface microlayers
  - Foam formation with wind or turbulence



PFAS-1, Section 16.5 Surface Water Foam
PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Transport in Surface Water: Foam

PFAS-Containing Foam Considerations

- **Transport** as “foam islands” to a new location
- Collapse of foam and **dissolution of PFAS** back into water column
- PFAS concentration in foam > water column
- PFAS in foam potentially leads to **additional exposure pathways** – both human and ecological receptors

*Note – foams can be produced by natural processes in the absence of PFAS as well; not all surface water foam is guaranteed to contain PFAS.

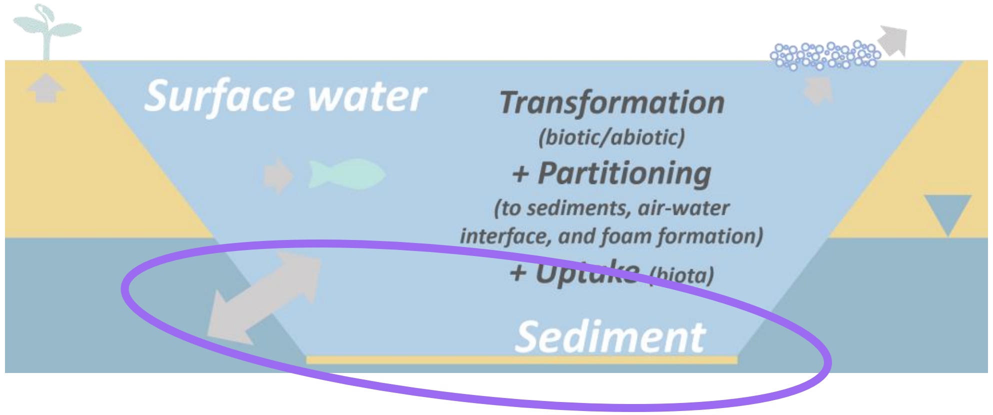
Photographs courtesy of R. Higgins, MPCA. Used with permission.

PFAS-1, Section 16.5, Surface Water Foam

Transport Between Surface Water and Groundwater

Transitions zones between SW and GW tend to have changes in conditions

- Low oxygen GW → oxygen-rich SW
  - Increased microbial activity
  - Increased precursor transformation
  - Increased proportion of PFAAs
- Differences in organic and mineral content between soils and sediments
  - Sorption to sediments and colloids
  - Changes in salinity affect sorption
- Potential for dilution and mixing depending on type of water body



More research needed

PFAS-1, 2023 Section 5.3. New content for groundwater – surface water interaction.
PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission

Co-contaminant considerations

Petroleum co-contamination common at AFFF sites and can occur at other PFAS sites

PFAS may partition into LNAPL or accumulate at water/LNAPL interface

- Can lead to greater retention of PFAS

Petroleum contamination leads to reducing conditions

- Slows down precursor transformation
- Shifts precursor transformation to anaerobic processes/pathways

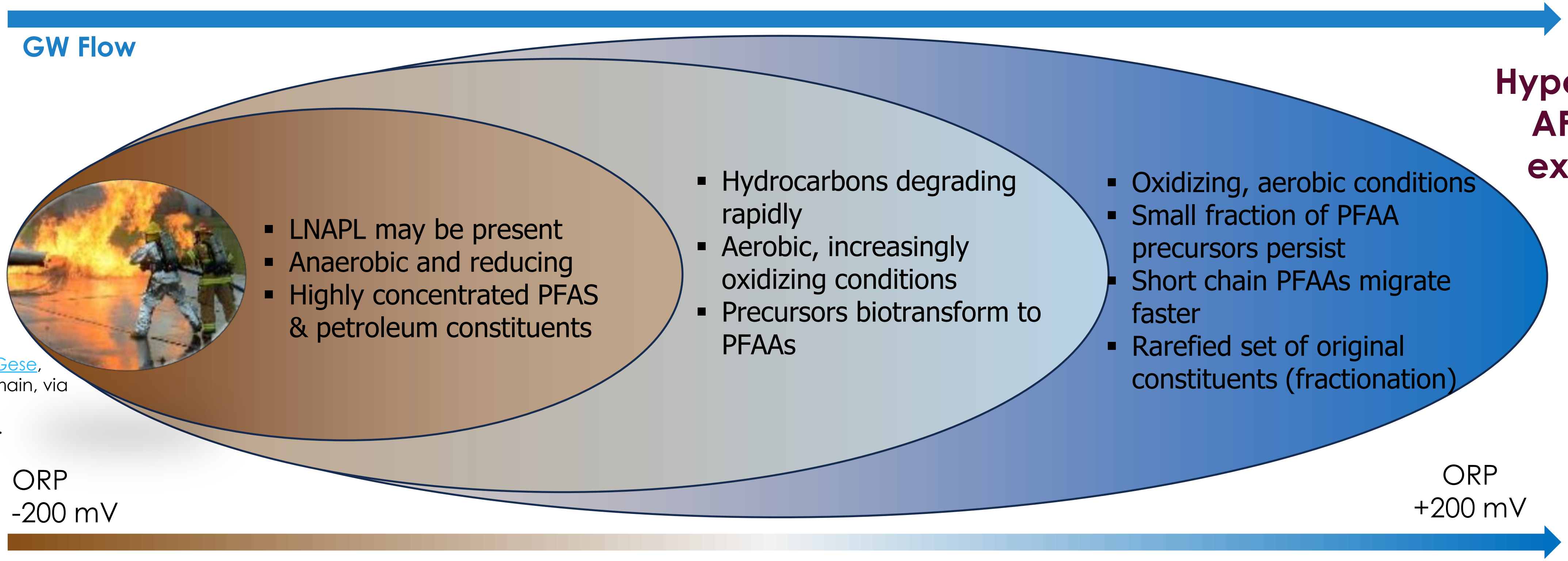
If petroleum remediation has occurred, may alter redox to oxidizing conditions (e.g., air sparge) or change ionic concentrations (e.g., ISCO)

- Can alter rates of precursor transformation

DNAPL co-contamination can also result in increased PFAS retention

Environmental Fractionation

- Differential transport and precursor transformation lead to environmental fractionation
- As PFAS move downgradient from source area, composition of PFAS changes
- Source type and hydrogeochemical parameters influence type and rates of change



GW Flow

Hypothetical AFFF site example

- LNAPL may be present
- Anaerobic and reducing
- Highly concentrated PFAS & petroleum constituents

- Hydrocarbons degrading rapidly
- Aerobic, increasingly oxidizing conditions
- Precursors biotransform to PFAAs

- Oxidizing, aerobic conditions
- Small fraction of PFAA precursors persist
- Short chain PFAAs migrate faster
- Rarefied set of original constituents (fractionation)

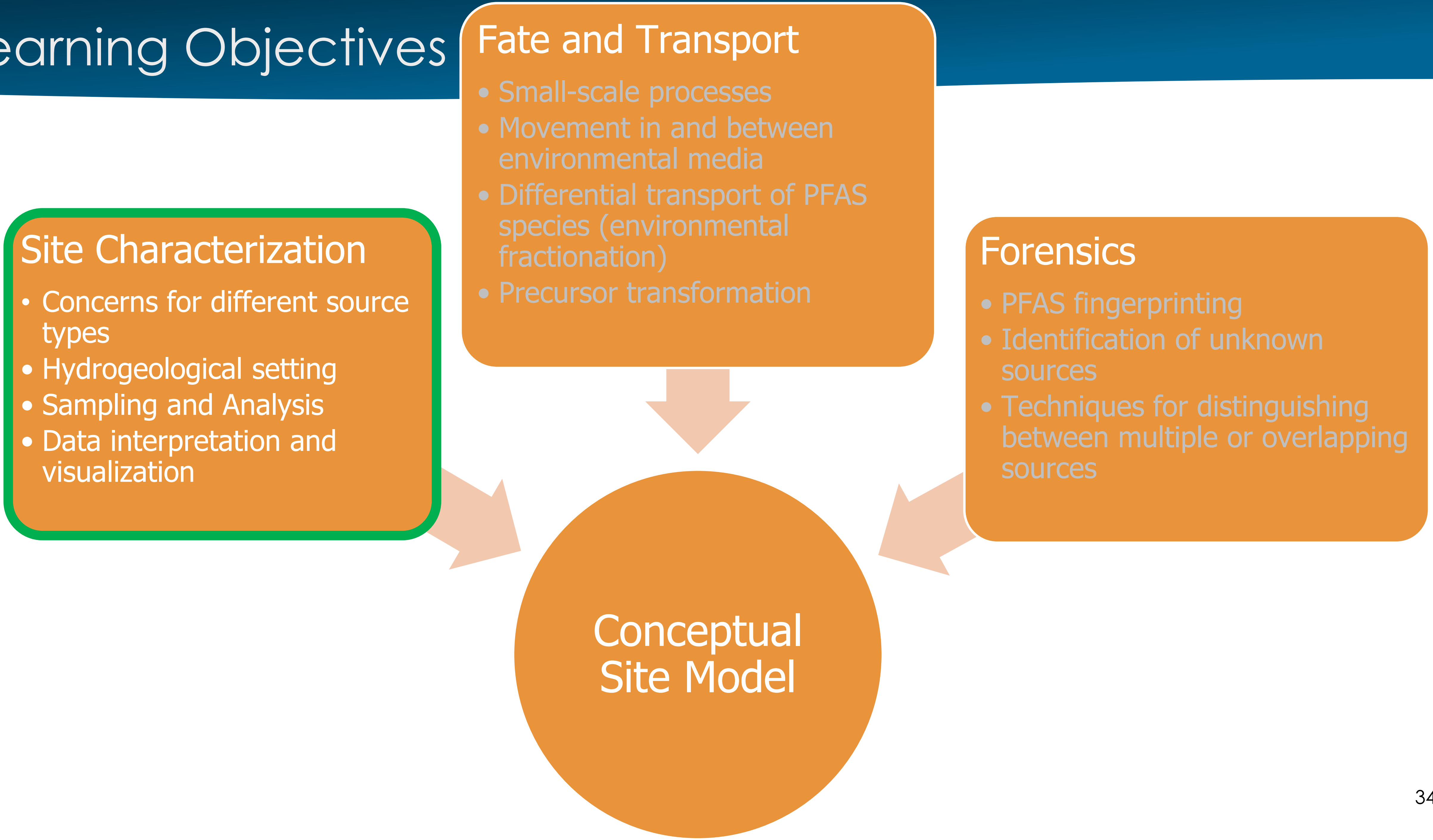
ORP
-200 mV

ORP
+200 mV

A1C Kyle Gese, Public domain, via Wikimedia Commons.

Site Characterization

Learning Objectives



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- PFAS fingerprinting
- Identification of unknown sources
- Techniques for distinguishing between multiple or overlapping sources

Conceptual Site Model

Work Plan and Conceptual Site Model (CSM)

Initial step in Site Characterization is CSM development to inform Data Quality Objectives

CSM development should consider:

- Site characteristics
- Properties of contaminants

Use CSM to identify data gaps and sampling needs

PFAS-1, Section 10.2 Initial Steps.

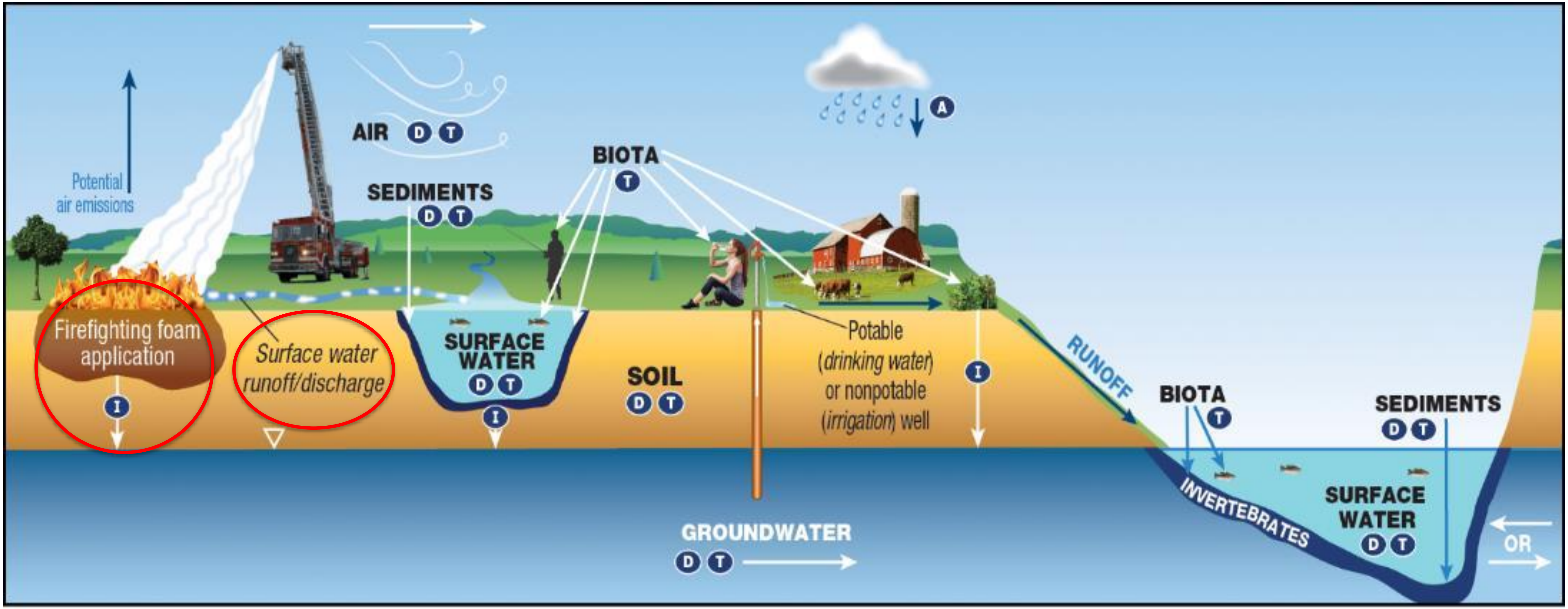
Main Sources of PFAS Release to the Environment

*Industrial sites include primary and secondary manufacturing

For additional information on biosolids, please see "*Biosolids: Sources, Transport, and Management of PFAS Surface Releases*"

PFAS-1, Section 2.6 Releases to the Environment.

Fire Training & Response Sites

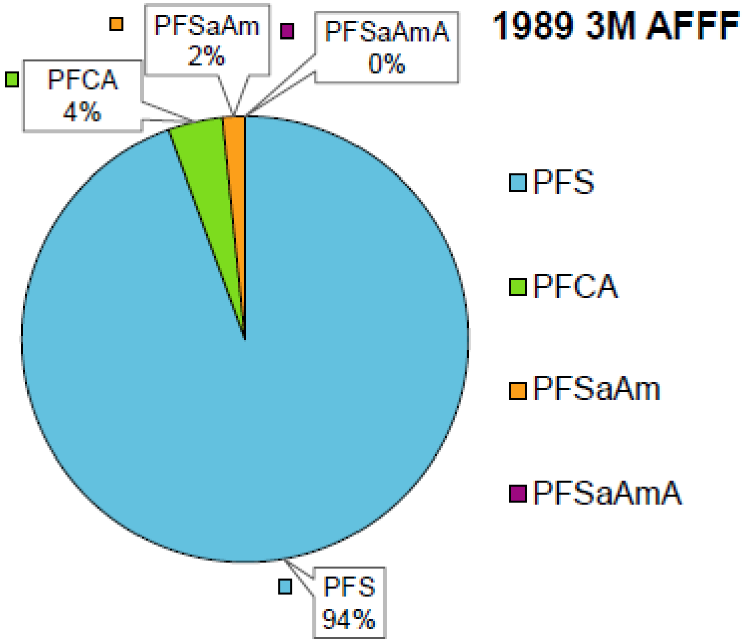


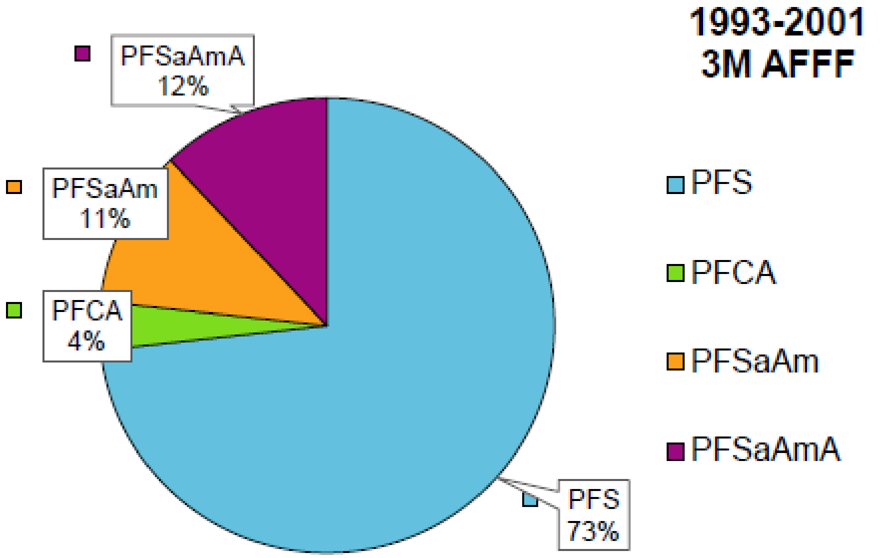
KEY Ⓐ Atmospheric Deposition Ⓓ Diffusion/Dispersion/Advection Ⓘ Infiltration Ⓣ Transformation of precursors (abiotic/biotic)

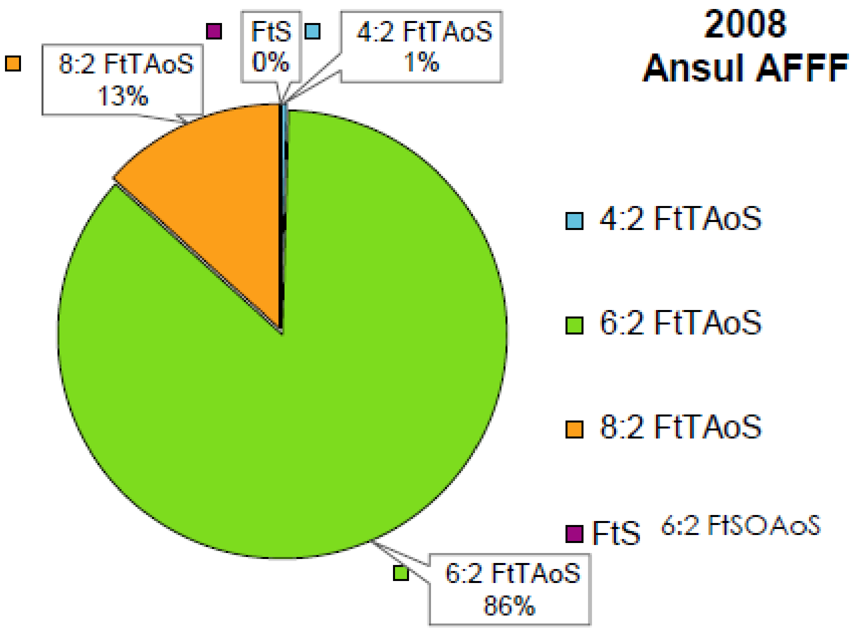
PFAS-1, Figure 2-19, CSM for fire training areas. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

AFFF Contains Highly Diverse Mixtures

AFFF product chemistry has changed over time







Electrochemical Fluorination

Fluorotelomerization

Table 3-1 of the ITRC PFAS Technical Regulatory Guidance document presents types of foam and composition.

Barzen-Hanson et. Al 2017. Environ Sci Tecnol 51: 2047-2057
Figures used with permission from J. Field, Oregon State.

Forensic Analysis of PFAS from AFFF Sources

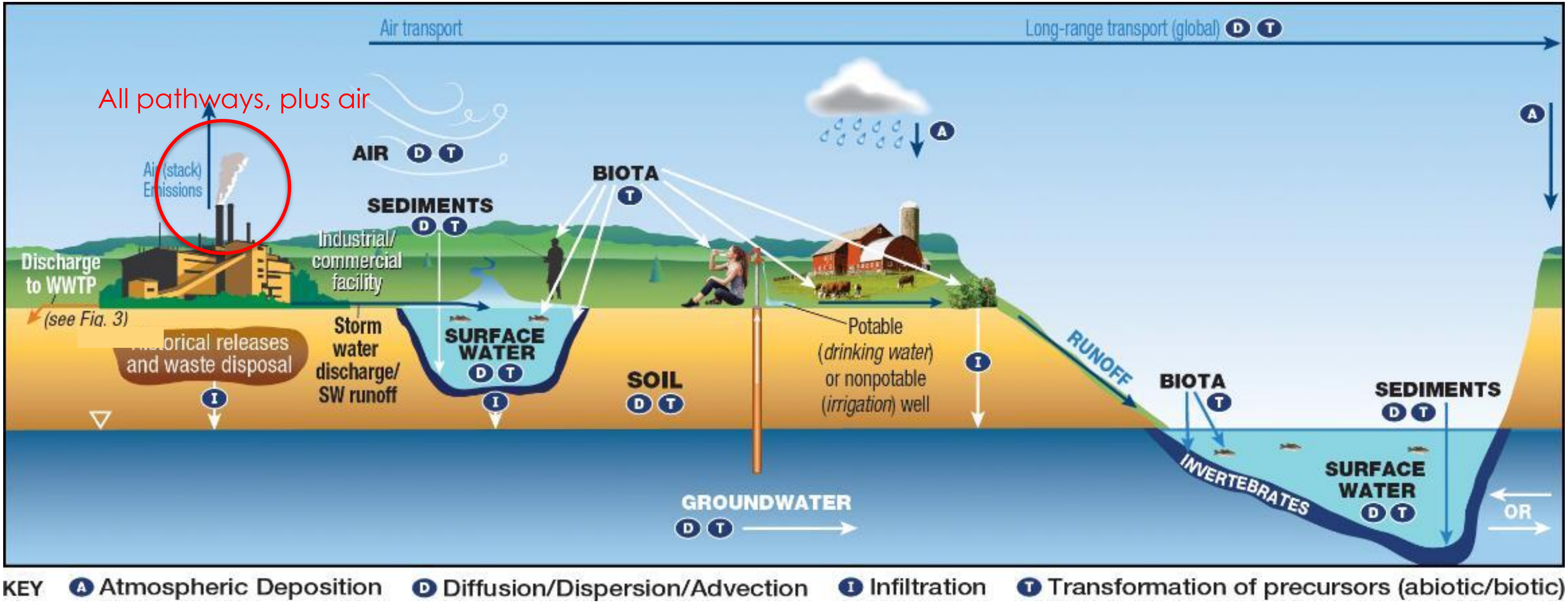
Forensic analysis of AFFF is based on fingerprinting the composition of unknown samples

Multiple lines of evidence and methods should be considered for site-specific fingerprinting:

- AFFF use history
- AFFF manufacturing processes
- Targeted PFAS analysis, TOP analysis for precursor transformation, and TOF analysis
- The effects AFFF source commingling and co-contaminants on fate and transport behavior

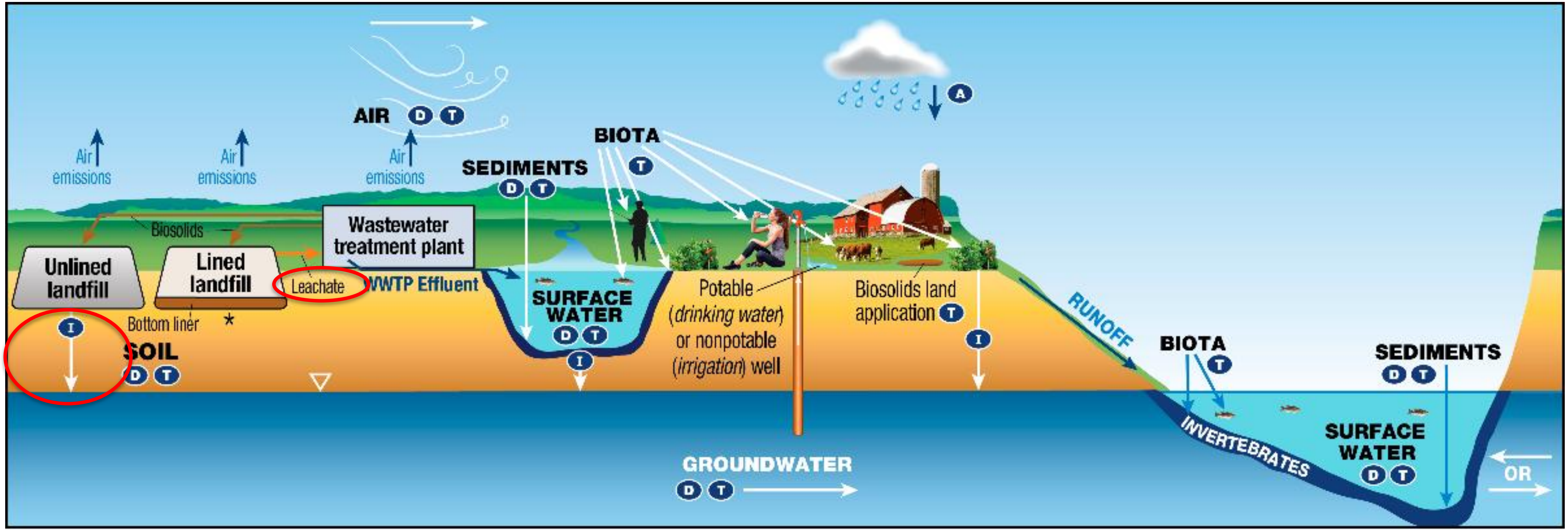
PFAS-1, Section 3.5 Forensic Analysis of AFFF.

Industrial Sites


All pathways, plus air

PFAS-1, Figure 2-18, CSM for industrial sites. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

Landfills and WWTPs



*Leachate release from lined landfills could occur in the event of a liner leak

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

PFAS-1, Figure 2-20, CSM for landfills and WWTPs. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

Source-specific considerations

AFFF

- Diverse mix of PFAS
- Manufacturing methods determine PFAS composition
- Fate and Transport affected by co-contaminants and historical remediation

Industrial

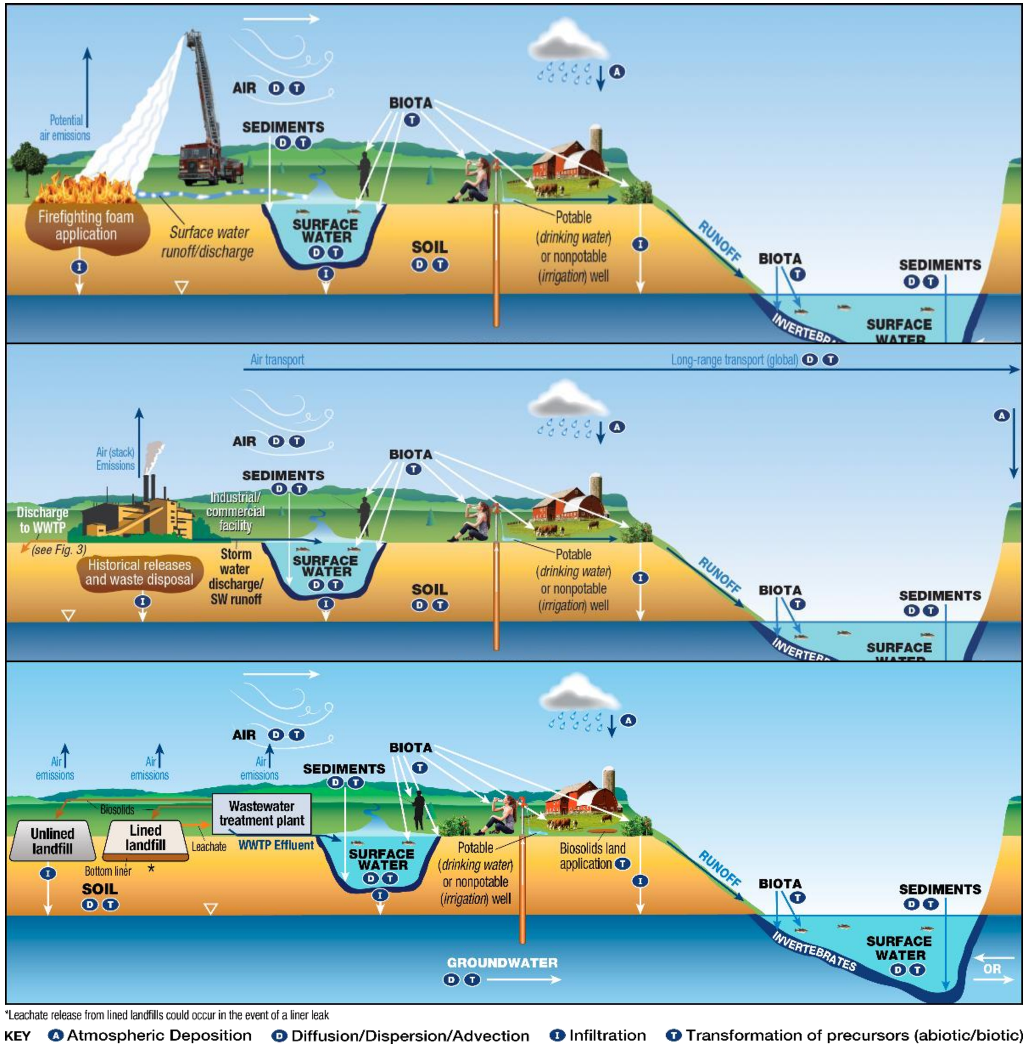
- PFAS mixture may be less diverse
- Site-specific process determines PFAS composition
- Air transport may be important (may cause diffuse soil sources from deposition)

Landfill

- 5:3 FTCA as "signature compound"
- May include volatile PFAS (FTOHs and PFBA; possible short-range deposition)
- Types of waste accepted determine PFAS composition and concentration

WWTP & Biosolids

- Short chains and terminal products may dominate (not always)
- Types of waste accepted AND treatment process determine PFAS mix



*Leachate release from lined landfills could occur in the event of a liner leak

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

PFAS-1, Section 2.6 Releases to the Environment.

Site Characterization: General Considerations

Conceptual Site Model

Review existing data and information

Site history, PFAS use/types, release locations, mixtures released, co-contaminants

Nature and location of potential receptors

Hydrogeologic setting

- Topography/Drainage
- Soil type
- Depth to water
- Nature of aquifer system & characteristics – unconfined/confined; permeability, porosity, velocity
- Nature of GW discharge – seeps, tributaries, rivers, lakes, supply wells

Surface Water

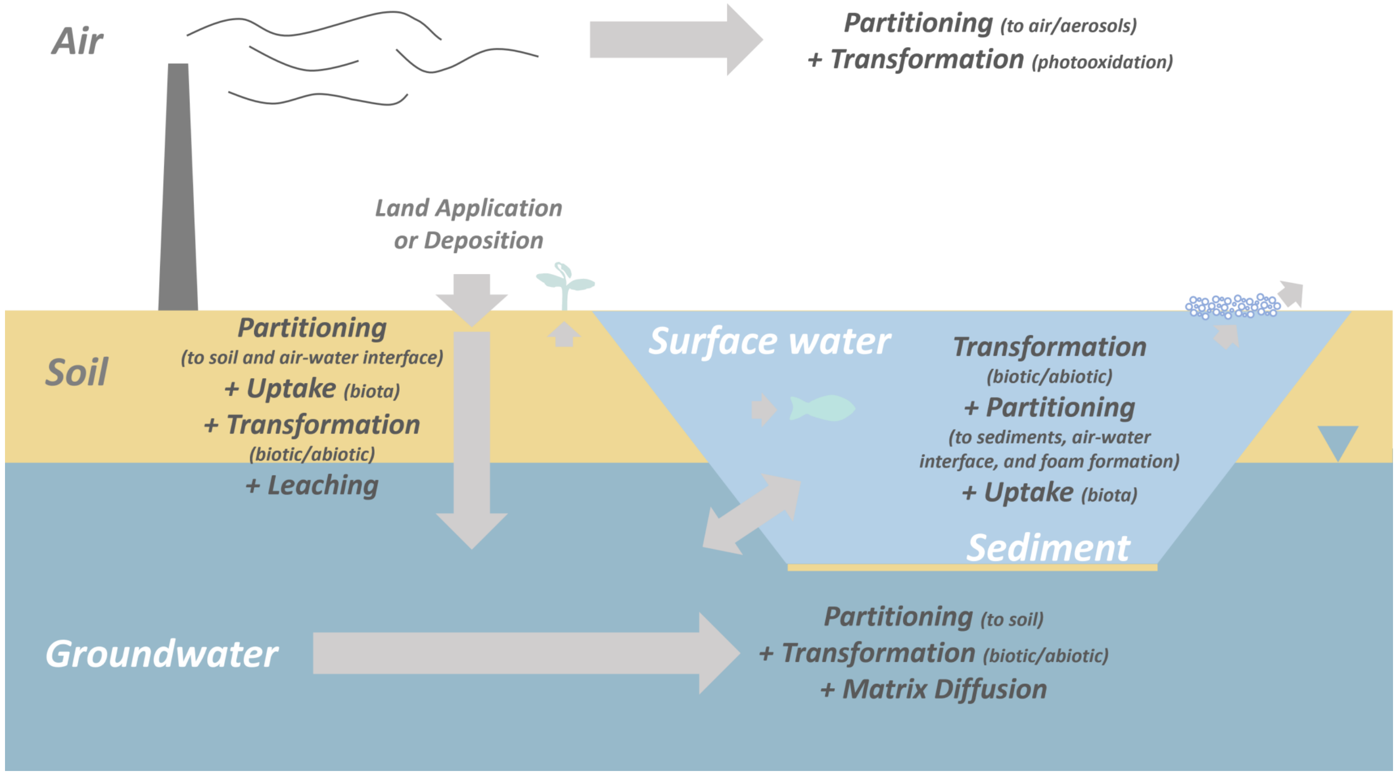
Relevant regulations, permits, standards

PFAS-1, Section 10 Site Characterization.

Site Characterization: General Considerations

Transport Pathways

- Release to GW
  - Vadose Zone – Depth to water; soil type (sands vs. clays; clay layering); organic carbon content; pH; ion exchange capacity
  - Air-Water Interface – Grain size; moisture content
  - GW System – Soil type; pH; TDS/salts/divalent cations, co-contaminants; confining units
- Release to SW
  - GW discharge
  - Storm runoff



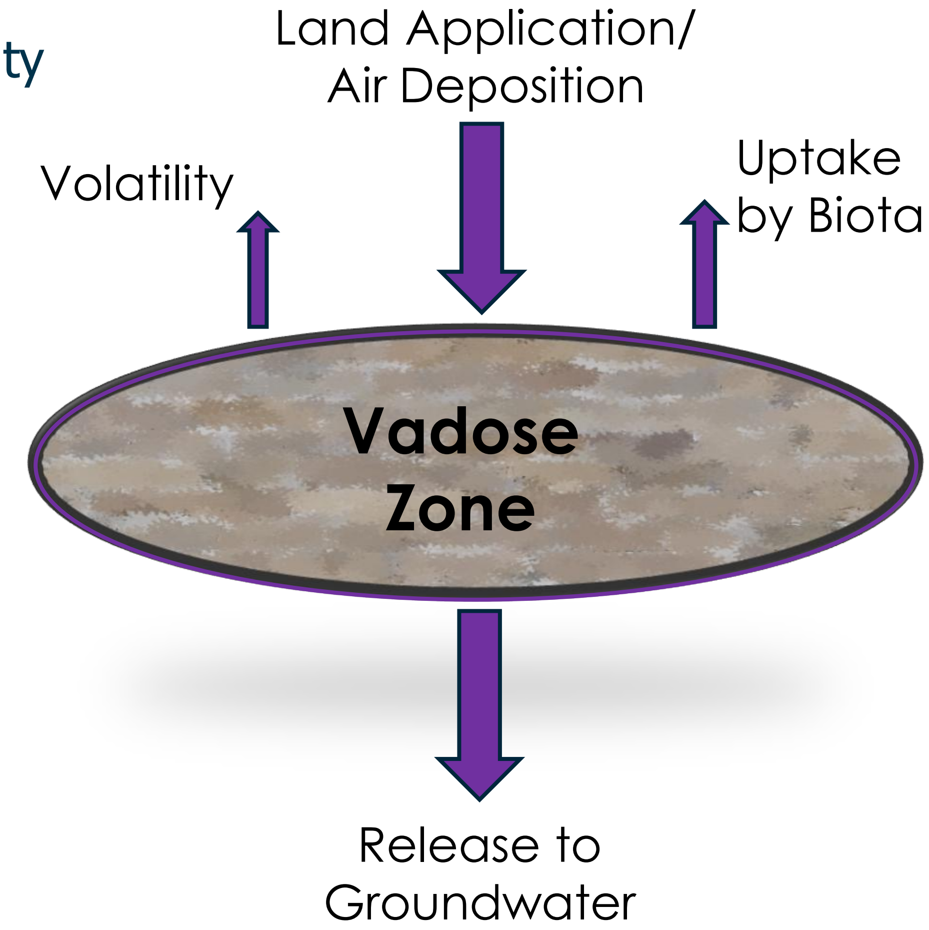
PFAS-1, Section 5.3. New content for groundwater – surface water interaction.
PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission

What to Analyze

VADOSE ZONE

- Soil type/particle size/porosity
- Moisture content
- Cation Exchange Capacity (CEC)
- Surface charge
- Multivalent cations
- Soil pH
- Organic Carbon
- Depth to GW

* Focus on air-water interface and clay lenses and layers



SATURATED GROUNDWATER SYSTEM

- pH, TDS, salts, turbidity, multivalent cations, co-contaminants
- GW gradient and velocity
- Depth to basement (unconfined vs confined conditions)
- Presence and depth to fractured rock, if applicable

* Focus on potential influences to GW movement (nearby pumping wells, GW-SW interactions, etc)

PFAS-1, Section 10.3.1 Development of Site Investigation Work Plan.

Potential for PFAS Sample Contamination

Some supplies and equipment may contain PFAS

Analyzing at extremely low detection limits

Collect equipment rinseate and other QC samples

- Waterproof coatings containing PFAS
- Fluorinated ethylene-propylene (FEP)
- Low-density polyethylene (LDPE)
- Polyvinylidene fluoride (PVDF)
- Polytetrafluoroethylene (PTFE)
- Pipe thread compounds and tape

PFAS-1, Section 11.1.2 Equipment and Supplies.

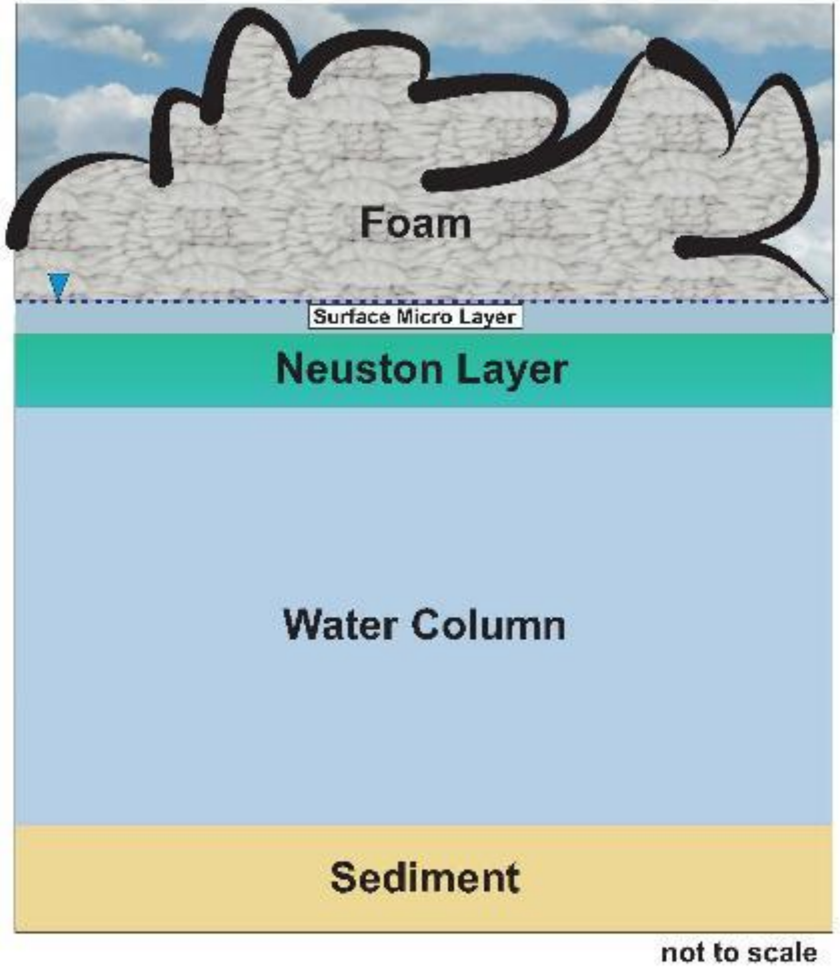
PFAS-Containing Foam – Four Layers

Foam – contains higher concentrations of PFAS than the underlying layers; as foam is formed, it removes PFAS from the water column.

Surface micro layer – about 50 µm thick - includes the air-water interface. Likely highest concentration of PFAS in water column

Neuston Layer – zone directly below surface micro layer. Rich in aquatic organisms

Underlying water column



PFAS-1, Section 16.5 Figure 16-2 PFAS foam on surface water.

Analytical Method Differences

Method	Sample Preparation	Quantitation Scheme	Evaluation of Transition Ion Required?	# PFAS Analytes	Quantitation Limits (analyte dependent)
EPA Method 537.1	SPE	Internal Standard	No	18	0.53 to 6.3 ng/L
EPA Method 533	SPE	**Isotope Dilution**/EIS	No	25	1.4 to 13 ng/L
SW-846 8327	Solvent Dilution	External Standard	Yes	24	
DoD AFFF01	SPE	**Isotope Dilution**	Yes	2 PFOA/PFOS	
EPA 1633-Aqueous	SPE	**Isotope Dilution**/EIS	Yes	40	Landfill leachate: 10-250 ng/L Other: 2-50 ng/L
EPA 1633-Solid	Solvent Extraction	**Isotope Dilution**/EIS	Yes	40	Soil/Sediment: 0.2-5 ug/kg Biosolids: 2-50 ug/kg Tissue: 0.5-12.5 ug/kg

SPE = Solid Phase Extraction
EIS = Extracted Internal Standard
LC/MS/MS = Liquid Chromatography/Dual Mass Spectrometry
ng/L = nanograms per liter (ppt)
ug/kg = micrograms per kilogram (ppb)

All use LC/MS/MS

PFAS-1, Section 11.2.1.3 Sample Analysis and Table 11-3.

TOP Assay (qualitative)

Analysis of PFAS using EPA 1633 can significantly underestimate PFAS mass

Total Oxidizable Precursor (TOP) Assay

Analyze sample normally and then after oxidation

Total precursors = $\text{PFAS}_{\text{treated}} - \text{PFAS}_{\text{untreated}}$

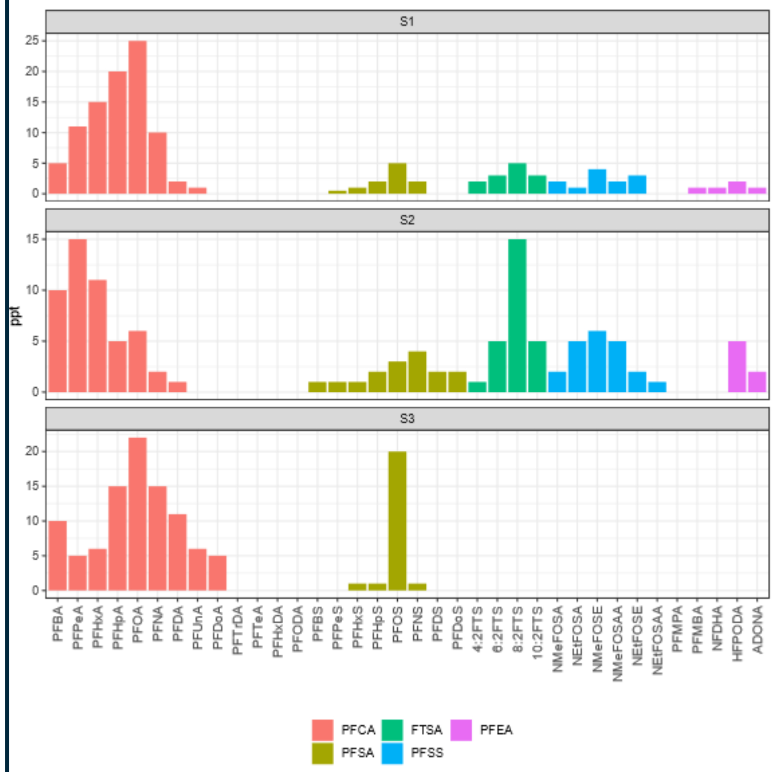
Reporting Limits: same as EPA 1633 (~2 ng/L)

- Estimate concentrations of oxidizable precursors in sample.
- Precursors can transform to measurable PFAAs. TOP Assay oxidation forces transformation.
- Predominant precursor transformation products are perfluorocarboxylic acids (PFCAs).
- Increased concentrations of PFCAs after oxidation provide estimate of oxidizable precursors.
- Potential low biases:
  - Incomplete oxidation
  - Lack of quantification of PFCAs < C4

PFAS-1, Section 11.2.2.2 TOP Assay

Data Visualization: PFAS Chemical Profiles

Many different methods to visualize PFAS profiles (all based on the same data)

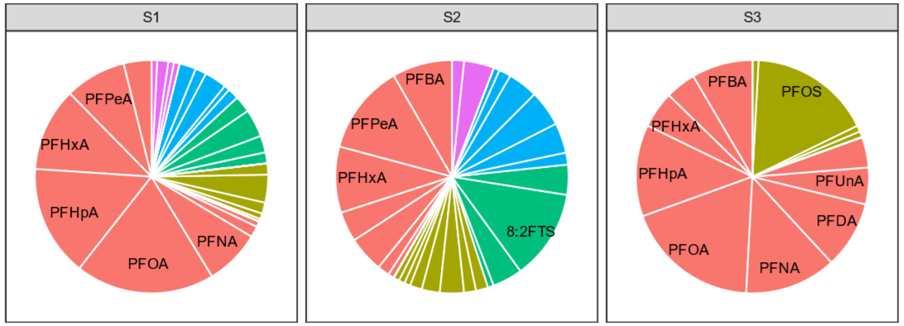


Bar Charts

- Grouped by PFAS class and ordered by MW
- Y-axis allows consideration of concentrations
- Can get cluttered with many samples

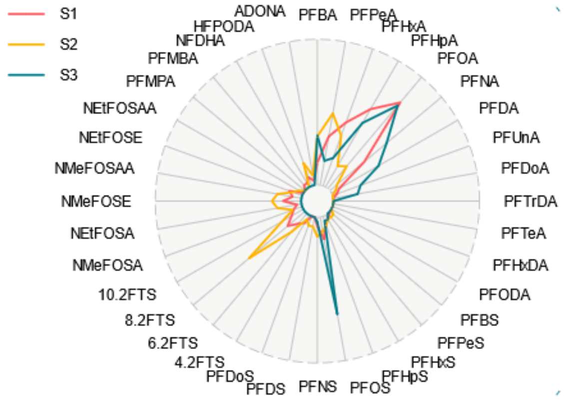
Pie Charts

- Grouped by PFAS class and ordered by MW
- Limited space to label compounds with large compound list
- Can be difficult to compare samples
- Easier to interpret with 10 or fewer compounds



Radar/Spider Charts

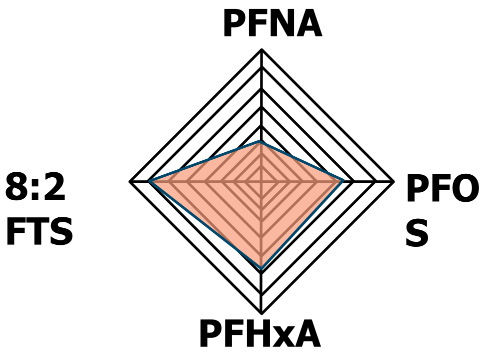
- Ordered by PFAS class ordered by MW
- Limited space to label compounds with a large compound list
- Easy to compare 3-5 samples, gets cluttered with more samples in a single plot
- Easier to interpret with 10 or fewer compounds

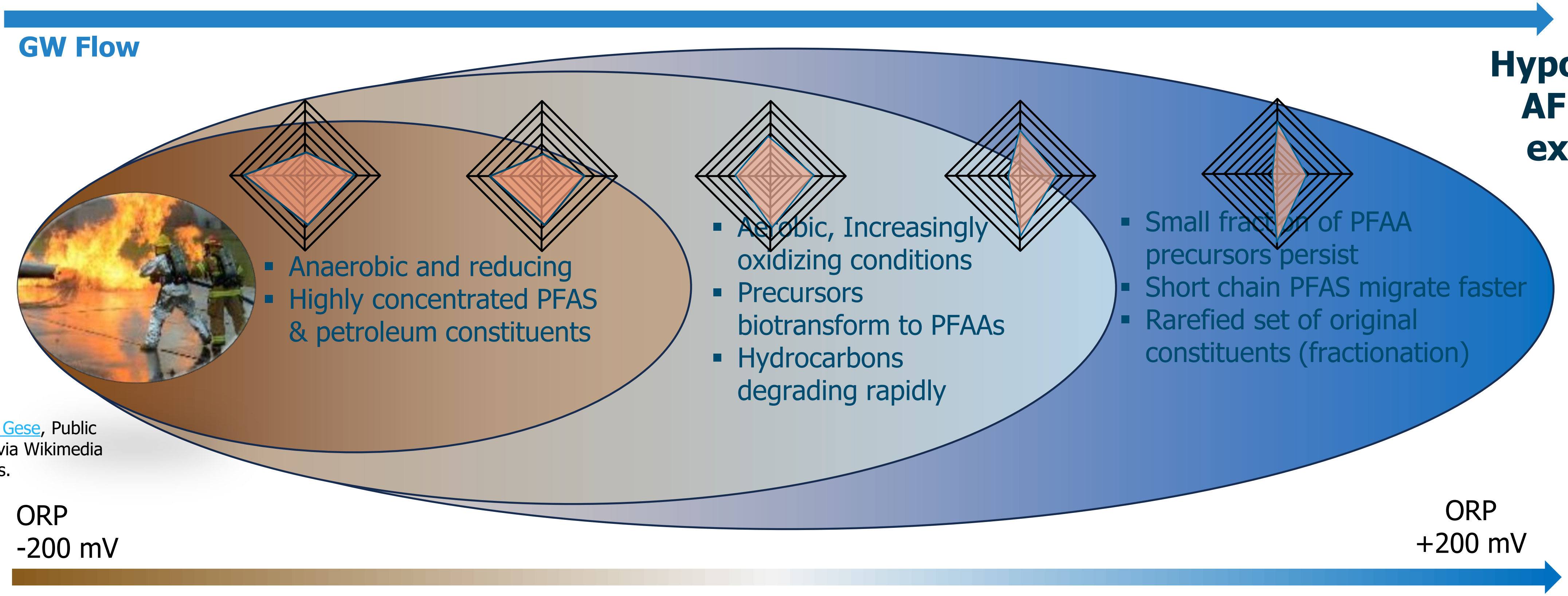


Bar Chart figures adapted from PFAS-1 Figure 10-2. Source M. Benotti, NewFields. Used with permission. Figures source: Michael Bock, Verdantas. Used with permission.

Data Visualization: Spatial Coordinates

- Chemical data visualization enhanced when placed in spatial context.
- Hypothetical example below shows subset of four PFAS.
- Downgradient pattern changes clearer when shown on a map of the plume.





- Anaerobic and reducing
- Highly concentrated PFAS & petroleum constituents

- Aerobic, Increasingly oxidizing conditions
- Precursors biotransform to PFAAs
- Hydrocarbons degrading rapidly

- Small fraction of PFAA precursors persist
- Short chain PFAS migrate faster
- Rarefied set of original constituents (fractionation)

Hypothetical AFFF site example

A1C Kyle Gese, Public domain, via Wikimedia Commons.

Visual Representations of Data: Case Study 1

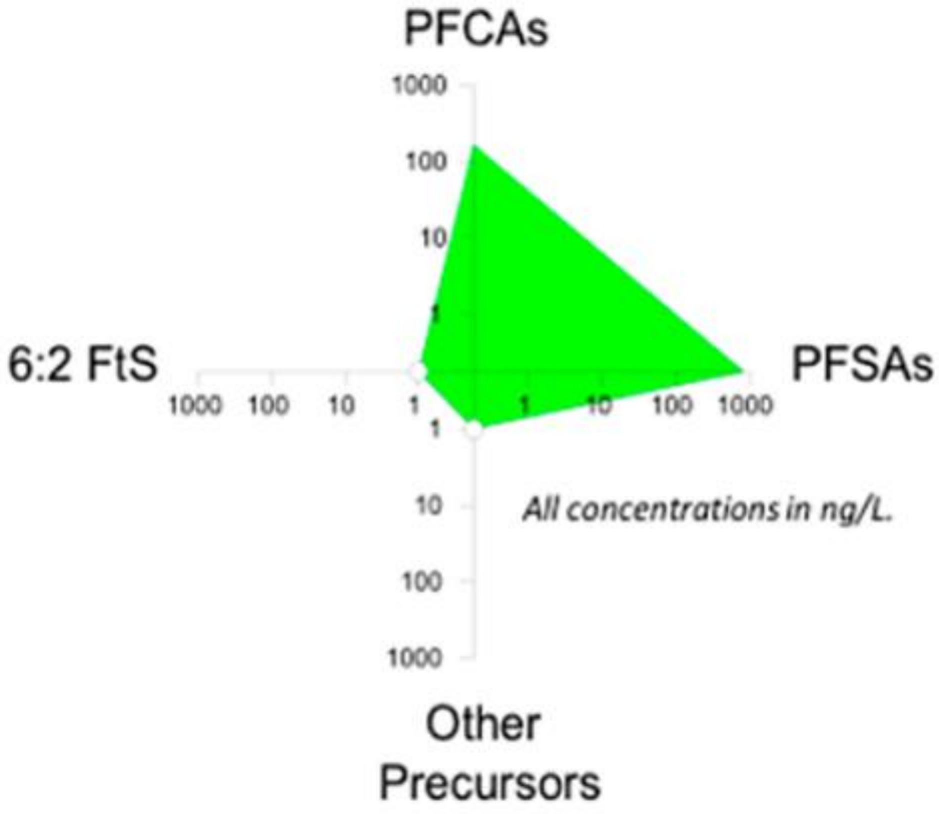
Example is from a site in Sweden where multiple fire training areas impacted groundwater

Rather than percent abundance, axes display a log-based 10 scale

Total PFCAs and PFSAs shown instead of individual compounds, to identify general group patterns

6:2 FTS differentiated from other precursors due to site-specific considerations

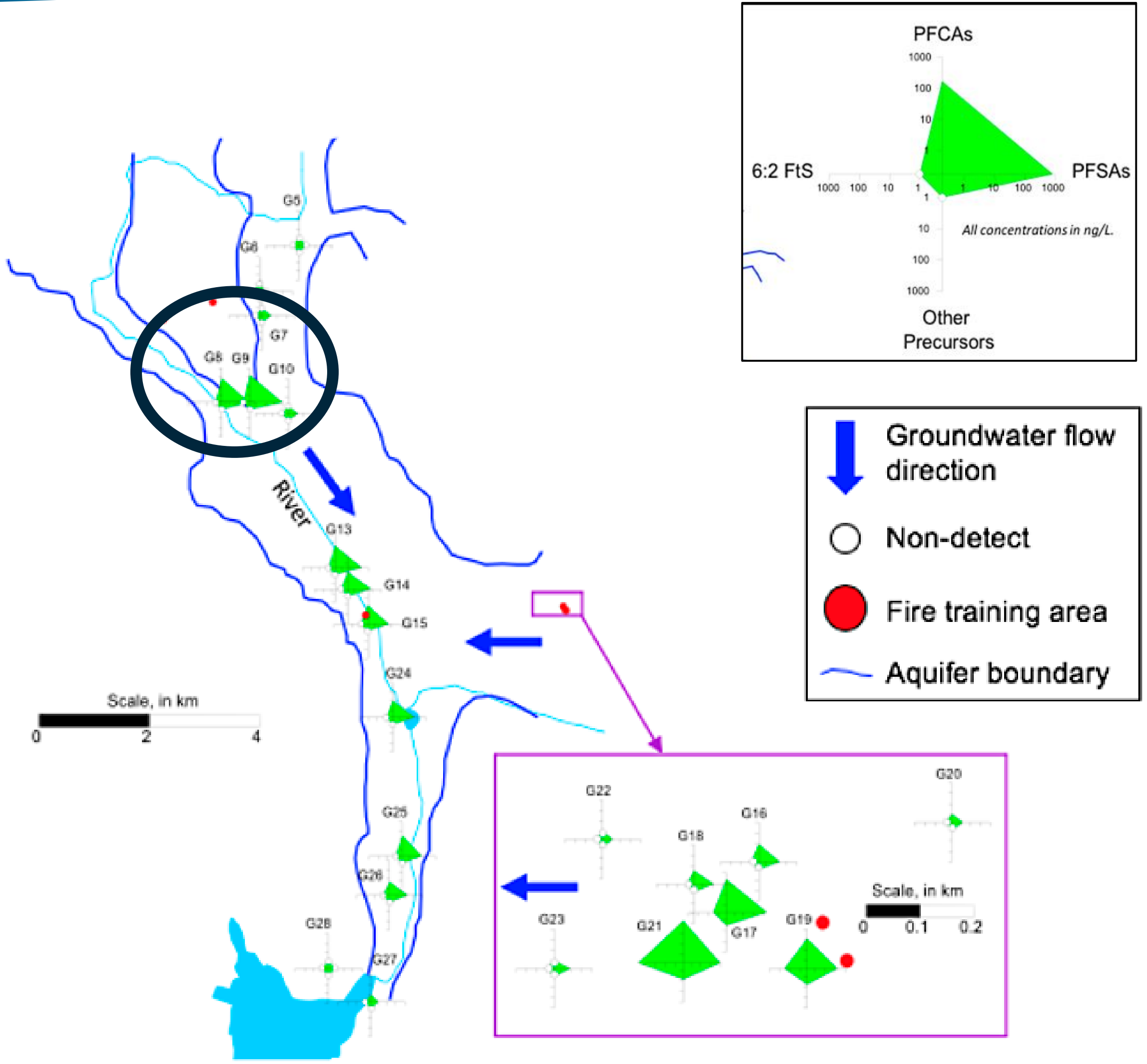
Patterns in shape pertain to precursors vs. PFCA/PFSA relationships



PFAS-1, Figure 15-3. PFAS composition in groundwater. Source: G. Carey, Porewater Solutions. Used with permission.

Data Visualization: Case Study 1

- All chemical-specific precursors non-detect in main aquifer channel, attenuated near fire training areas.
- PFSA and PFCA concentrations decline along the main flow channel (for example, downgradient of G8 and G9).
- Concentrations of precursors in the vicinity of the fire training areas shown in the inset map are much higher than in the main groundwater flow channel.
  - Sorption
  - Biotransformation of 6:2 FTS and other precursors
  - Possibly groundwater – surface water interactions
- Elevated PFCAs, PFSAs, and 6:2 FtS near at least two fire training areas: AFFFs produced using telomerization used at one point.



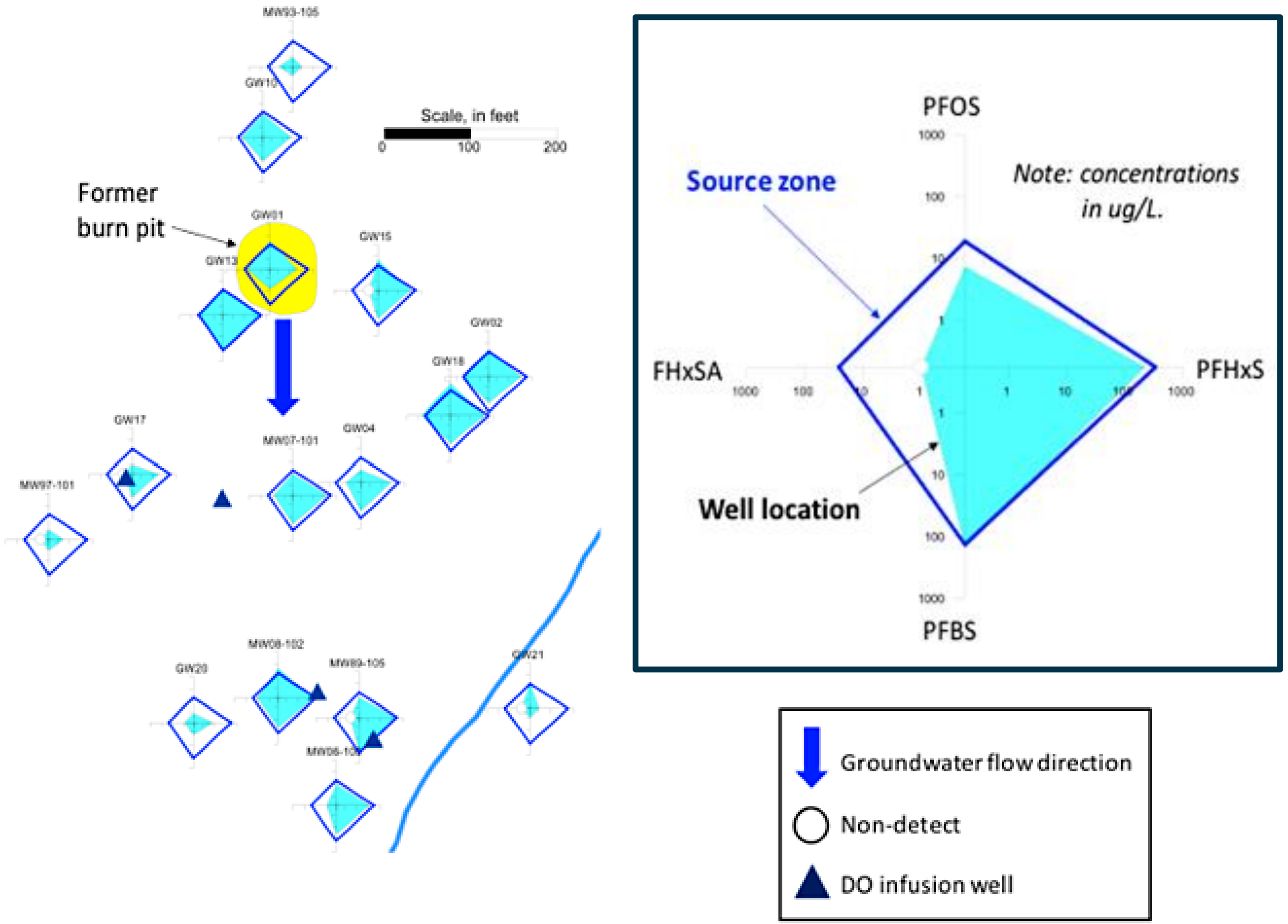
PFAS-1, Figure 15-3. PFAS composition in groundwater.
Source: G. Carey, Porewater Solutions. Used with permission.

Data Visualization: Case Study 2

- Comparison of source zone concentrations (dark blue outline) vs. downgradient samples (light blue fill) show changes due to
    - Migration
    - Dissolved Oxygen infusion wells

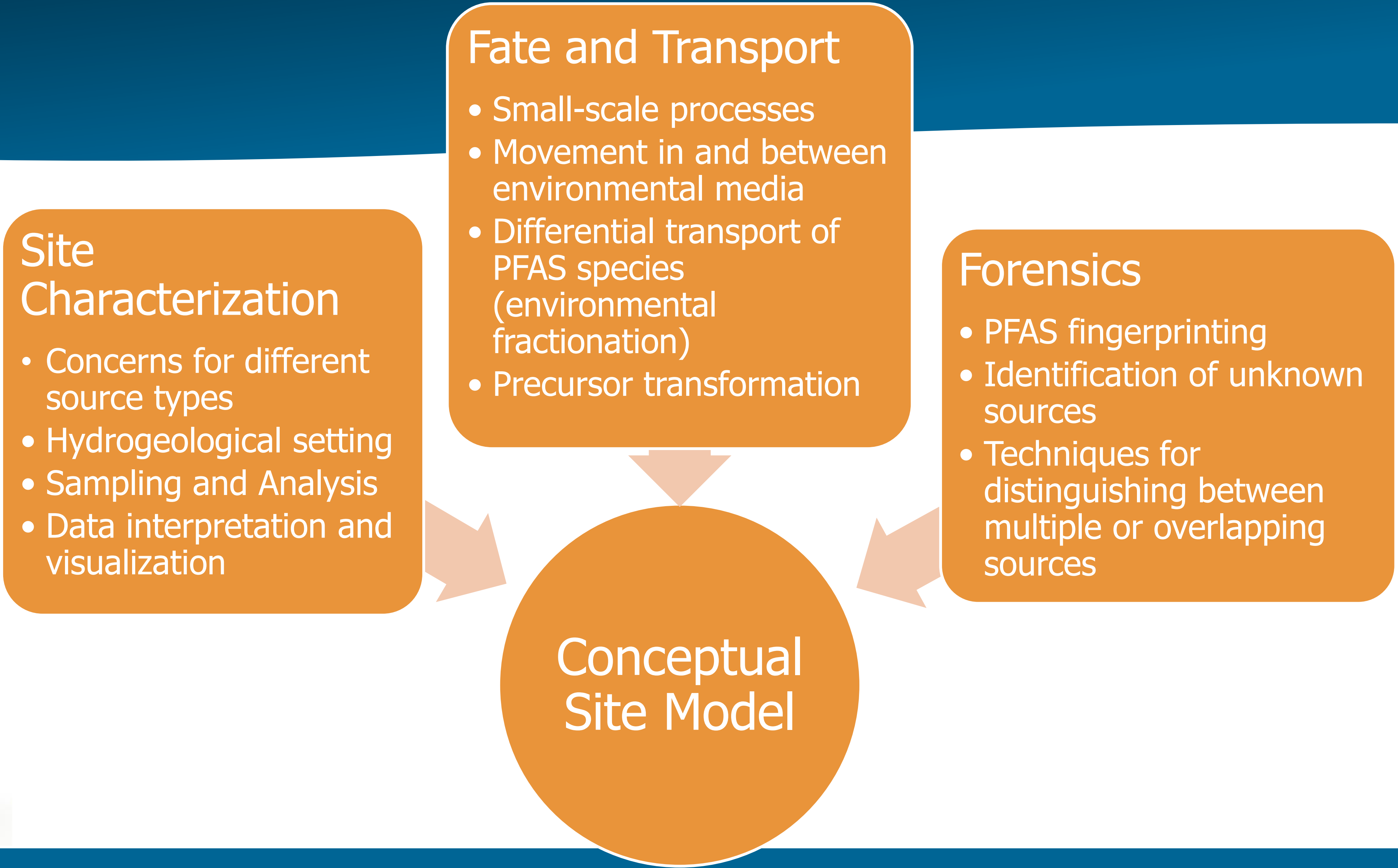
- Introduction of oxygen → transformation of precursor compound FHxSA.

- Some differential transport of short and long chains.



PFAS-1, Figure 15-2. Radial diagrams illustrating PFSA trends at an AFFF release site. Source: G. Carey, Porewater Solutions. Used with permission.

Questions



Fate and Transport

- Small-scale processes
- Movement in and between environmental media
- Differential transport of PFAS species (environmental fractionation)
- Precursor transformation

Site Characterization

- Concerns for different source types
- Hydrogeological setting
- Sampling and Analysis
- Data interpretation and visualization

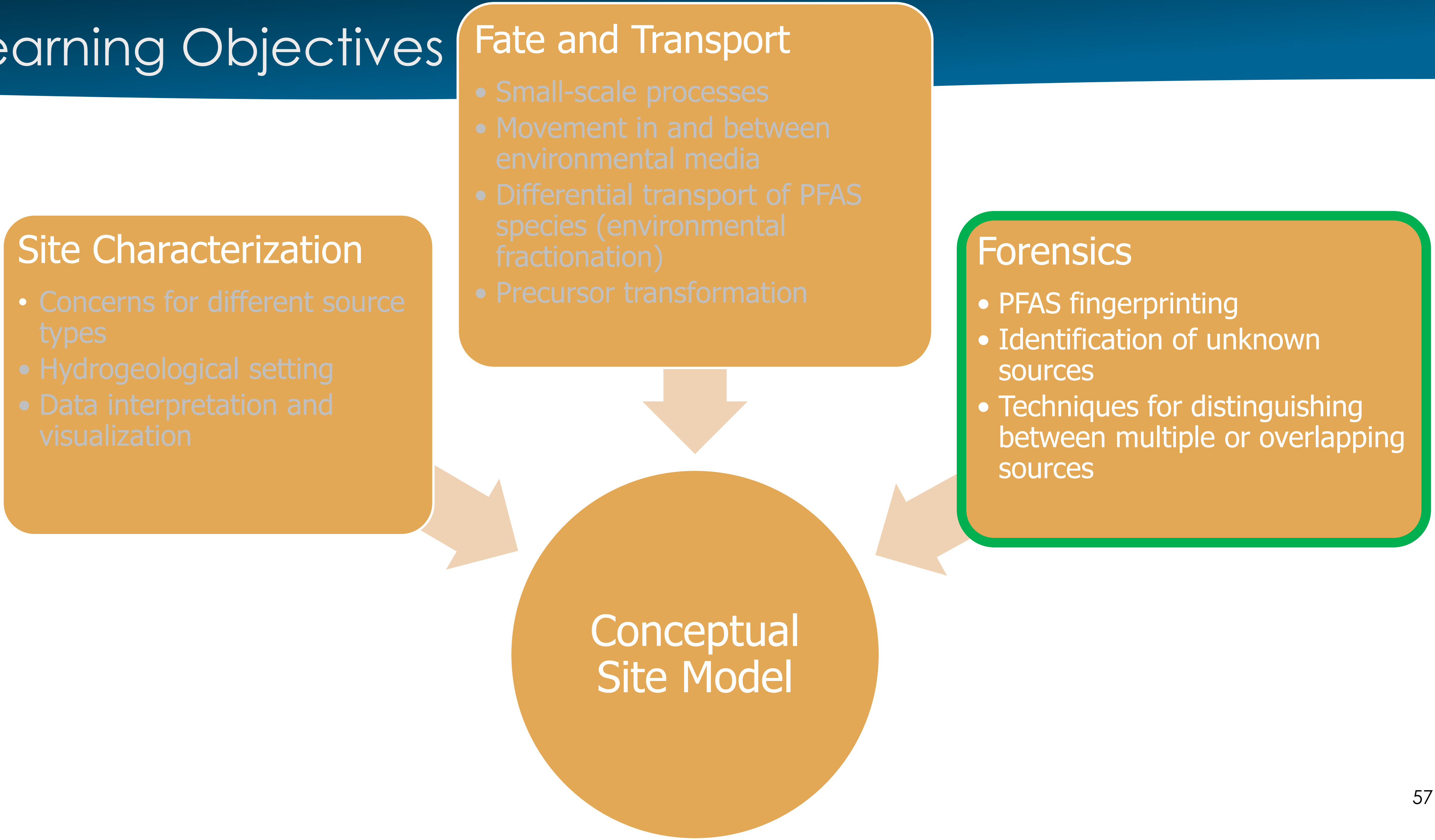
Forensics

- PFAS fingerprinting
- Identification of unknown sources
- Techniques for distinguishing between multiple or overlapping sources

Conceptual Site Model

Understanding PFAS Sources

Learning Objectives



Fate and Transport

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Site Characterization

- Concerns for different source types
- Hydrogeological setting
- Data interpretation and visualization

Forensics

- PFAS fingerprinting
- Identification of unknown sources
- Techniques for distinguishing between multiple or overlapping sources

Conceptual Site Model

What is Environmental Forensics?

Environmental forensics is the application of the scientific method to answer questions about contamination events and their origin.

Link contamination to a source

Distinguish between multiple sources

Estimate the contribution from multiple individual sources to overlapping plumes

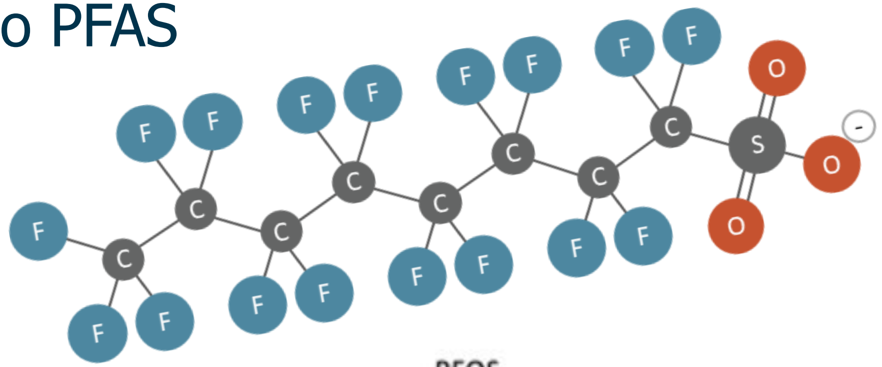
Evaluate effects of remediation or natural attenuation

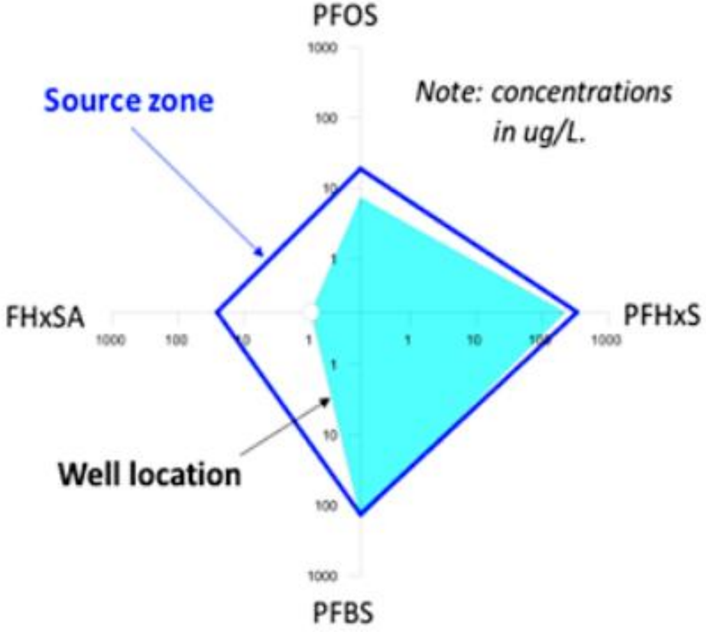
Predict or model site-specific fate and transport of contaminants

PFAS-1, Section 10.5 Source Identification.

PFAS Forensics Applications

- PFAS Forensics: application of environmental forensics to PFAS
  - Arguably in its nascent stages
- Applications so far include:
  - Source identification
  - Differentiation of overlapping sources
  - Evaluation of environmental fractionation
  - Identifying the types of AFFF used at a site
  - Identifying transport-related signatures
- Setting and history are very important





PFAS-1, Figure 15-2 Radial diagrams illustrating PFSA trends at an AFFF release site. Source: G. Carey, Porewater Solutions. Used with permission.
PFAS Figure Source: M. Olson, Trihydro. Used with permission.

Source Identification and Differentiation

Source Identification: process of finding or identifying a source of contamination.

- Often applied when contamination is discovered without prior knowledge of source

Forensic methods can also be applied to source differentiation

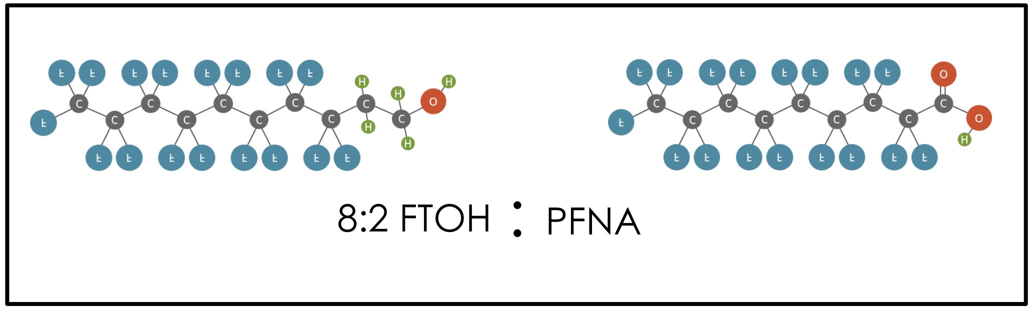
- Two plumes from different sources overlap
- Anomalous data within known plume points to other undiscovered sources
- Distinguish between point and nonpoint (i.e., diffuse) sources – use caution

PFAS-1, Section 10.5 Source Identification.

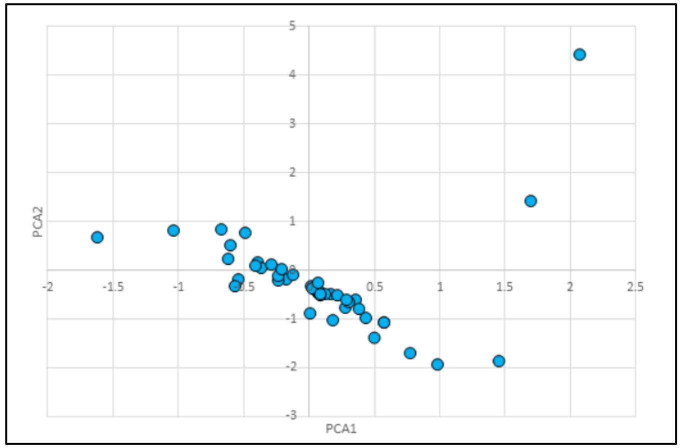
PFAS Forensics Techniques

- Diagnostic ratios of PFAS mixtures
  (e.g., PFOS:PFOA)
- Data visualization techniques
  (e.g., radial diagrams, bar charts)
- Specialized analytical techniques
  (e.g., non-target analysis, linear/branched speciation)
- Advanced multivariate statistics
  (e.g., PCA, cluster analysis, receptor models)

Diagnostic ratio



PCA scores plot



PFAS-1, Figure 10-4 PCA scores plot of the analysis of a PFAS data set. Source: M. Benotti, NewFields. Used with permission.
PFAS Figures Source: M. Olson, Trihydro. Used with permission.

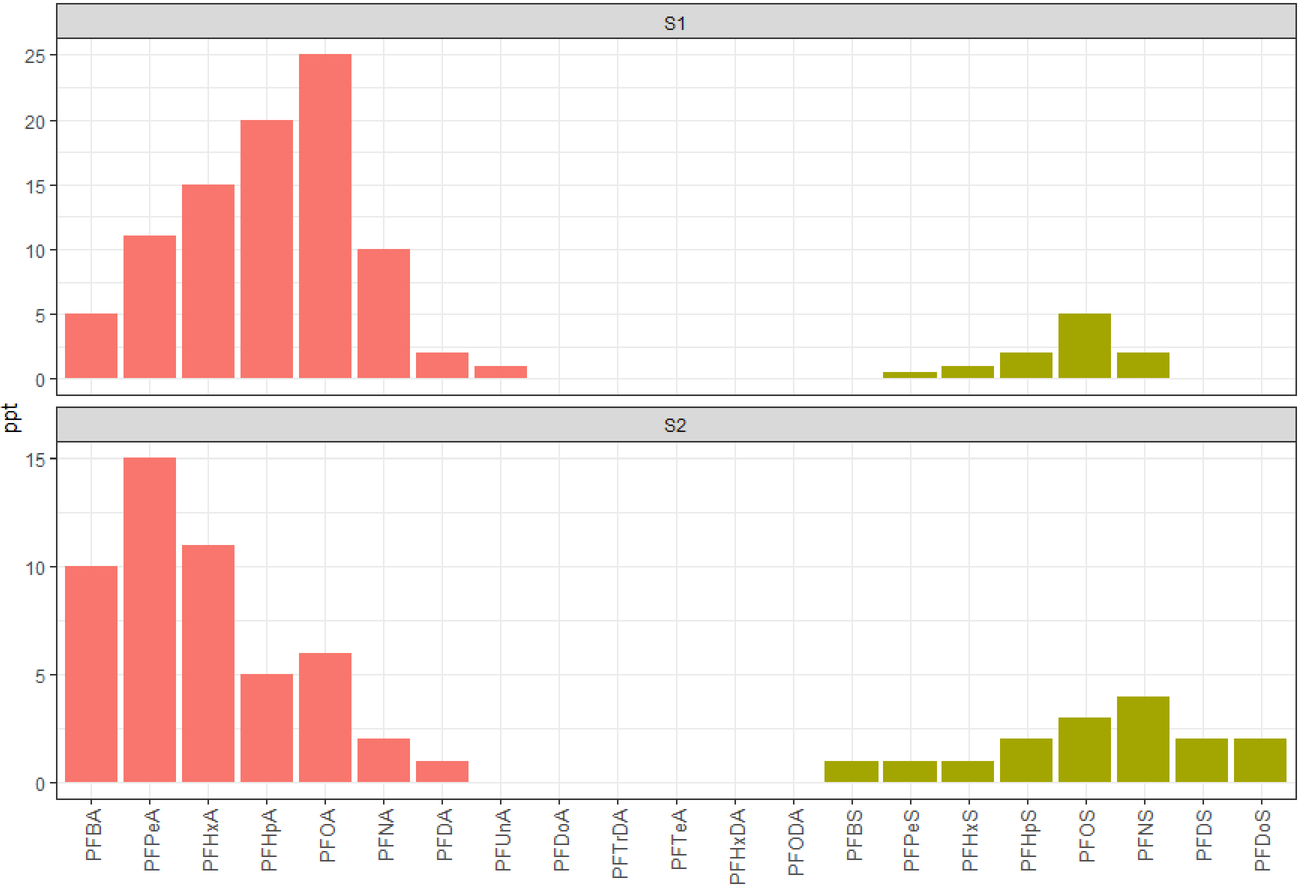
Diagnostic ratios of PFAS mixtures

Table 10-1. Example diagnostic ratios to compare PFAS signatures of Sample A or Sample B

	Sample A	Sample B
Relative Abundance of PFCAs	0.062	0.93
Relative Abundance of PFSAs	0.94	0.041
Relative Abundance of FTSs	0	0.029
PFCAs/PFSAs	0.066	22
PFOA/PFOS	0.0217	13

PFAS-1, Table 10-1. Example diagnostic ratios to compare PFAS signatures of Sample A and Sample B.

PFAS Profiles: Bar Charts

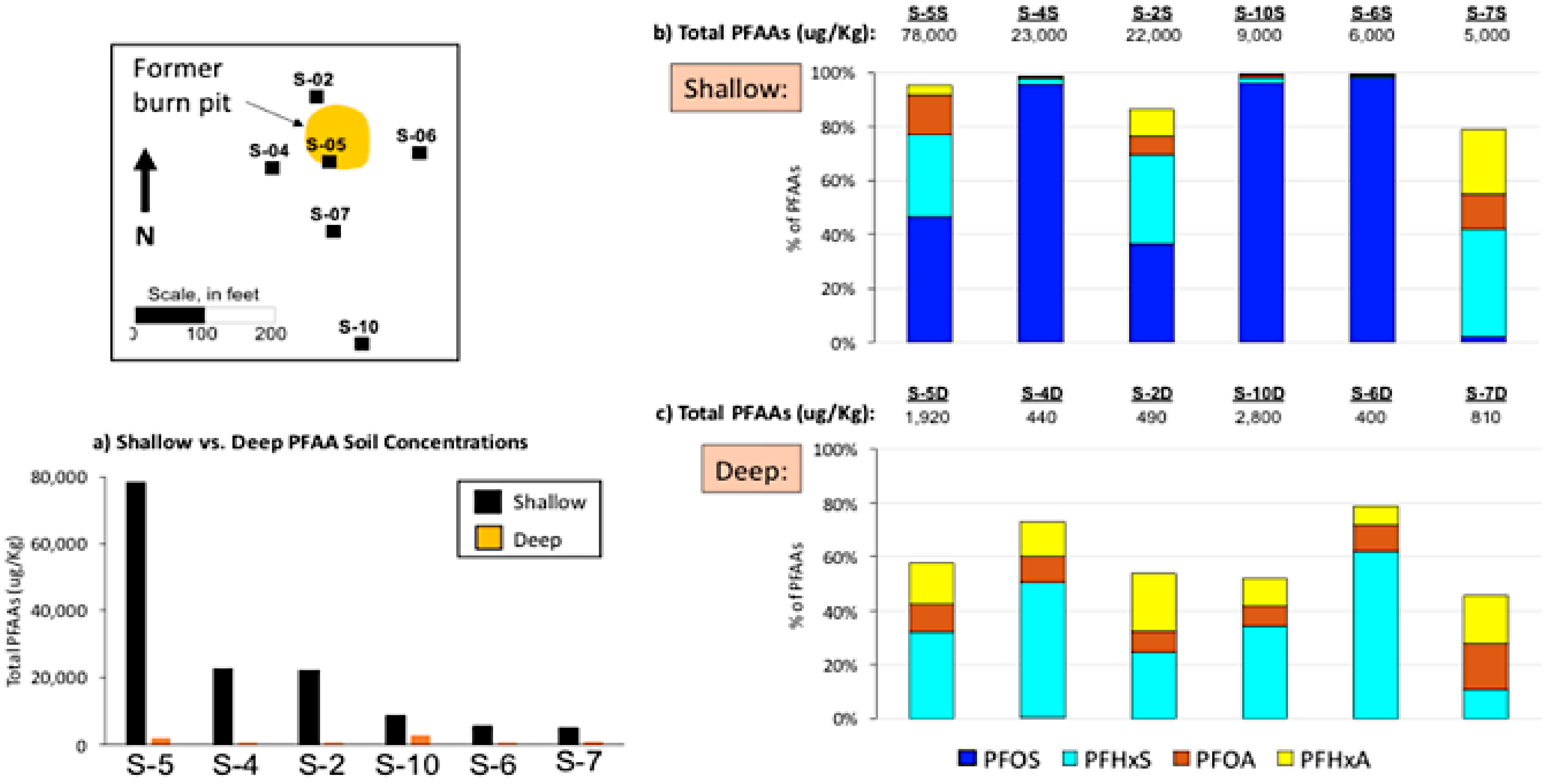


- Comparison of PFAS signatures in individual samples using “unstacked” bar graphs
- Bars are scaled to show relative contributions, but y-axis can be used to ascertain concentrations
- Can be used as a quick way to compare PFAS profiles between one or several environmental samples

PFAS-1, Section 10.5.1.2 Figures adapted from PFAS-1 Figure 10-2. Source M. Benotti, NewFields. Used with permission.
Figure source: Michael Bock, Verdantas. Used with permission.

Diagnostic ratios of PFAS mixtures: Stacked Bar Charts

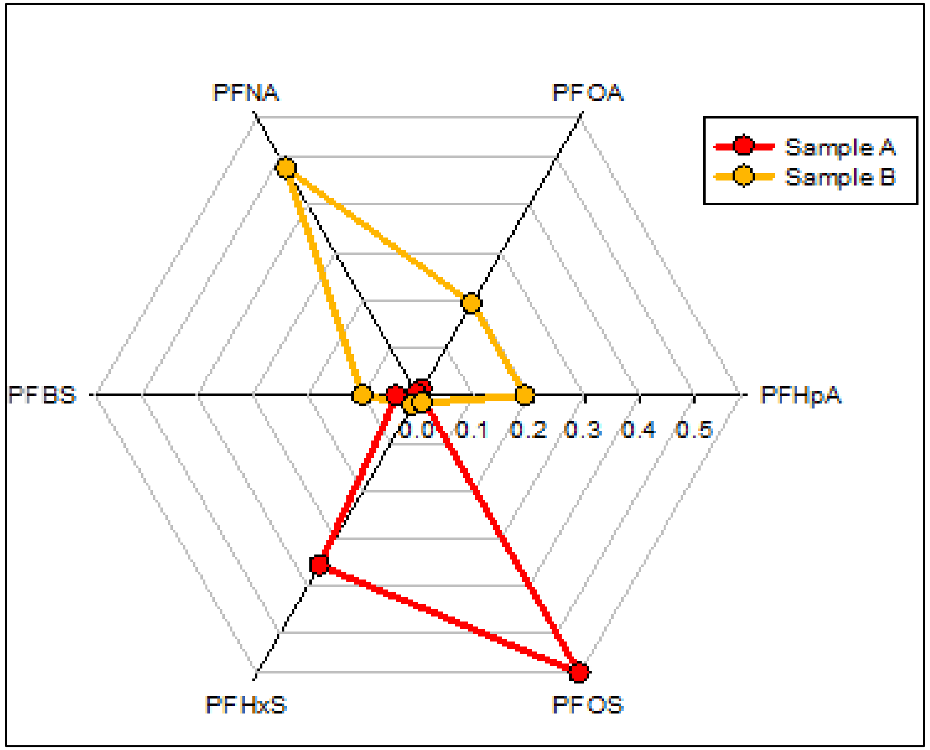
- Stacked bar charts show compositional differences in PFAS.
- Removes the effect of total concentration, permitting similar fingerprints (e.g., potential sources) to plot together regardless of magnitude.
- Can be used as a quick way to compare PFAS profiles between few environmental samples



PFAS-1, Figure 15-1. Comparison of shallow and deep soil samples at an AFFF release site. Source: G. Carey, Porewater Solutions. Used with permission.

Data Visualization: Radial Diagrams

- Radial diagrams (a.k.a., radar charts, spider plots) – useful for quick visual reference
  - Can be useful beyond source differentiation.
  - Section 15.1 of ITRC PFAS-1 has two case studies showing environmental fractionation.
- Comparison of PFAS signatures in hypothetical Sample A and B using Radial Diagrams.
- Plotting position is PFAS percent relative abundance (concentration divided by total PFAS).
- Can be used as a quick way to compare PFAS profiles between few environmental samples on one graph, or many on a map.



PFAS-1, Section 10.5.1.2
Figure 10-3 Comparison of PFAS Signatures. Source: M. Benotti, NewFields. Used with permission.

Multivariate statistics

- In **PCA** correlated variables are transformed into a small number of uncorrelated variables. These principal components are used to simplify the visual representation of the variability in the dataset
- In **factor analysis/receptor models**, end member/factors that characterize the underlying structures in the dataset are identified. End members/factors are used to simplify the visualization of the variability in the dataset.
- In **cluster analysis**, the similarity/dissimilarity between samples are calculated and used to define clusters of similar samples in a larger dataset.

Sample	PFOS	PFOA	PFBA	PFBS	PFNA
1					
2					
3					
4					
5					
6					
7					
8					

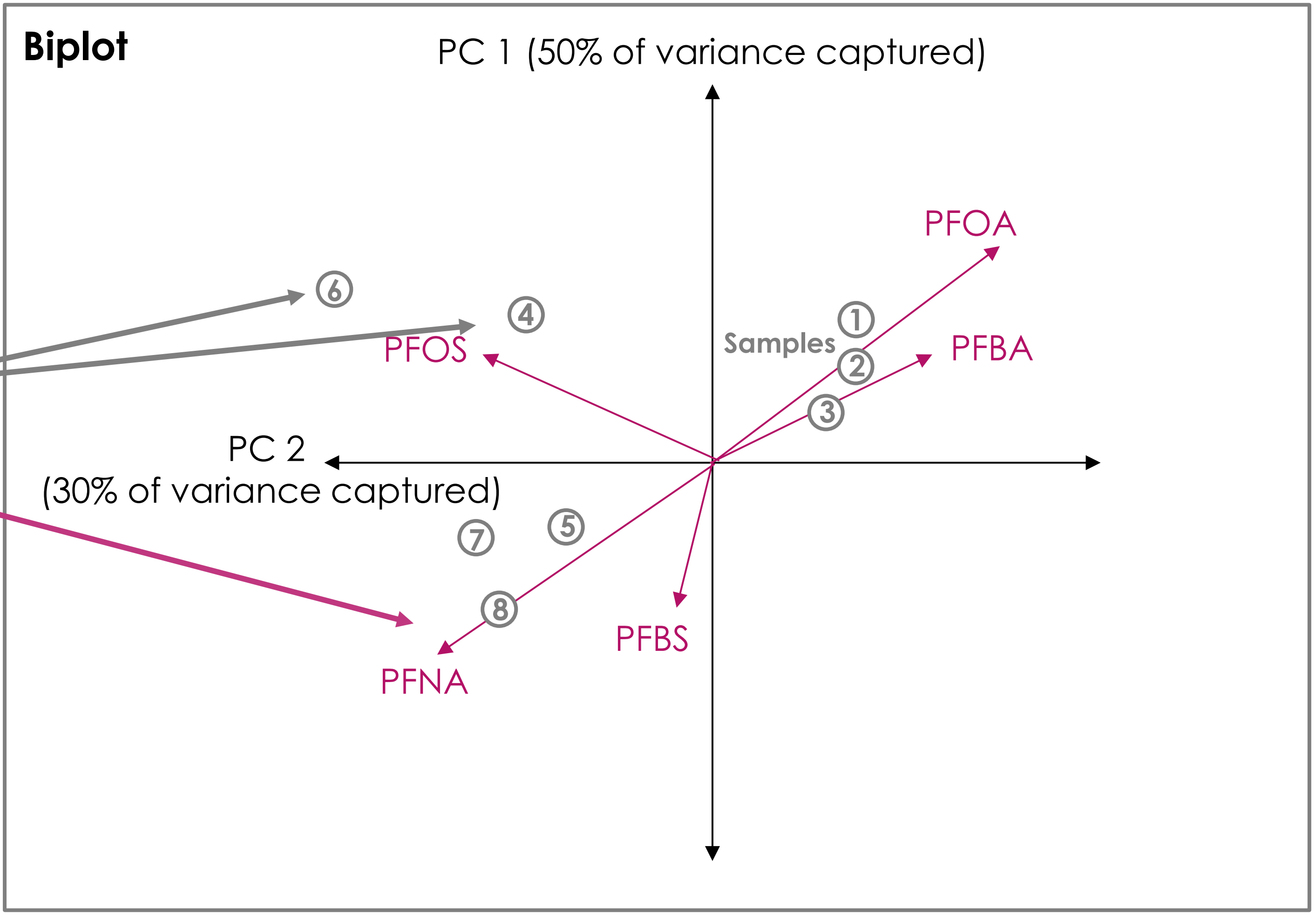
Analytical data

PFAS-1, Section 10.5 Source Identification. Illustration of generalized data table.

Advanced multivariate statistics: Principal Component Analysis (PCA)

Scatter plot of the data compressed into PCs, for visualization in 2D or 3D.

- Data rows (samples) are points.
- Columns (analytes) are arrows.



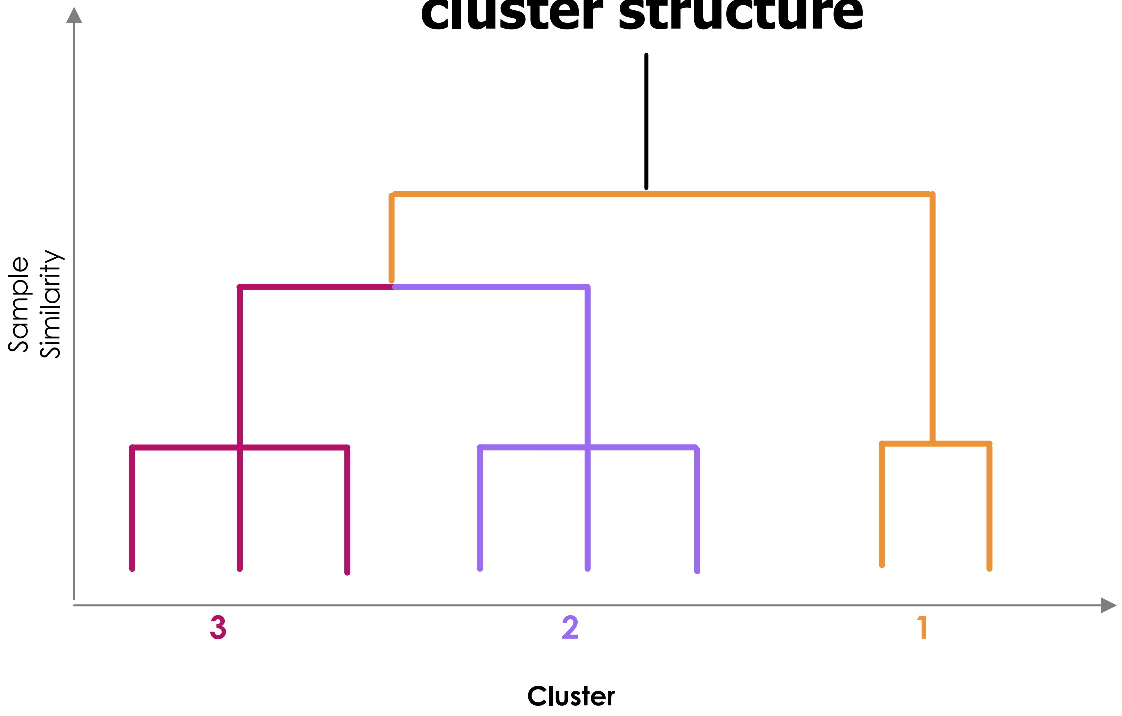
PFAS-1, Section 10.5 Source Identification. Illustration of generalized Principal Components Analysis biplot.

Advanced multivariate statistics: Clustering Analysis (CA)

Groups samples based on similarity/dissimilarity (i.e., chemical profile similarity)

- Not all clusters are sources. They may also reflect:
    - Site-specific fate-and-transport processes
    - Background/ambient
    - A mixture of sources found at similar proportions in large groups of samples

Dendrogram of hierarchical cluster structure

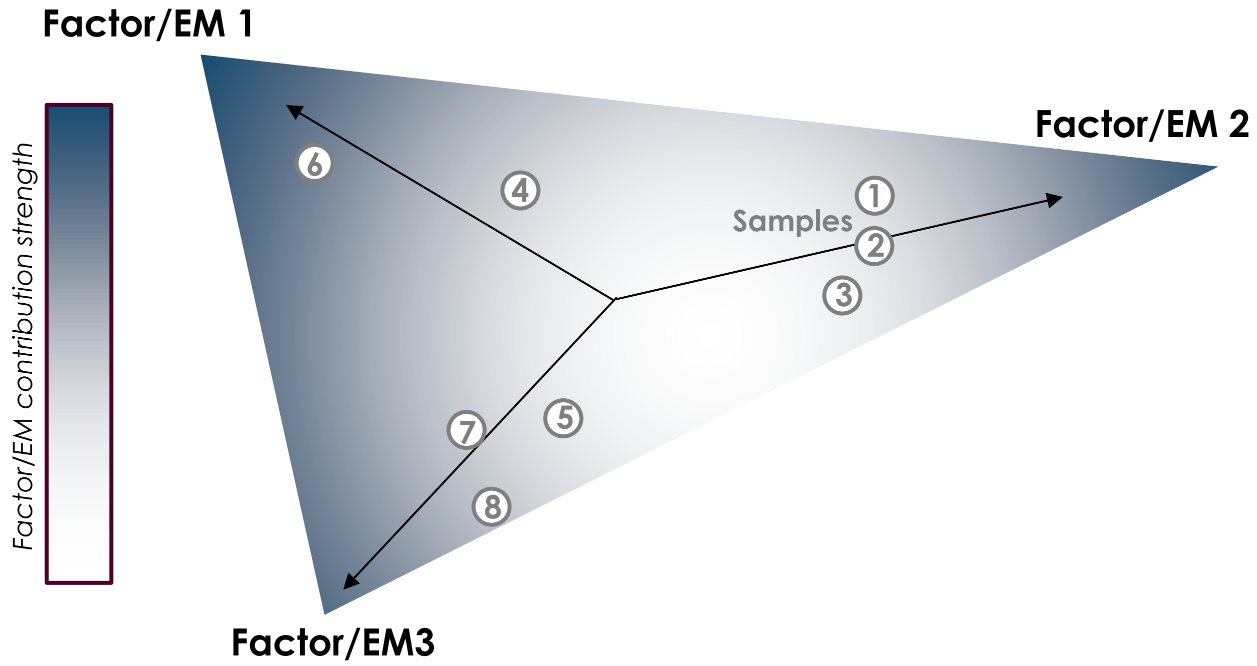


PFAS-1, Section 10.5 Source Identification. Illustration of generalized clustering.

Advanced multivariate statistics: Factor Analysis (FA) and receptor models

Blind Source Separation

- Estimate number of factors/end members
- Estimate profiles for each factor/end member
- Estimate contribution of each factor/end member to each sample
- Not all end members are sources – some may be weathering or transformation patterns, etc.

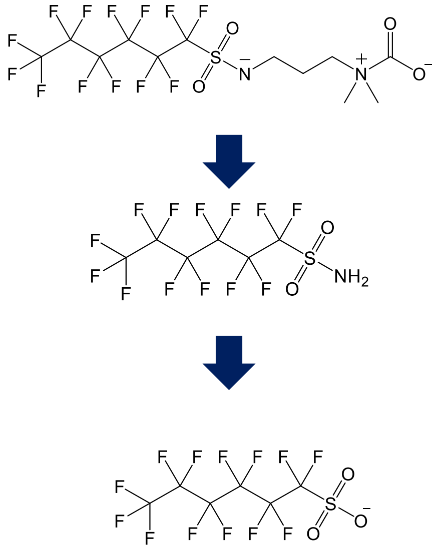


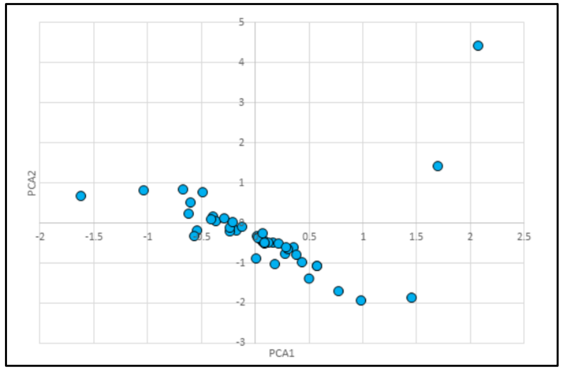
PFAS-1, Section 10.5 Source Identification. Illustration of generalized factor analysis.

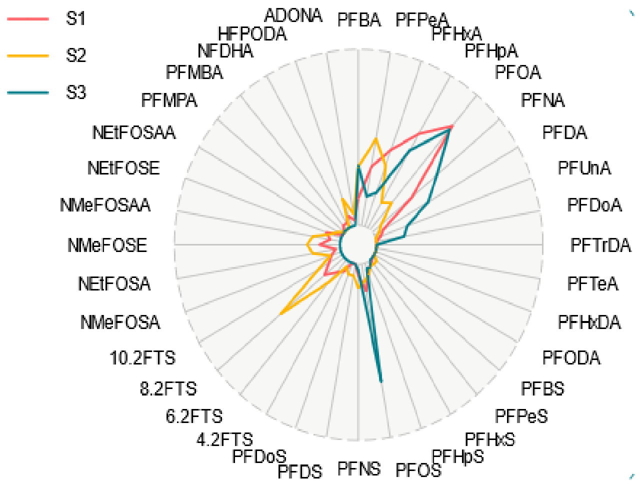
Advanced multivariate statistics: Limitations

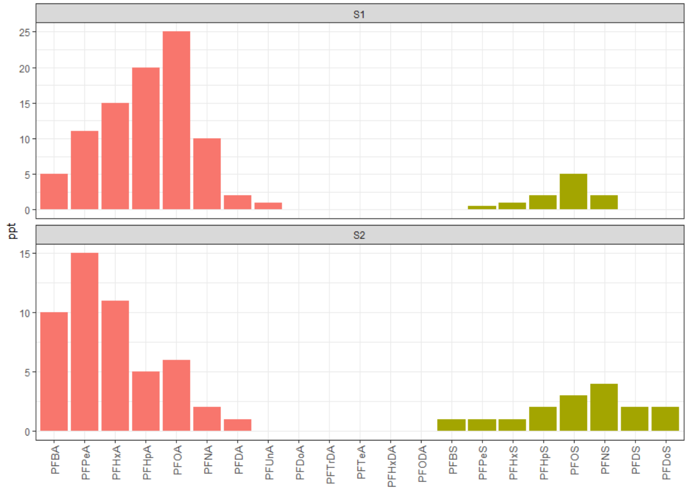
No method, including multivariate statistics, is a silver bullet

- Factor analysis and clustering typically require user to specify number of factors or clusters.
- Iterative process to find a realistic solution.
- Practitioner must interpret results (clusters or factors don't inherently "mean" anything).









PFAS-1, Section 10.5 Source Identification. Illustration of generalized clustering. PFAS-1, Figure 10-4 PCA scores plot of the analysis of a PFAS data set. Source: M. Benotti, NewFields. Used with permission. Bar Chart figures adapted from PFAS-1 Figure 10-2. Source M. Benotti, NewFields. Used with permission.
Bar charts and radar charts figure source: Michael Bock, Verdantas. Used with permission.
PFAS molecule diagrams. Christopher Olivares, UC Irvine. Used with permission.

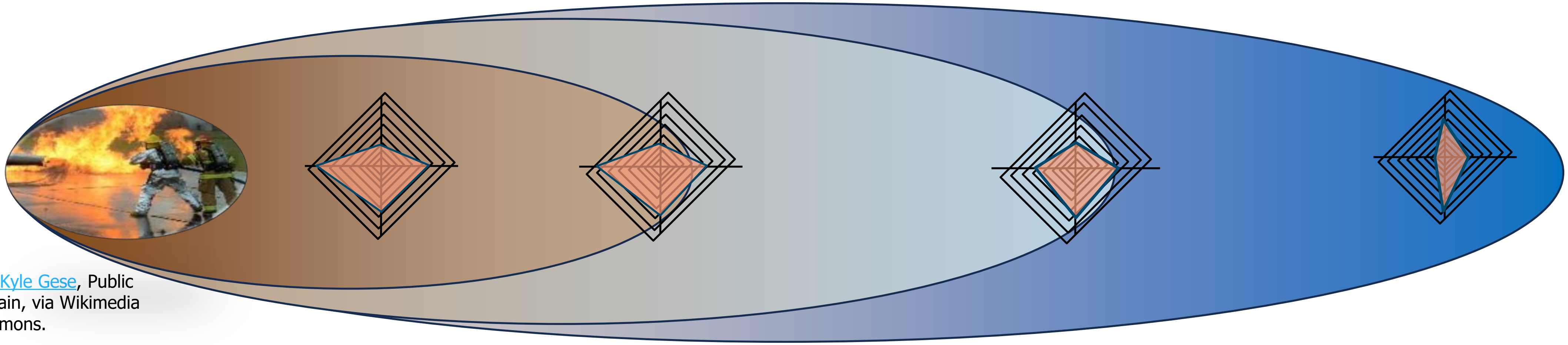
Advanced multivariate statistics: Limitations

Site conditions often produce many non-source signatures:

- Diffuse (ambient) signatures or stable mixtures found in large numbers of samples
- Patterns due to environmental fractionation or differential transport
- Chemical (i.e., precursor) transformations

Always use multiple lines of evidence

- Other lab analyses
- Spatial / temporal trends
- Site-specific history and analytical records
- etc.



A1C Kyle Gese, Public domain, via Wikimedia Commons.

PFAS-1, Section 10.5 Source Identification. Illustration of generalized clustering.

Environmental Factors affecting PFAS Forensics

Sites typically contain mixtures of PFAS that exhibit wide range of physical and chemical properties

- PFAS transported from source zones are redistributed downgradient

Groundwater transport depends on:

- Soil characteristics (OM, pH, minerology, etc)
- PFAS characteristics (chain length, functional groups, molecular structure, etc.)

PFAS Forensics Examples

Examples of fingerprinting studies for source identification include:

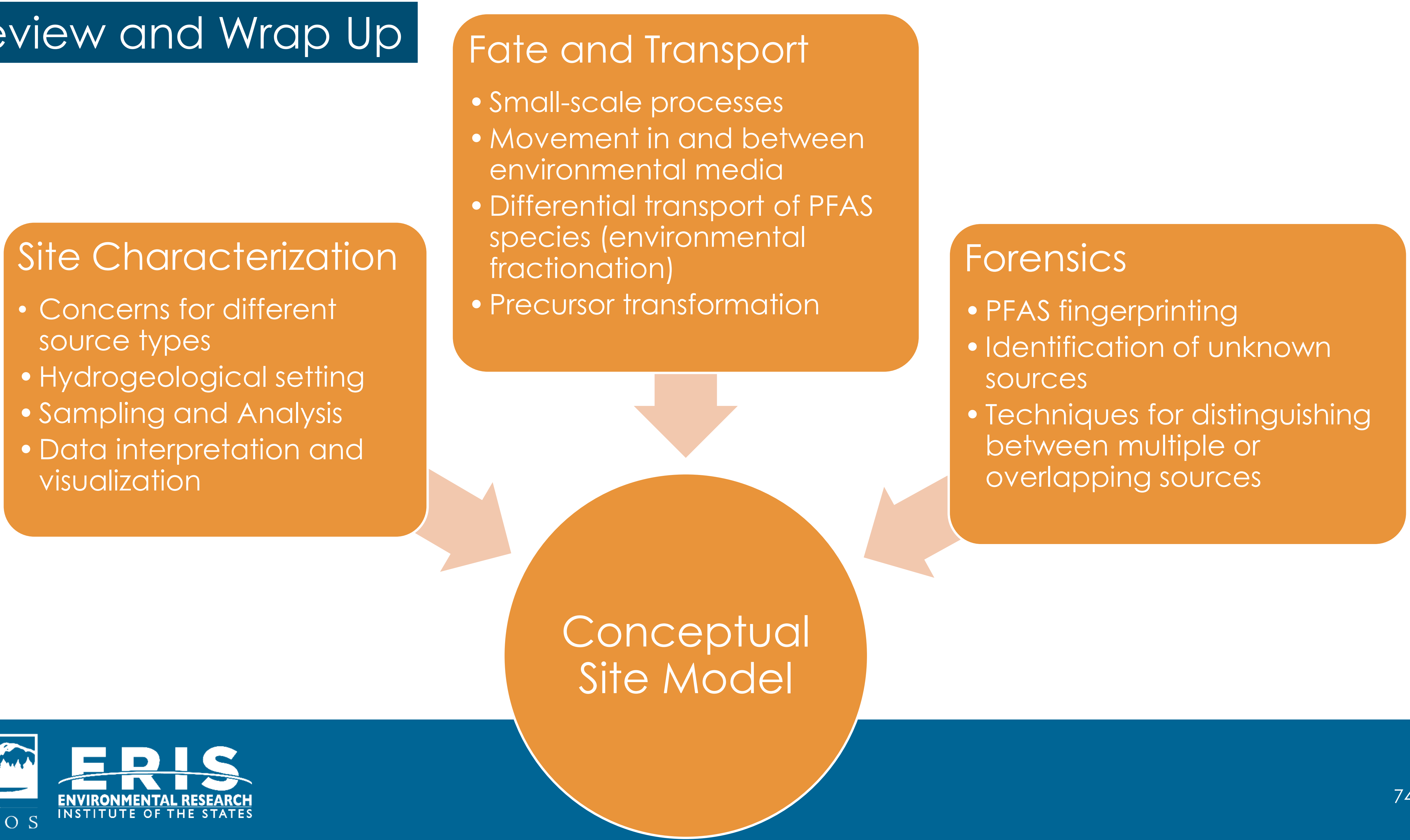
HRGCMS was used to assign the identity of 14 major compounds that accounts for a majority of the detectable PFAS in contemporary AFFF.

(Ruyle et al 2021)

PFAS profiles have been developed for different sources, including various AFFF formulations.

(Dasu et al 2022)

Review and Wrap Up



Fate and Transport

- Small-scale processes
- Movement in and between environmental media
- Differential transport of PFAS species (environmental fractionation)
- Precursor transformation

Site Characterization

- Concerns for different source types
- Hydrogeological setting
- Sampling and Analysis
- Data interpretation and visualization

Forensics

- PFAS fingerprinting
- Identification of unknown sources
- Techniques for distinguishing between multiple or overlapping sources

Conceptual Site Model

ITRC PFAS Resources

ITRC PFAS: https://pfas-1.itrcweb.org/

Guidance Document

13 Fact Sheets

External Tables

PFAS Introductory Training

- Clu-In Archive: https://www.clu-in.org/conf/itrc/PFAS-Introductory/

Other video resources

- Available through links on: https://pfas-1.itrcweb.org
- Quick Explainer Videos
- Longer PFAS Training Modules
- Archived Roundtable Sessions

Questions

Feedback Form & Certificate:
www.clu-in.org/conf/itrc/PFAS-BTB-FT/

PFAS
"Beyond the Basics"
TRAINING

2025

SAMPLING & ANALYSIS, SW ANALYSIS, AIR OCCURRENCE
February 25 2025
1:00-3:00 PM ET

HUMAN HEALTH EFFECTS, ECOLOGICAL TOXICITY, REGULATIONS
March 25 2025
1:00-3:00 PM ET

SOURCE ID, SITE CHARACTERIZATION, FATE & TRANSPORT
April 24 2025
1:00-3:00 PM ET

BIOSOLIDS, SOIL LEACHING, & MOBILITY
May 20 2025
1:00-3:00 PM ET

TREATMENT TECHNOLOGIES
June 3 2025
1:00-3:00 PM ET