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PFAS: Beyond the Basics Training

Biosolids

- **Source Zones**
- **Fate and Transport**
- **Characterization and Treatment**

Today's PFAS Trainers

Chris Evans, M.S./LG
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Anchor QEA
slaroe@anchorqea.com

ITRC PFAS Resources

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

Guidance Document

13 Fact Sheets

External Tables

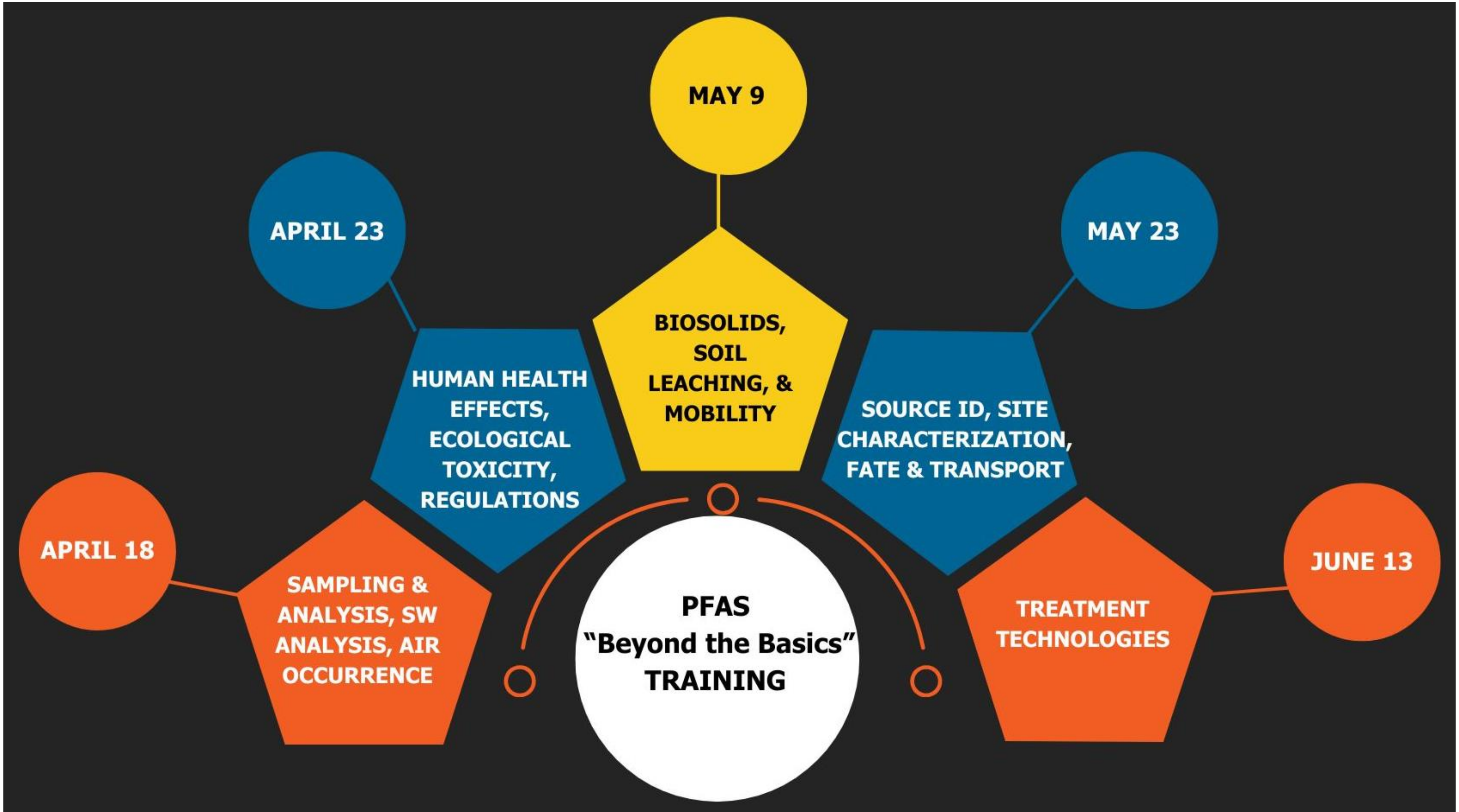
PFAS Introductory Training

- 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

ITRC PFAS Team:
2024 "Beyond the Basics" Training Modules



Biosolids & PFAS Fate and Transport in the Vadose Zone

- Source Zone Characteristics
- Vadose Zone Controls on Mobility
- Field Scale Fate, Transport, Uptake
- Characterization and Treatment

Additional Biosolids Considerations & Summary

Biosolids

Source Zones

Fate and Transport

Characterization and Treatment

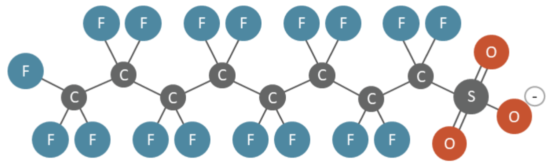
PFAS (per- and polyfluoroalkyl substances)

<u>Per</u>fluoroalkyl substances

- PFAAs typically in anionic form
  - Sometime named based on acid or salt
- Mobility
  - PFCAs >PFSAs
  - Short chain >long chain
  - PFAAs may be present in linear or branched form - change in structure also affects sorption/mobility in the environment
- See Sections 2.2 and Section 4.3 for detail

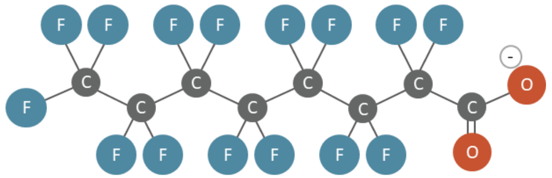
Perfluoroalkyl acids, or PFAAs

PFSAs (perfluoroalkane sulfonates)



PFOS (perfluorooctane sulfonate)

PFCAs (perfluoroalkyl carboxylates)

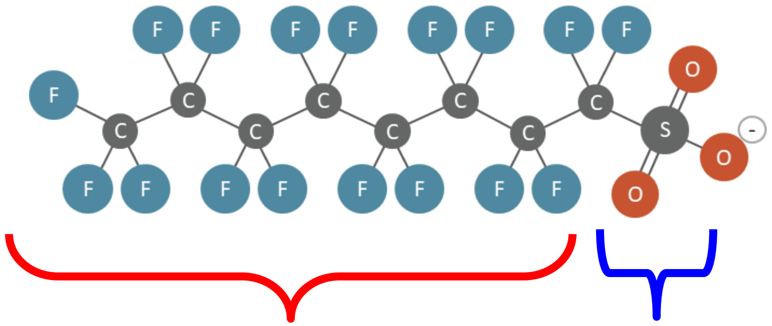


PFOA (perfluorooctane carboxylate)

PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs) and Section 2.2.4 Polyfluoroalkyl Substances. Source: M. Olson, Trihydro. Used with permission.

The Heads and Tails of PFAAs

Perfluorooctane sulfonate (PFOS)



Perfluorinated "Tail"
Hydrophobic/Lipophobic

Anionic "Head" group
Polar/Hydrophilic

Perfluoroalkyl acids (PFAAs) are extremely persistent in the environment and are mobile in groundwater

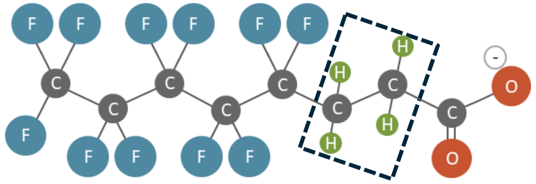
PFAS images used with permission from Mitchell Olson, Trihydro.

PFAS (per- and polyfluoroalkyl substances)

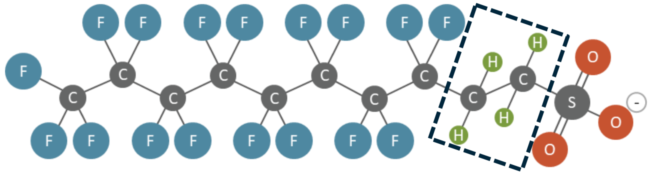
<u>Poly</u>fluoroalkyl substances

- Fluorotelomers (FT…), sulfonamide/sulfoanamido groups, diPAPs
- Neutral, anions, cations, zwitterions
- “Precursors”

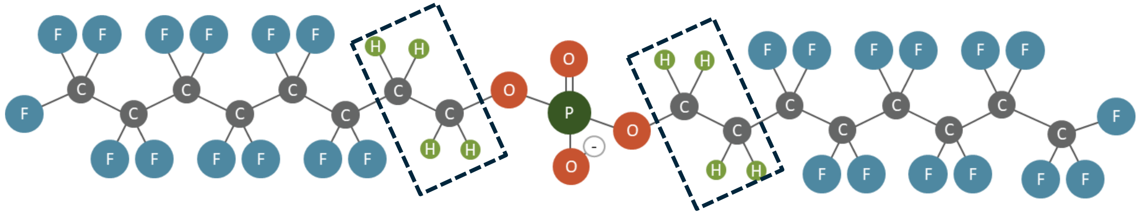
5:3 Fluorotelomer carboxylate (5:3 FTCA)



8:2 Fluorotelomer sulfonate (8:2 FTS)



6:2 Polyfluoroalkyl Phosphate Diester (6:2 diPAP)



PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs) and Section 2.2.4 Polyfluoroalkyl Substances. Source: M. Olson, Trihydro. Used with permission.

Biosolids and PFAS Fate and Transport in the Vadose Zone

Source Zone Characteristics

Vadose Zone Controls on Mobility

Field Scale Fate, Transport, Uptake

Characterization and Treatment

Additional Biosolids Considerations & Summary

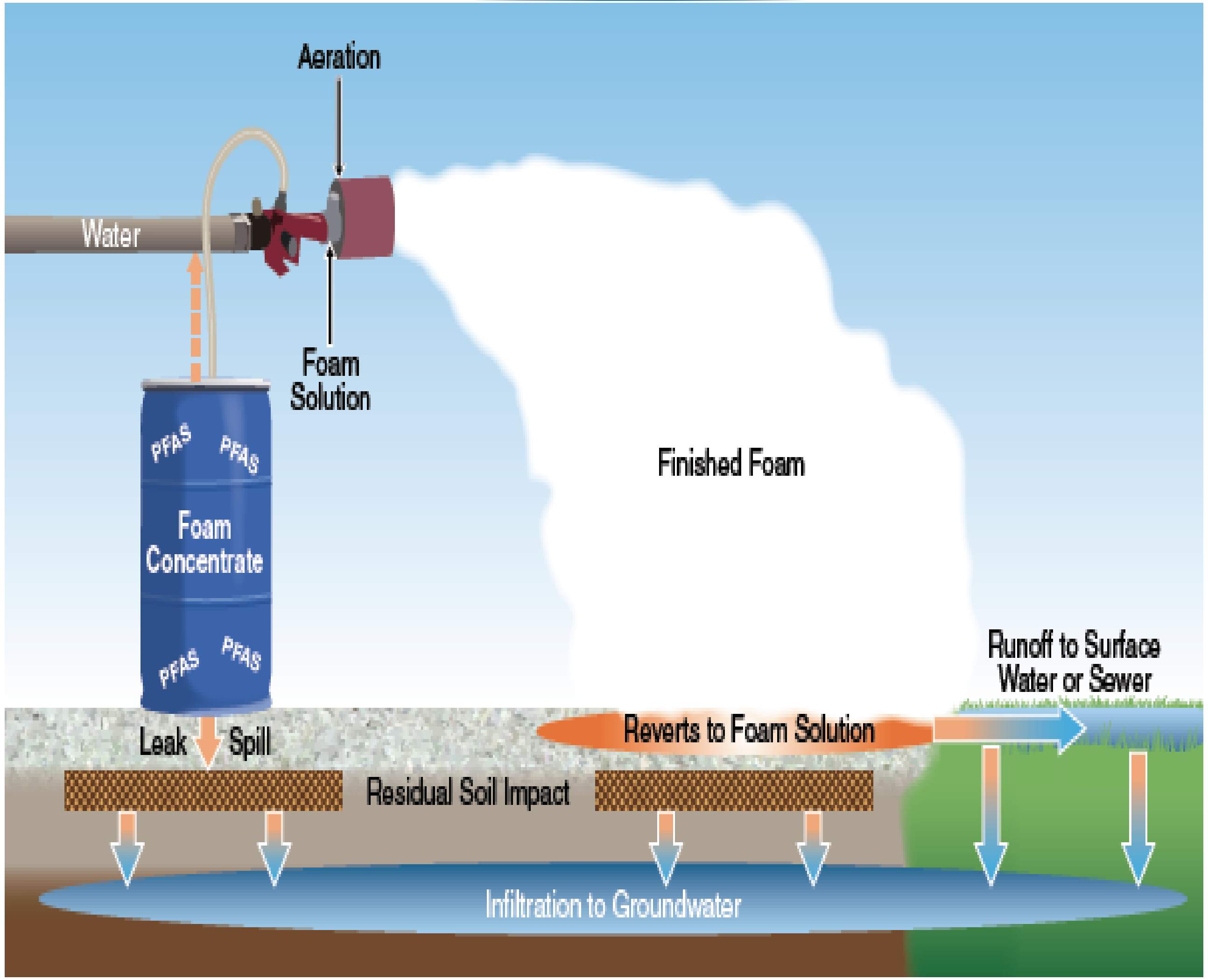
Biosolids

Source Zones

Fate and Transport

Characterization and Treatment

Aqueous Film Forming Foams (AFFF) Source Zones



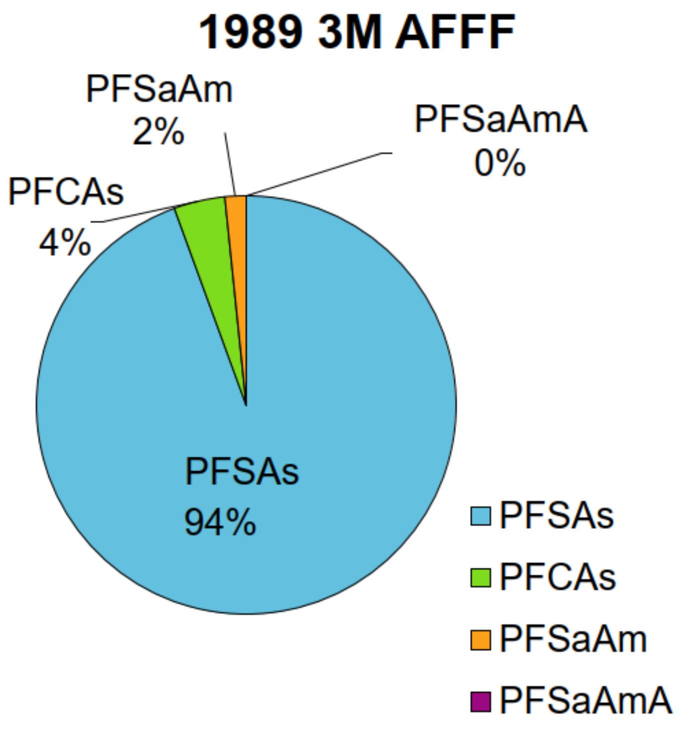
PFAS-1, Figure 3-4 Release of firefighting foam.
Source: Adapted from figure by J. Hale, Kleinfelder, used with permission.

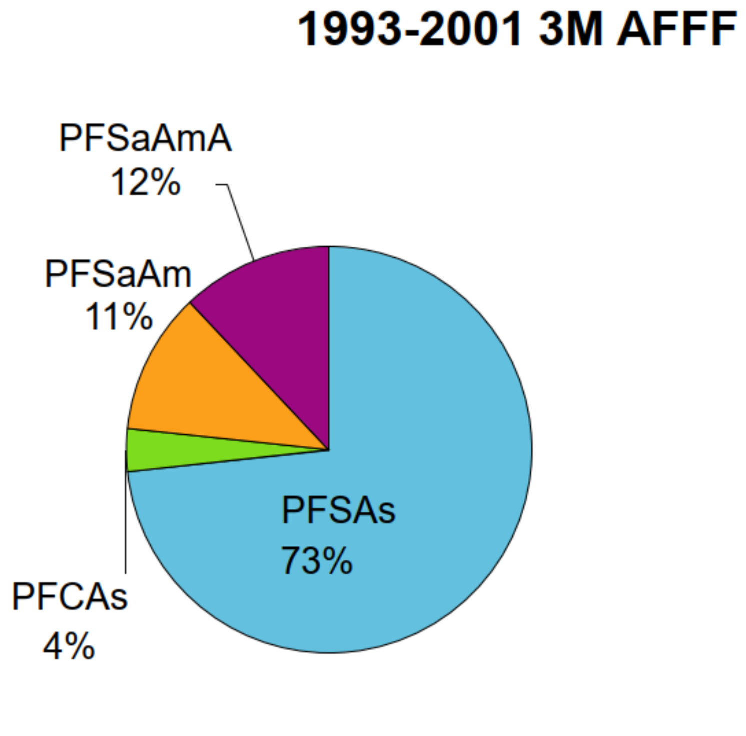
PFAS-1, Section 3.3 Mechanisms for Release to the Environment.

Foam release:

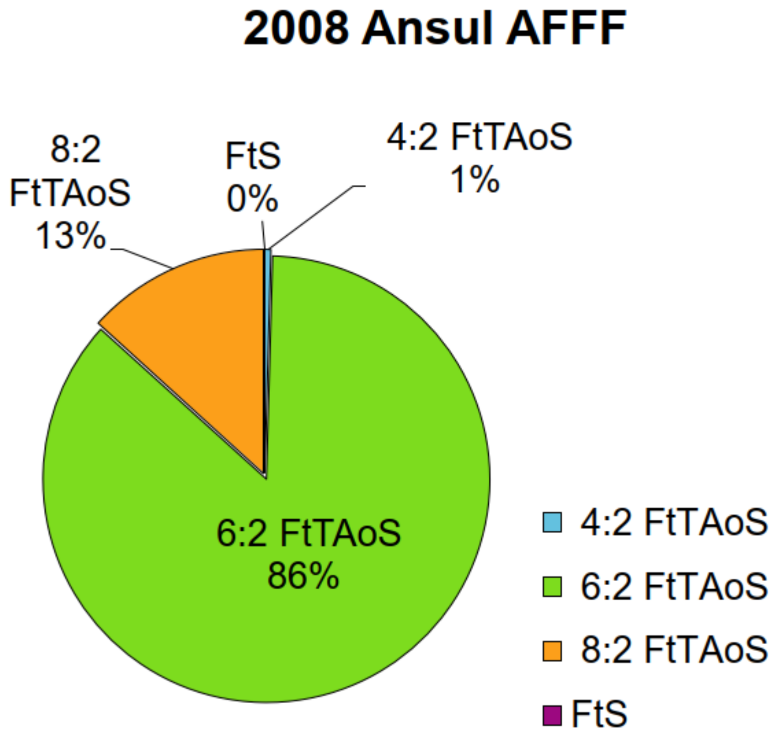
- **Spills, Leaks**
  - Low volume releases of foam concentrate
- **Firefighting Operations**
  - Moderate volume discharge of foam solution
  - Infrequent high-volume, broadcast discharge
- **Historic Training Operations, Equipment Checks**
  - Periodic, high volume, broadcast discharge

AFFF Source Zones – Product Chemistry Changed





Electrochemical Fluorination



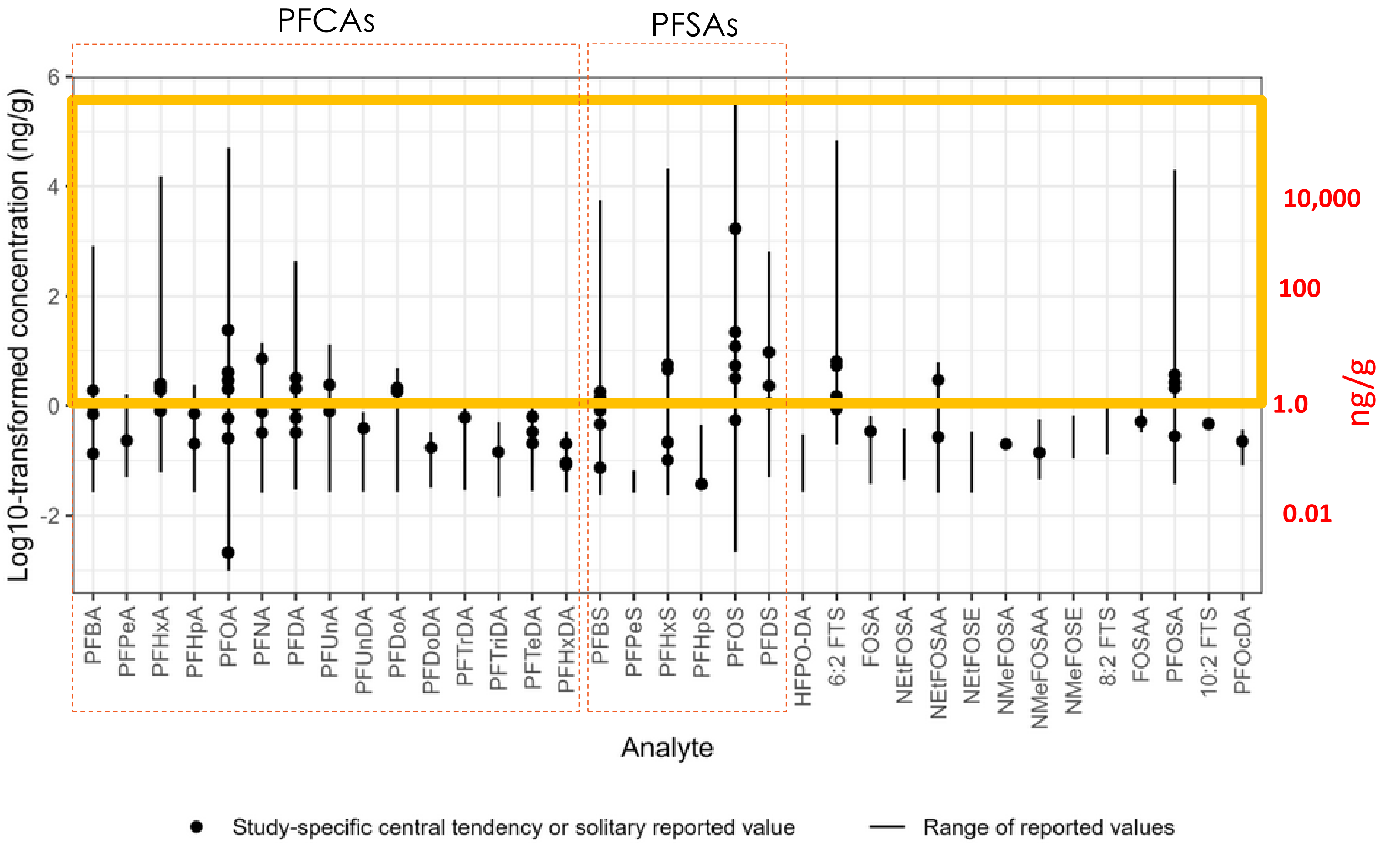
Fluorotelomerization

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

ITRC PFAS-1, Table 3-1.

AFFF Source Zones – PFAS Occurrence

- Suite of PFAS PFSAs, PFCAs most common
  - 6:2 FTS, PFOSA also present
- Upper bound of reported concentration in soil orders of magnitude greater than other sites
- Extent generally limited to application area (location of activity)
  - Impact extended by subsequent transport (runoff, infiltration)
  - Highest detections generally found in shallow soils



Sources: Brusseau et al. (2020), Groffen et al. (2019), Sanborn Head & Associates (2022), Sorengard et al. (2022), USGS (2022), Wang et al. (2018)

PFAS-1, 2023 Section 6 Figure 6-2A, Observed PFAS concentrations in site and anthropogenic background soil. Source: Figure developed using ggplot2 (Wickham 2016).

AFFF Source Zones – Vadose-Zone PFAS Transport

- High-concentration training area vs low-concentration (e.g., 1-time release at vehicle fire)
  - Higher source concentrations may = migration of PFAS to depths up to 30 m
  - Relative increase in short chain vs long chain PFAS with depth
- Biological/abiotic transformation of precursors to PFAAs
- Physical and chemical properties (PFAS and soils)

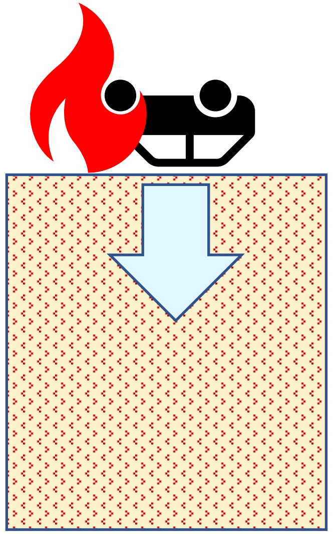
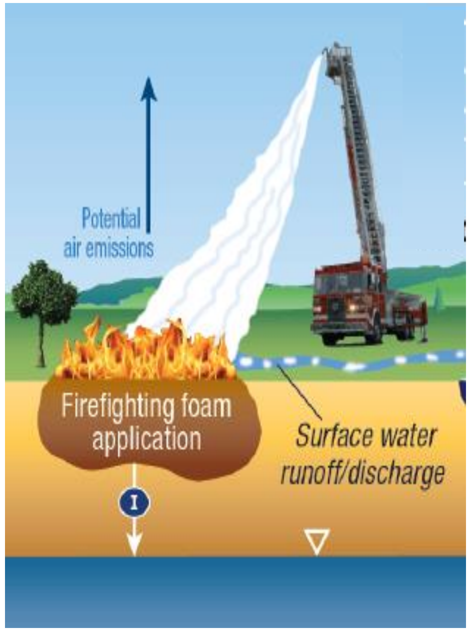


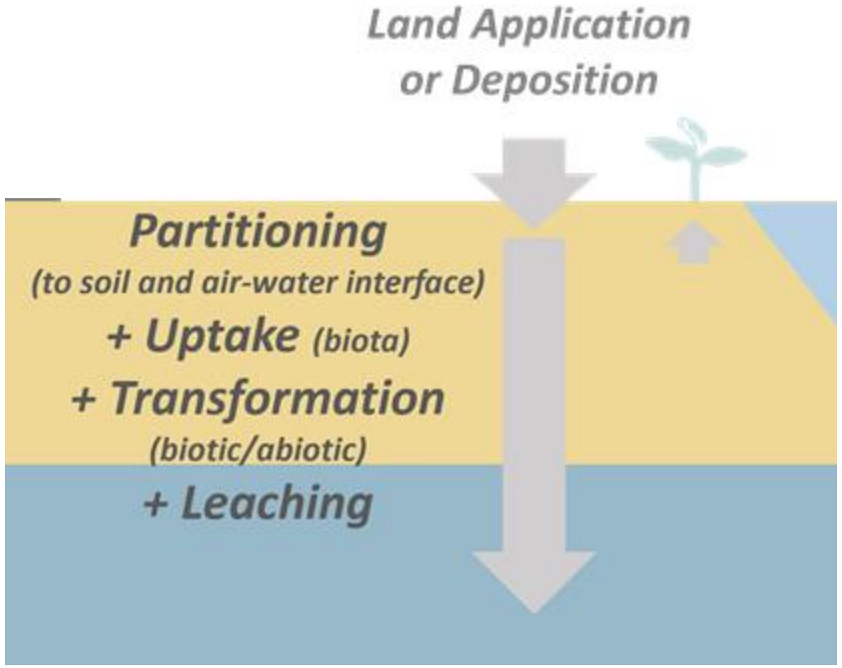
Figure Source: C. Evans, ME DEP, used with permission.



PFAS-1, Figure 2-19. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

https://pfas-1.itrcweb.org/15-case-studies/#15_1
Anderson et al 2016 PFAS1 # 161

Biosolids Source Zones – Land Application



1) Attributed to: Andrew Smith / *Muck-spreading on Little Down, Slindon* / CC BY-SA 2.0
2) PFAS-1, modified from Figure 5-1. Source: D. Adamson, GSI, used with permission.
3) Photo Source: C. Evans, ME DEP. Used with permission

What are Biosolids?

Class B : Treated to reduce pathogens but typically require a permit to land apply & have management practices governing their use on cropland, forestland , and land reclamation – not appropriate for lawns/gardens;

Treatment also includes meeting requirements for trace metals, currently no organics in Rules

Class A: Further treated to remove pathogens to levels safe for lawns and home gardens in many cases

PFAS-1, Section 2.6.4 Wastewater Treatment, Treatment Residuals and Biosolids.

Sources of PFAS in Wastewater and Biosolids

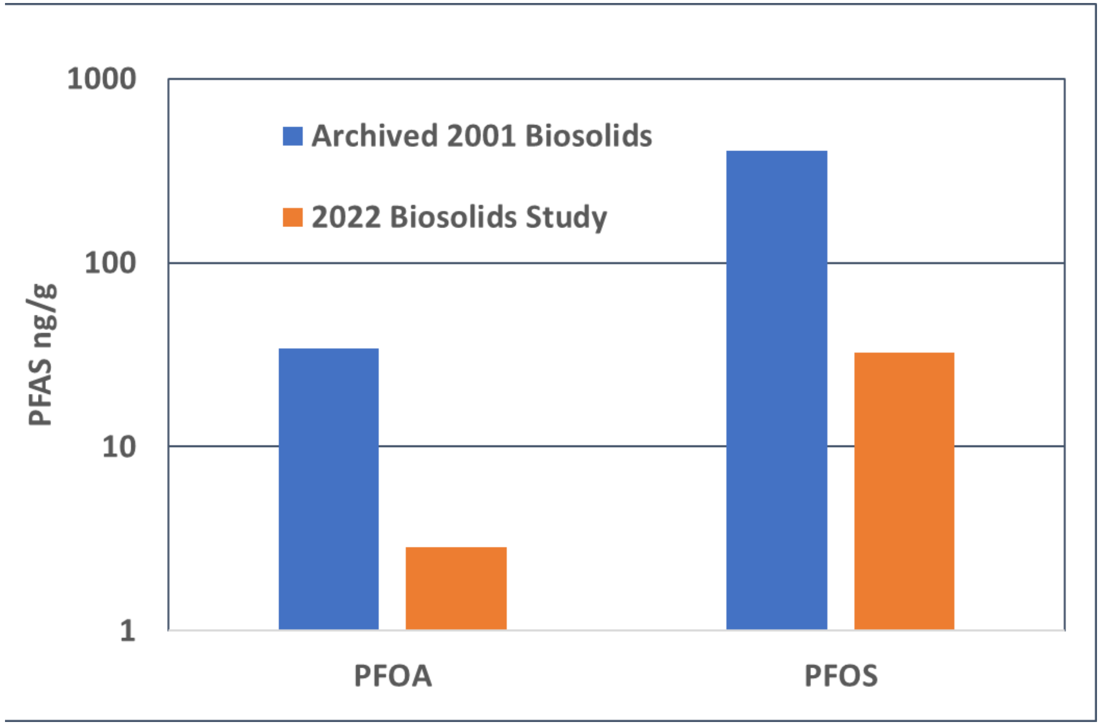
- All municipal/commercial wastewater contains some PFAS
  - leather tanning & finishing
  - plastics & synthetic fibers
  - pulp, paper & paperboard
  - textile mills

- Residential sources exist too

Photo taken by Watzmann (c) Günter Seggebäing. CC BY-SA 3.0 Via Wikimedia Commons

PFAS in Biosolids

- Biosolids tend to be enriched in longer chain (>C6) PFAAs but contain a wide range of precursor and non-target PFAS
- Decline of PFOS/PFOA
- Non-target PFAS/potential precursors represent 77-97% of total molar Fluorine
  - Fluorotelomer acids (often 8:2/6:2/4:2)
  - diPAPs (often 6:2 or 8:2)
  - Ultra Short Chain

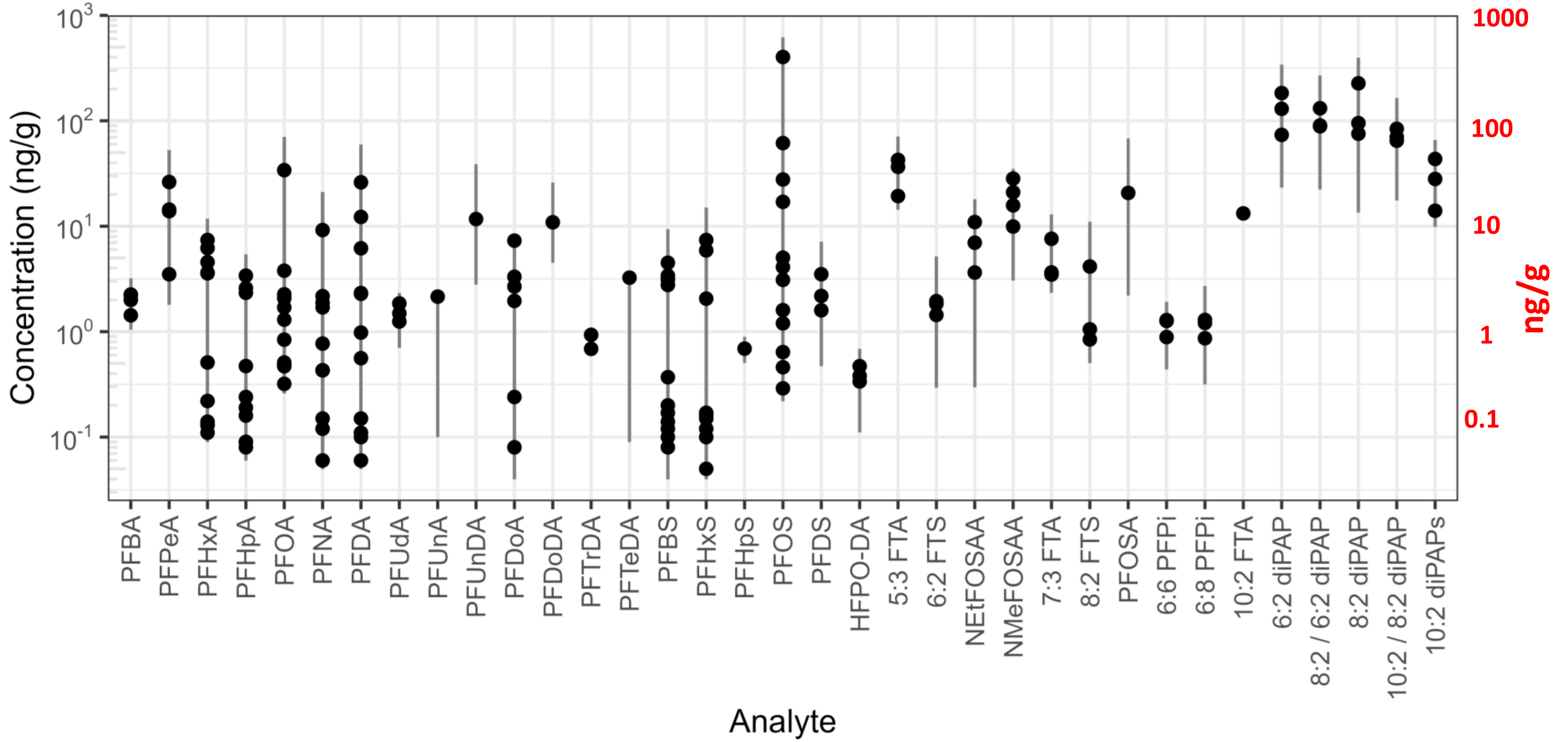


(1) And (2)

Graph Source: C. Evans, ME DEP, used with permission.

(1) Venkatesan, A.K., and R.U. Halden. 2013. Journal of Hazardous Materials 252-253:413-418
(2) Schaefer, C. E., et al Water Research 217:118405.

PFAS in Biosolids (Literature Range of Values)

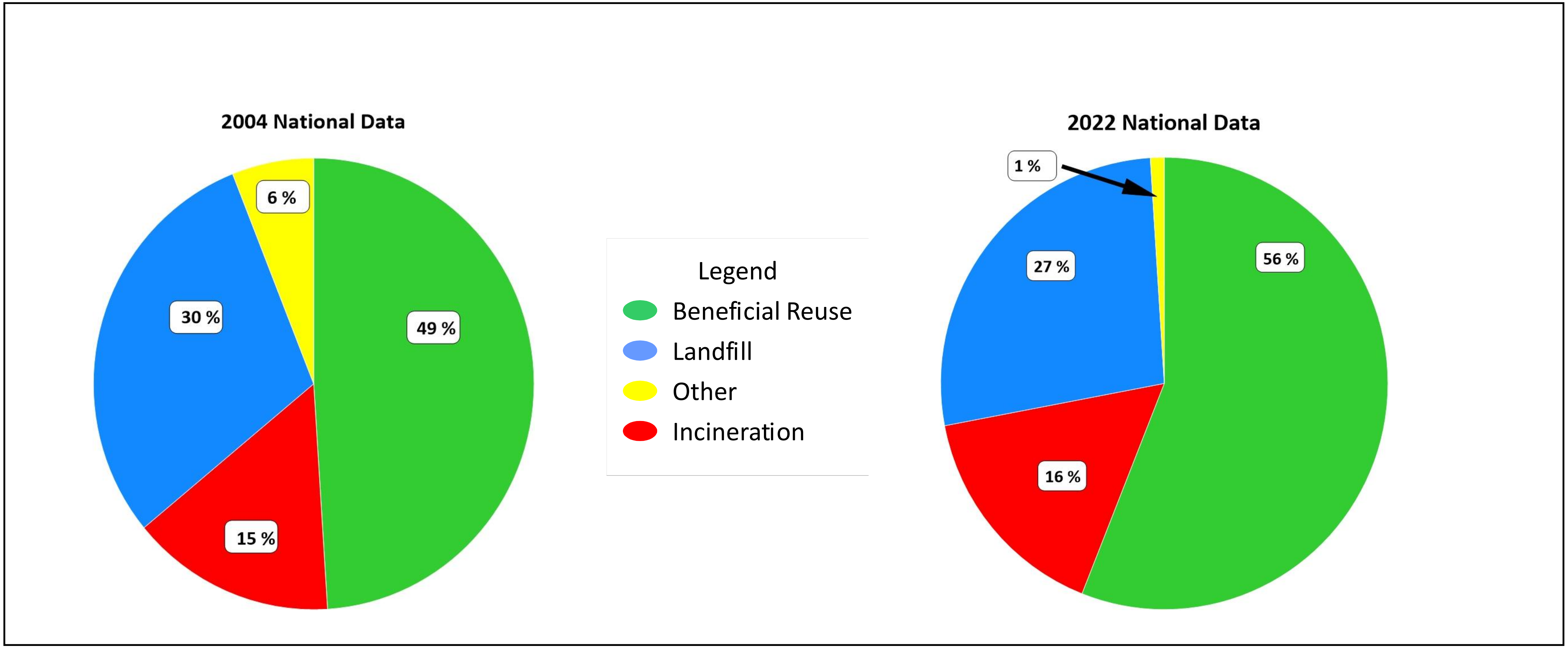


Sources: Pepper et al. (2021), Schaefer et al. (2022), Venkatsesan and Halden (2013), Venkatsesan and Halden (2014)

Composite ranges and study-specific averages are shown

PFAS-1, 2023 Section 6 Figure 6-2C, Range of values for common PFAS in Biosolids. Source: Figure developed using ggplot2 (Wickham 2016).

Disposal and Beneficial Reuse



PFAS-1, Section 2.6.4 Wastewater Treatment, Treatment Residuals and Biosolids.
Data from: 1) North East Biosolids and Residuals Association, 2007. A National Biosolids Regulation, Quality, End Use & Disposal Survey. July 20, 2007
2) www.epa.gov/biosolids/basic-information-about-biosolids

PFAS in Land Applied Soils

Direct Land Application

- Promoted by states, historically
- Potentially impacts water supplies in nearby residential homes
- Potential for exposure when fields redeveloped as housing
- Impacts may be significant when commercial or industrial inputs are large percent of total
- Persistence in farm soils – decades after application
- Use for land reclamation projects to incorporate organic matter

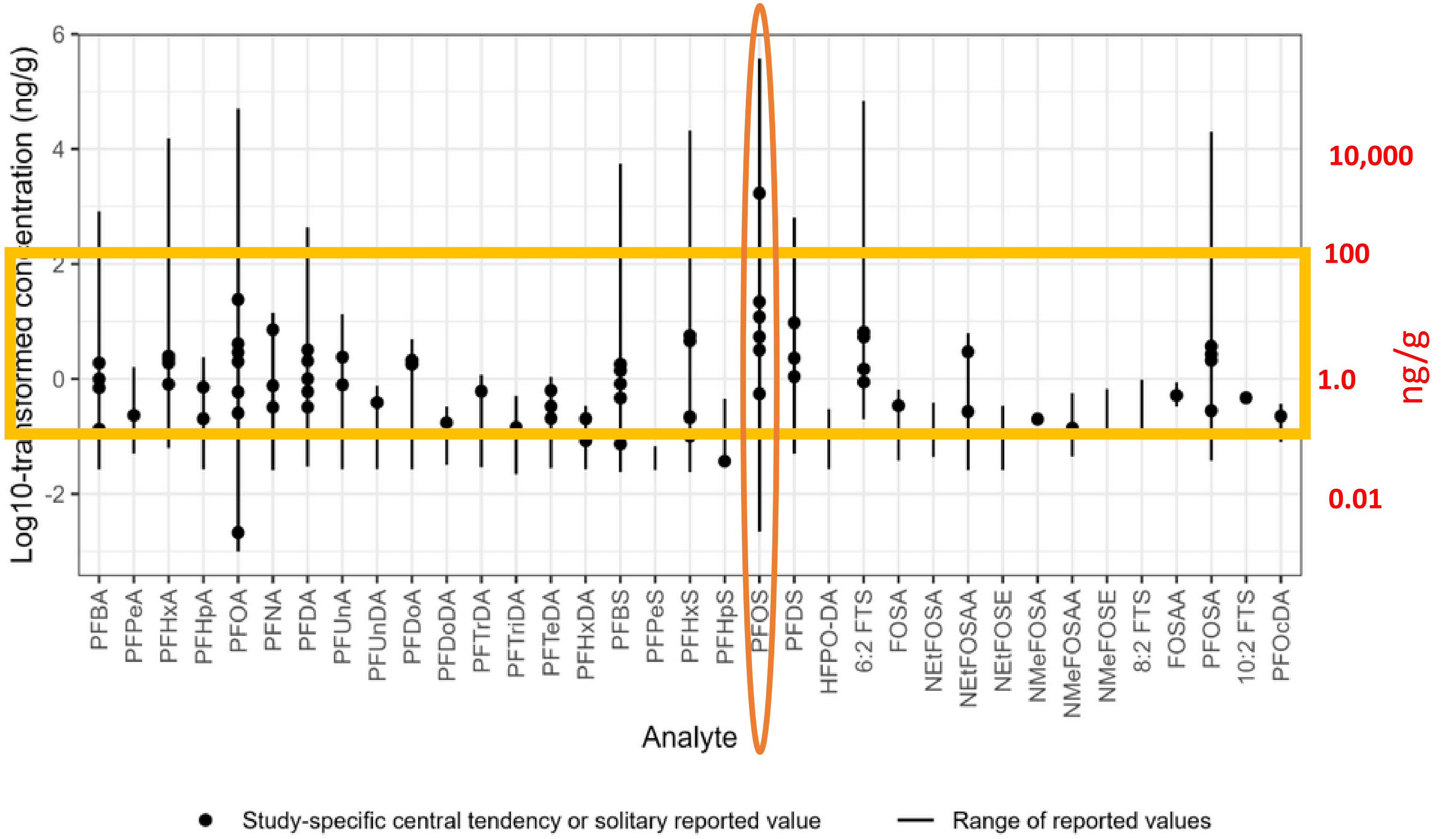
Biosolids processed in compost

- Less tracking
- Sold widely in commercial – retail settings
- Gardens, landscaping

Attributed to: Andrew Smith / *Muck-spreading on Little Down, Slindon* / CC BY-SA 2.0

PFAS in Land Applied Soil

- Highest concentrations found in surface soils
- PFOS still has high frequency of detection due to legacy application
- Field studies show preferential sorption of long chains vs short chains



Sources: Brusseau et al. (2020), Groffen et al. (2019), Sanborn Head & Associates (2022), Sorengard et al. (2022), USGS (2022), Wang et al. (2018)

PFAS-1, 2023 Section 6 Figure 6-2A, Observed PFAS concentrations in site and anthropogenic background soil. Source: Figure developed using ggplot2 (Wickham 2016).

PFAS in Land Applied Soil

Transport through the vadose zone at land application sites

Longer chain/precursors preferentially sorb in surface soil

Vertical Migration Extent Varies

- Studies report detectable PFAS to depth of 18 m but concentrations rapidly decrease with depth
- One study of FTOHs found no detectable concentrations in depth intervals below 10 cm

Composition of detected PFAS may change with depth, with greater PFCAs vs PFSAs detected

References in PFAS-1: Sepulvado, JG. et al, 2011; Johnson, GR. 2022; Washington, JW. et al. 2010.

Biosolids are different from AFFF sites!

	Biosolids	AFFF
Concentrations	Up to 618 µg/kg (Table 6-2C) *over large area (~10s-100s of acres)*	Up to 373,000 µg/kg (Table 6-2A) *over limited area (~<1 acre)*
Sources	PFAS in wastewater (municipal or industrial); 1980s to present	AFFF produced with PFAS; mid-1960s to present
Site Types	Mostly agricultural and other land application sites; broad area at limited frequency	Fire training/response areas at DoD, airports, oil-and-gas sites; higher application rate & frequency
Implications	Shallow soil impacts may affect crops and livestock, surface and groundwater	Local/regional sources may affect groundwater & drinking water

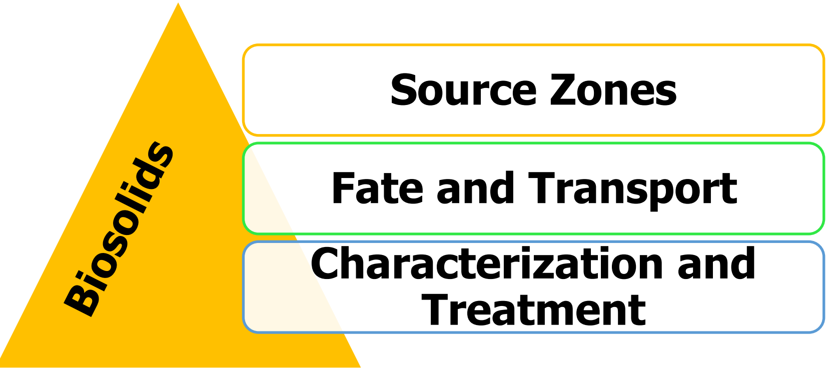
PFAS-1, Section 6.2 Soil, Sediment, and Biosolids.

*diPAPs - Polyfluoroalkyl Phosphoric Acid Diesters

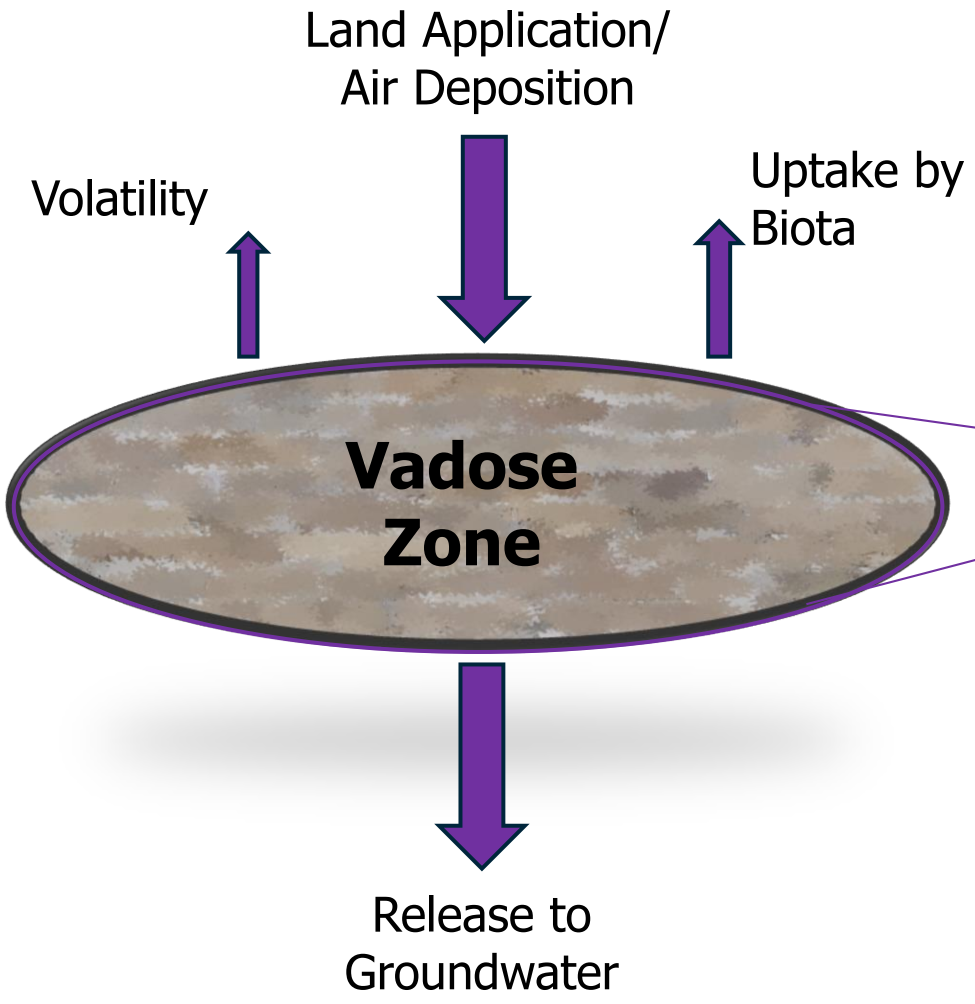
Biosolids and PFAS Fate and Transport in the Vadose Zone

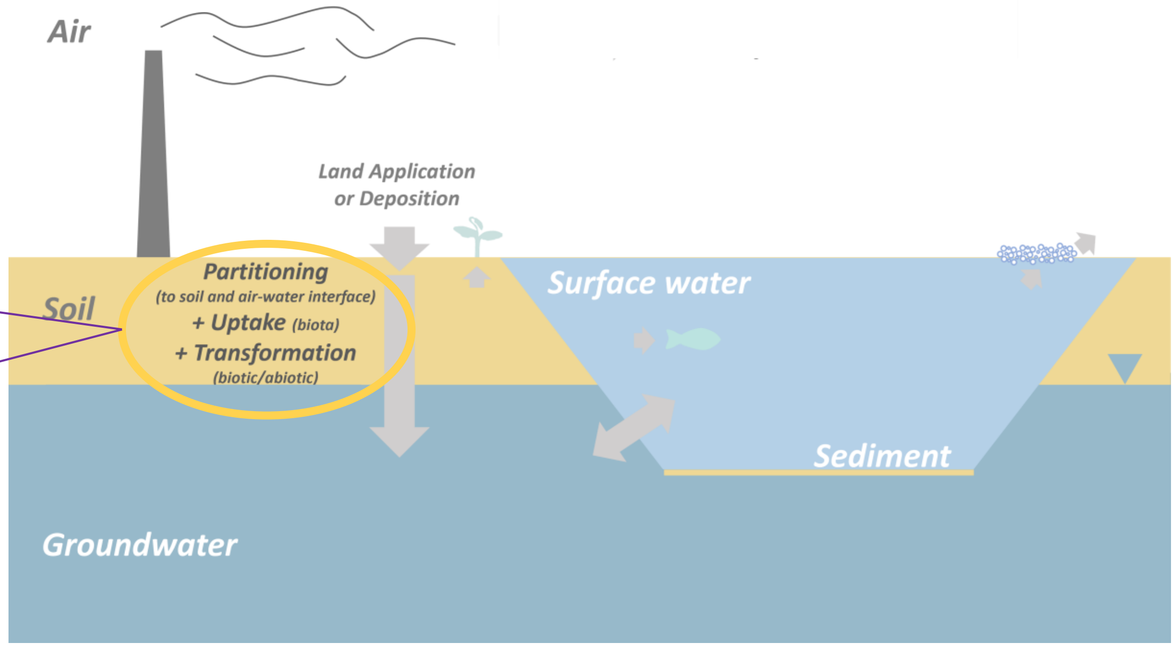
- Source Zone Characteristics
- **Vadose Zone Controls on Mobility**
- Field Scale Fate, Transport, Uptake
- Characterization and Treatment

Additional Biosolids Considerations & Summary



Macro-Scale Transport in the Vadose Zone



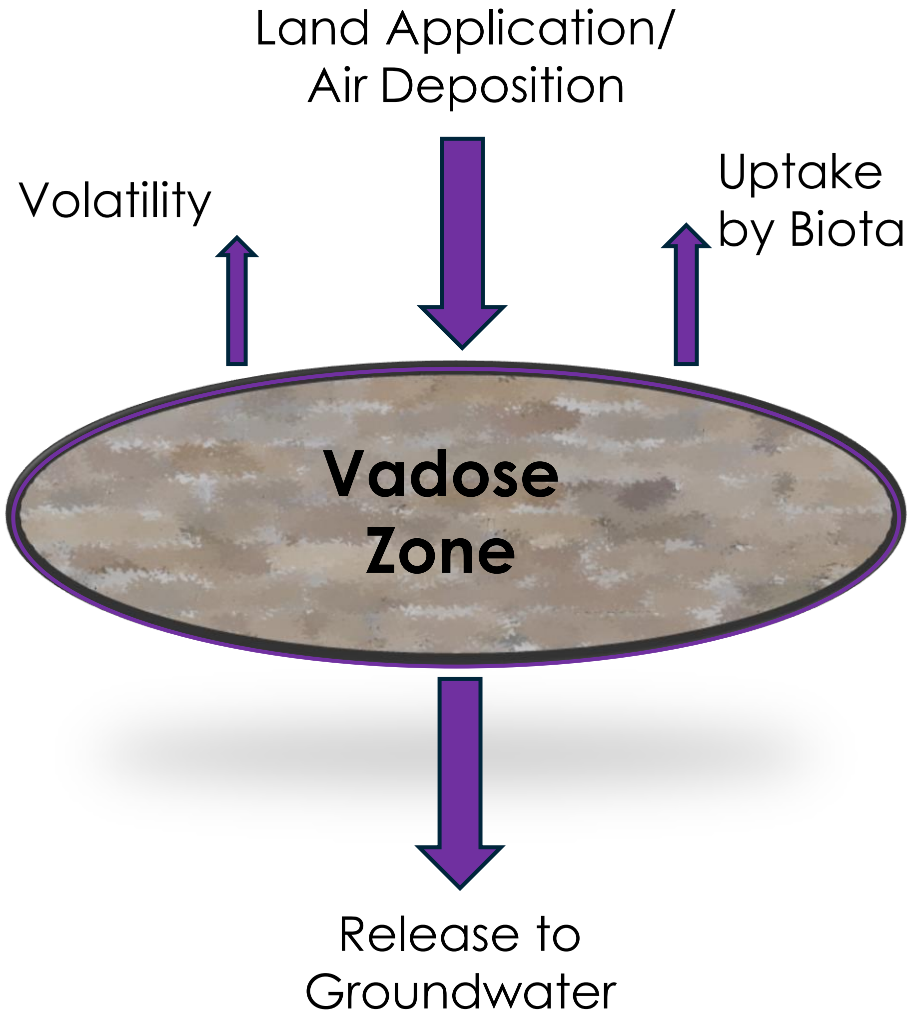


PFAS-1, Figure 5-1, Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Macro-Scale Factors Influencing PFAS Retention

Climate/Location

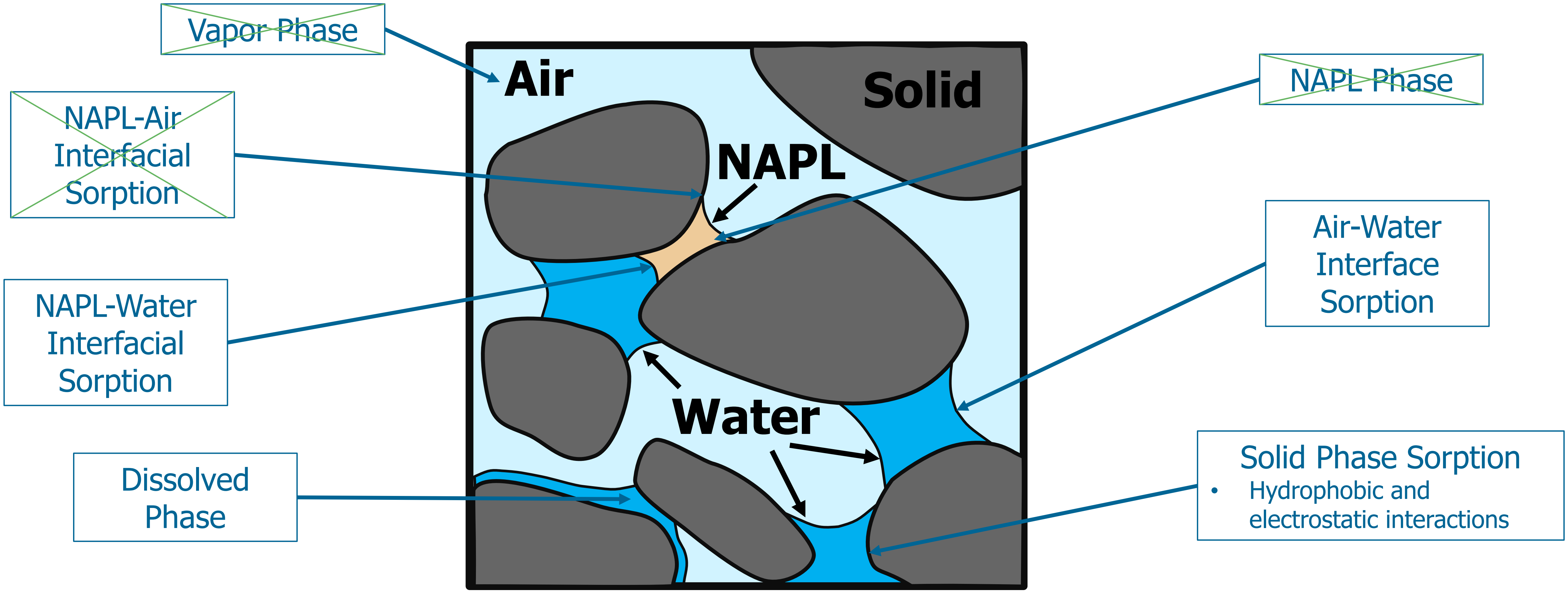
- Amount of precipitation
- Frequency of precipitation
- Depth to water
- Salinity
- Humidity



Soil Properties

- Surface Charge
- pH
- Heterogeneity
- Organic carbon content
- Soil type
- Degree of saturation

Micro-Scale Transport of PFAAs in the Vadose Zone

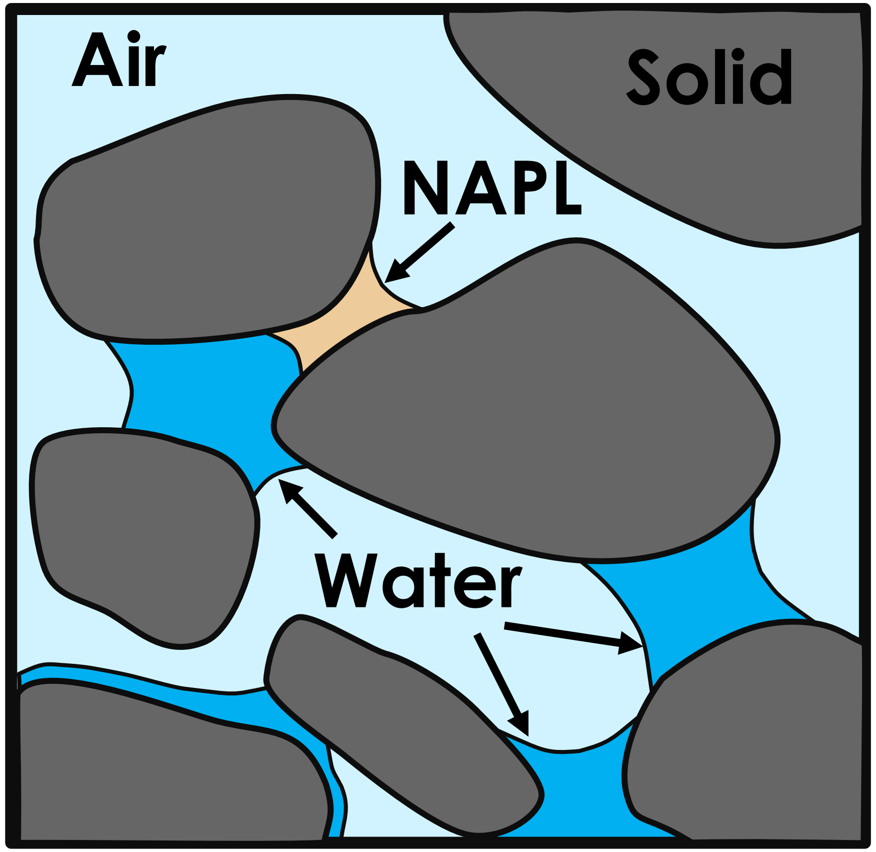


ITRC PFAS-1 Section 5.2

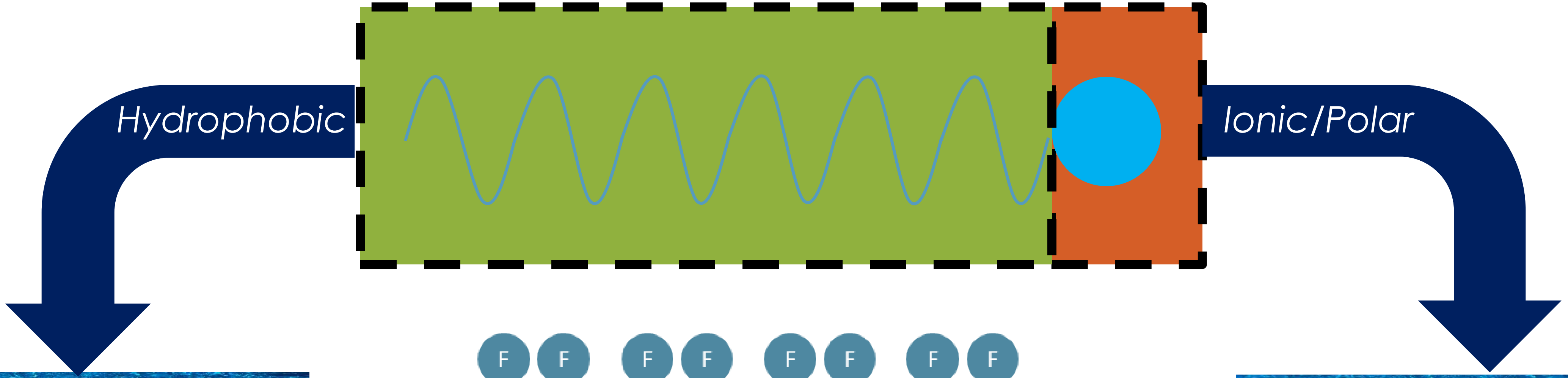
Micro-Scale Factors Influencing PFAS Retention

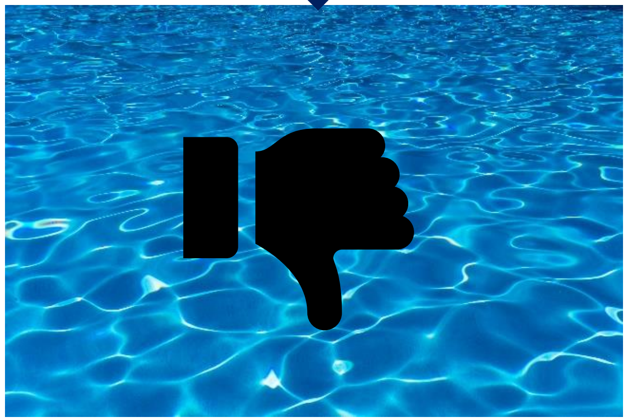
Properties of Solid Phase Sorption

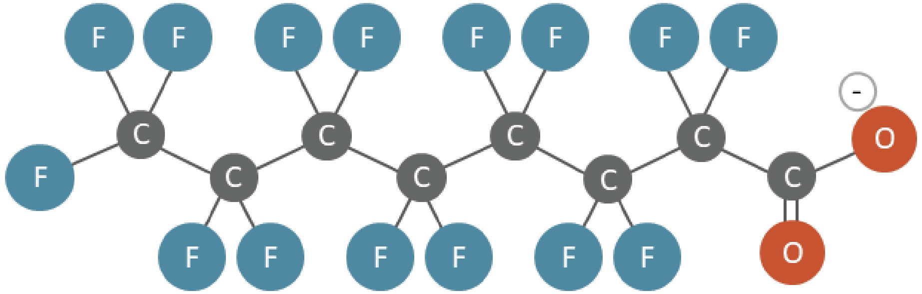
- Hydrophobic Partitioning
  - Longer chain PFAAs > shorter-chain PFAAs
  - PFSAs > PFCAs
  - Organic carbon dependent
- Electrostatic Interactions
  - Dependent on pH and ionic strength
  - Cationic/zwitterionic PFAS may strongly sorb
- Concentration dependent (nonlinear)
  - Sorption sites can become saturated
- Sorption properties change with precursor transformation



PFAA Surfactant Properties Are Important







Competing Interactions

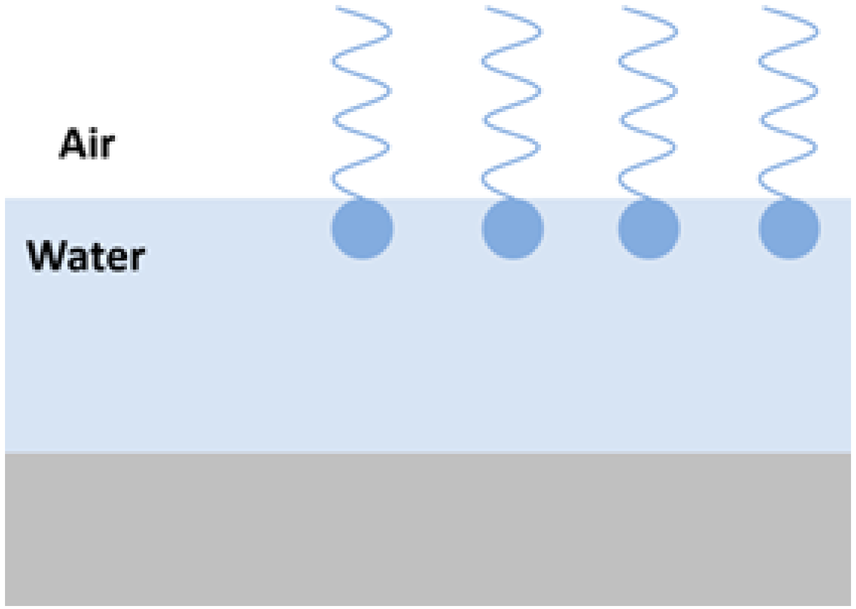
Molecule Figure Source: M. Olson, Trihydro. Used with permission.

PFAA Molecules Assemble at the Interface

Energetically favorable

Reduces the surface tension at the interface

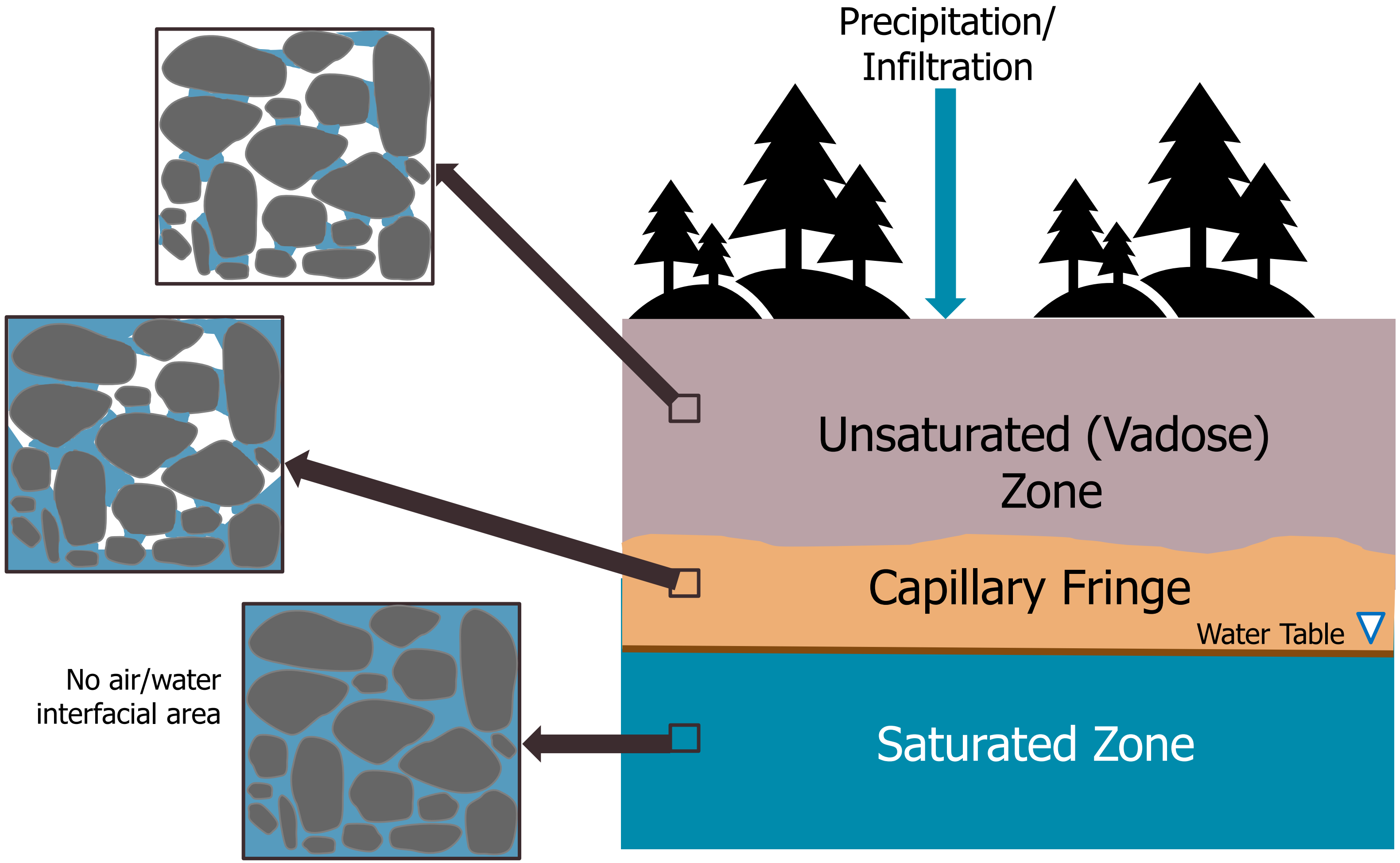
PFAAs have a greater affinity than traditional surfactants



ITRC PFAS-1, Figure 4-1, Example of expected orientation and accumulation of PFAS at air-water interface. Source: D. Adamson, GSI. used with permission.

ITRC PFAS-1 Section 5.2.4.1

PFAA Partitioning Depends on the Amount of Interfacial Area

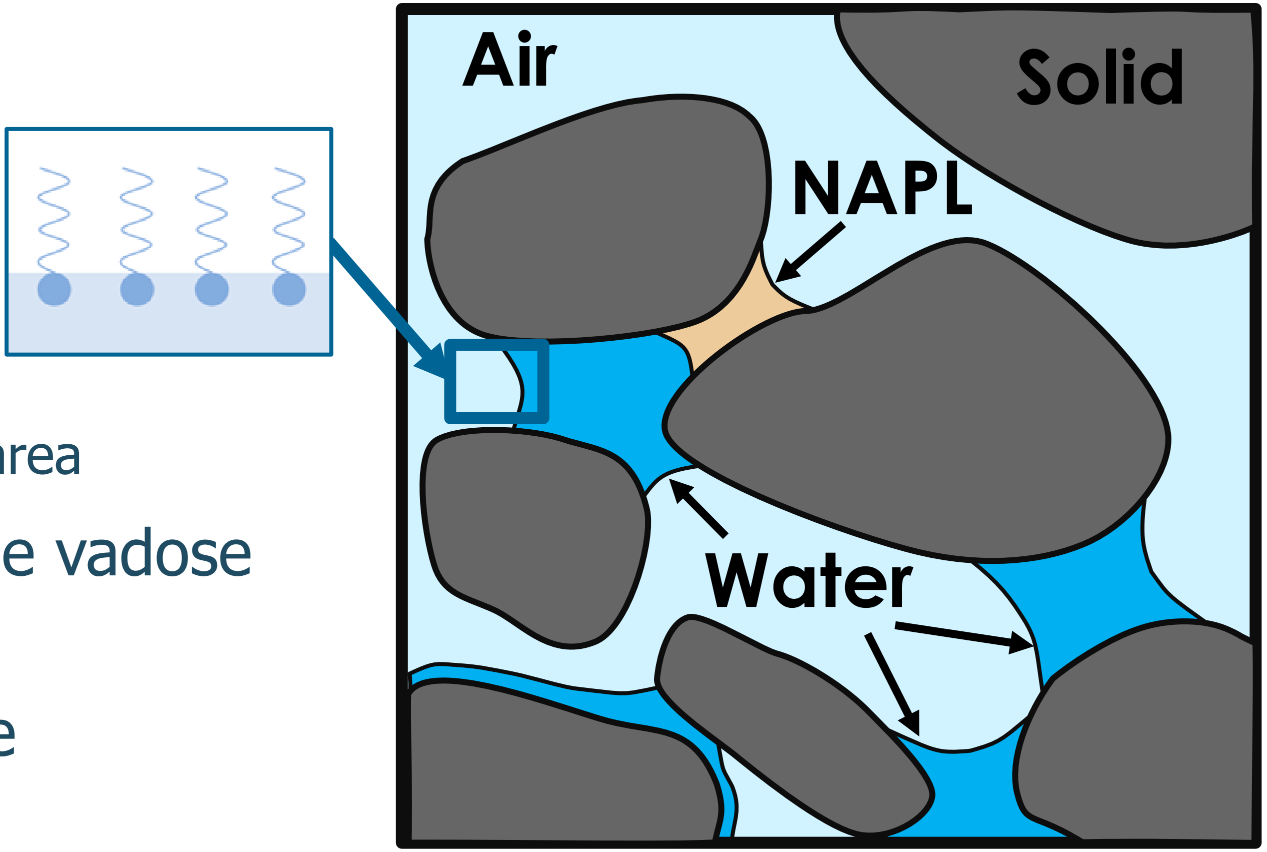


- Degree of water saturation affects the amount of interfacial area (nonlinear)
- Larger interfacial area enhances PFAA retention
- Factors affection A-W interfacial area:
  - Soil type
  - Grain size
  - Heterogeneity
  - Organic Content

ITRC PFAS-1, Sections 4.2.8, 5.2.4.1, 5.3.3

Studies/Support

- Many studies have shown that PFAAs can be highly enriched at the air-water interface
  - Enrichment increases with alkyl chain length
  - Concentration dependent
    - Nonlinear, inverse relationship
  - Increases with dissolved solids concentration
  - Dependent on extent of air-water interfacial area
- Studies point to long term retention in the vadose zone
- Relative importance of air-water interface partitioning is site specific



PFAS-1, Modified from Figure 4-1. Source: D. Adamson, GSI. used with permission.

ITRC PFAS-1, Sections 4.2.8, 5.2.4.1, 5.3.3

Micro-Scale Factors Influencing PFAA Retention

Air-Water Interface Sorption ≈? Solid Phase Sorption

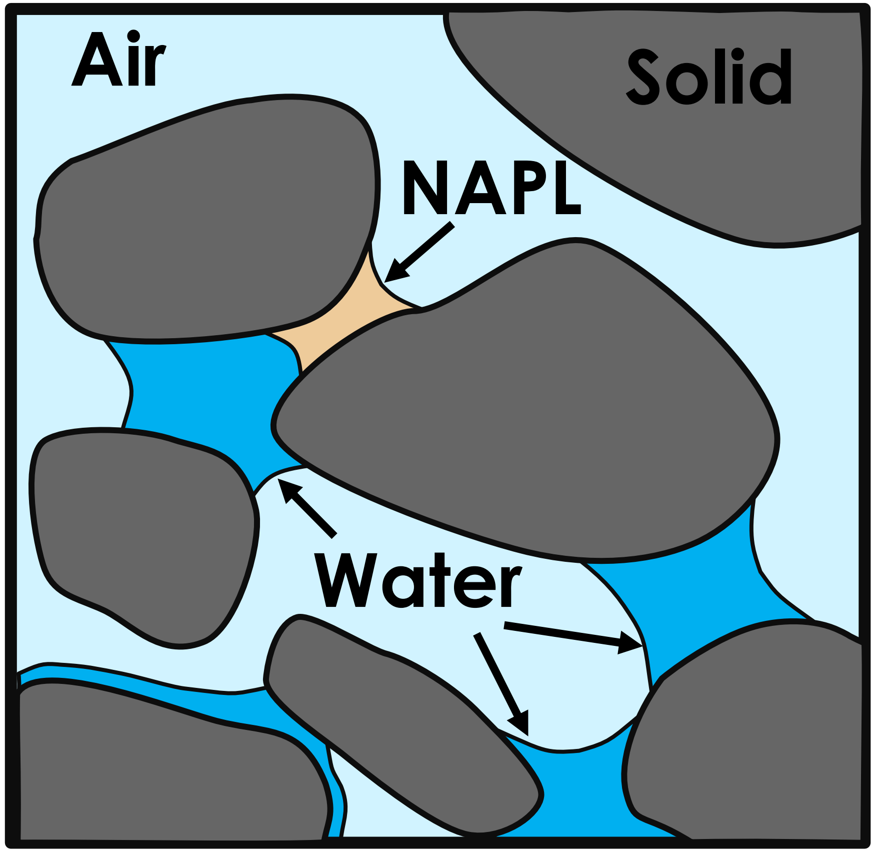
↓

Dissolved Phase ≈? NAPL-Water Interface Sorption

↓

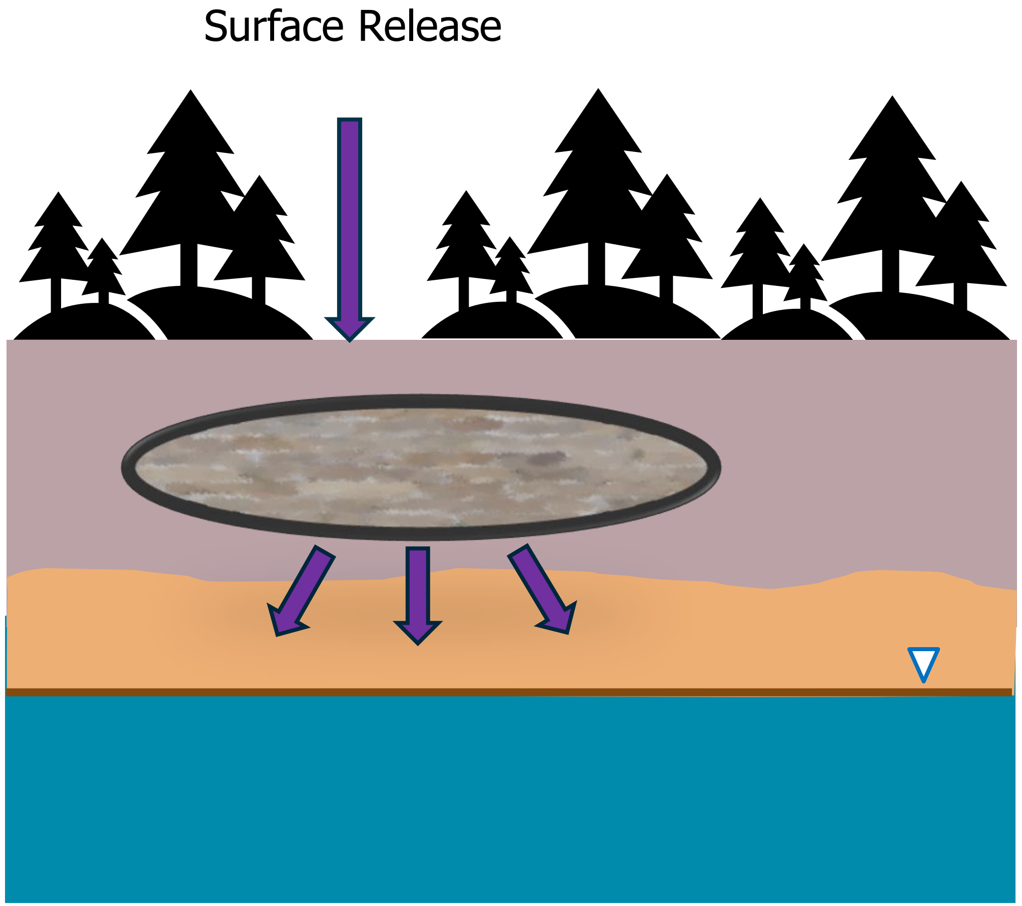
Vapor Phase | NAPL Phase | NAPL-Air Interface Sorption

Highly dependent on site conditions, concentration, PFAS compound, and other factors



Modeling

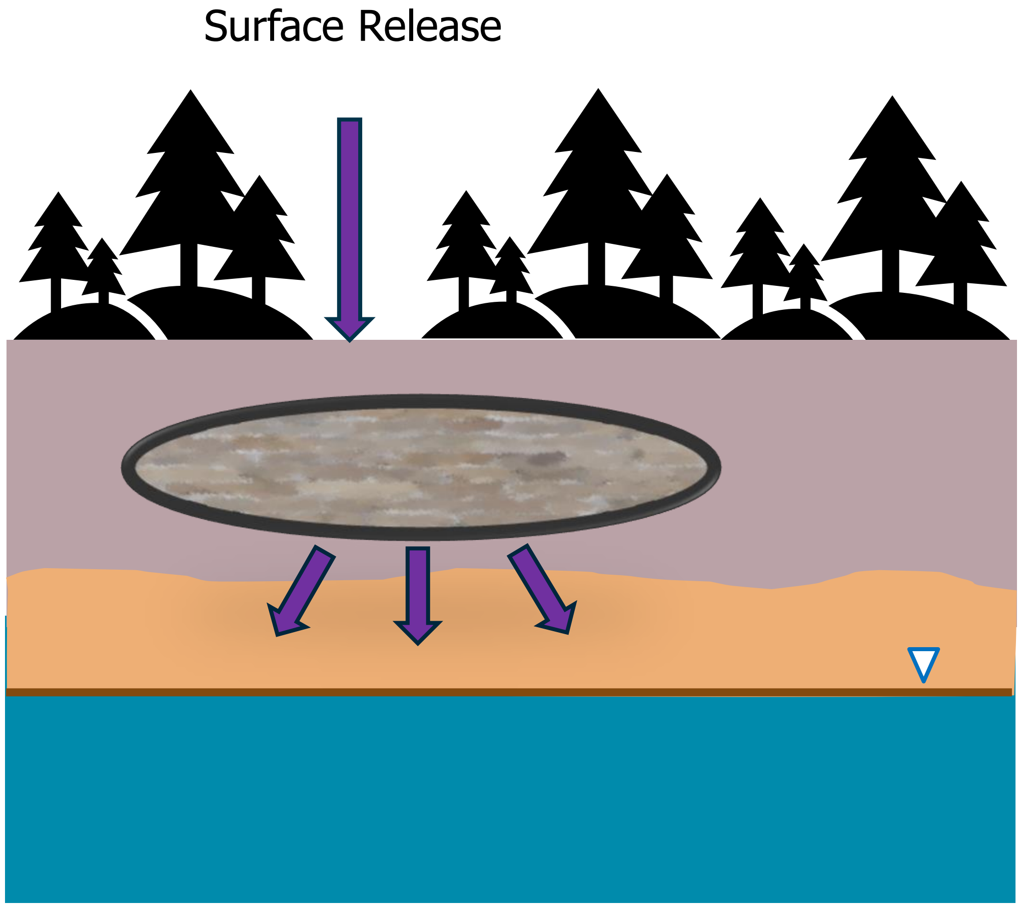
- Several researchers are developing models to understand fate and transport in the vadose zone
  - Consideration of air-water interfacial retention increases predictive accuracy
  - Highly dependent on prediction of site factors like air-water interfacial area
- Data gaps:
  - Role of micelle/hemimicelle formation
  - Other non-PFAA PFAS



PFAS-1 Section 10.4.1

Implications

- Transport of PFAS through the vadose zone after surface releases is an evolving topic
- Air-water interfacial sorption is likely a large contributor to vadose zone retention
  - Significant vadose zone retention is likely after a surface release like biosolids application
  - Creates a source zone that can contribute to groundwater on a long-term basis
- Still many unknowns with PFAS vadose zone retention



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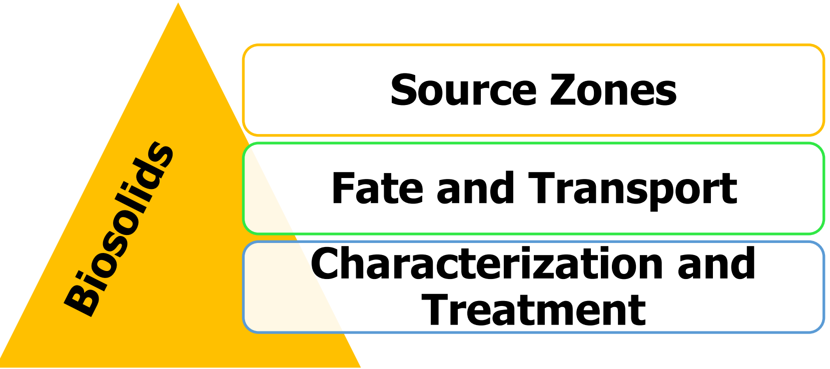
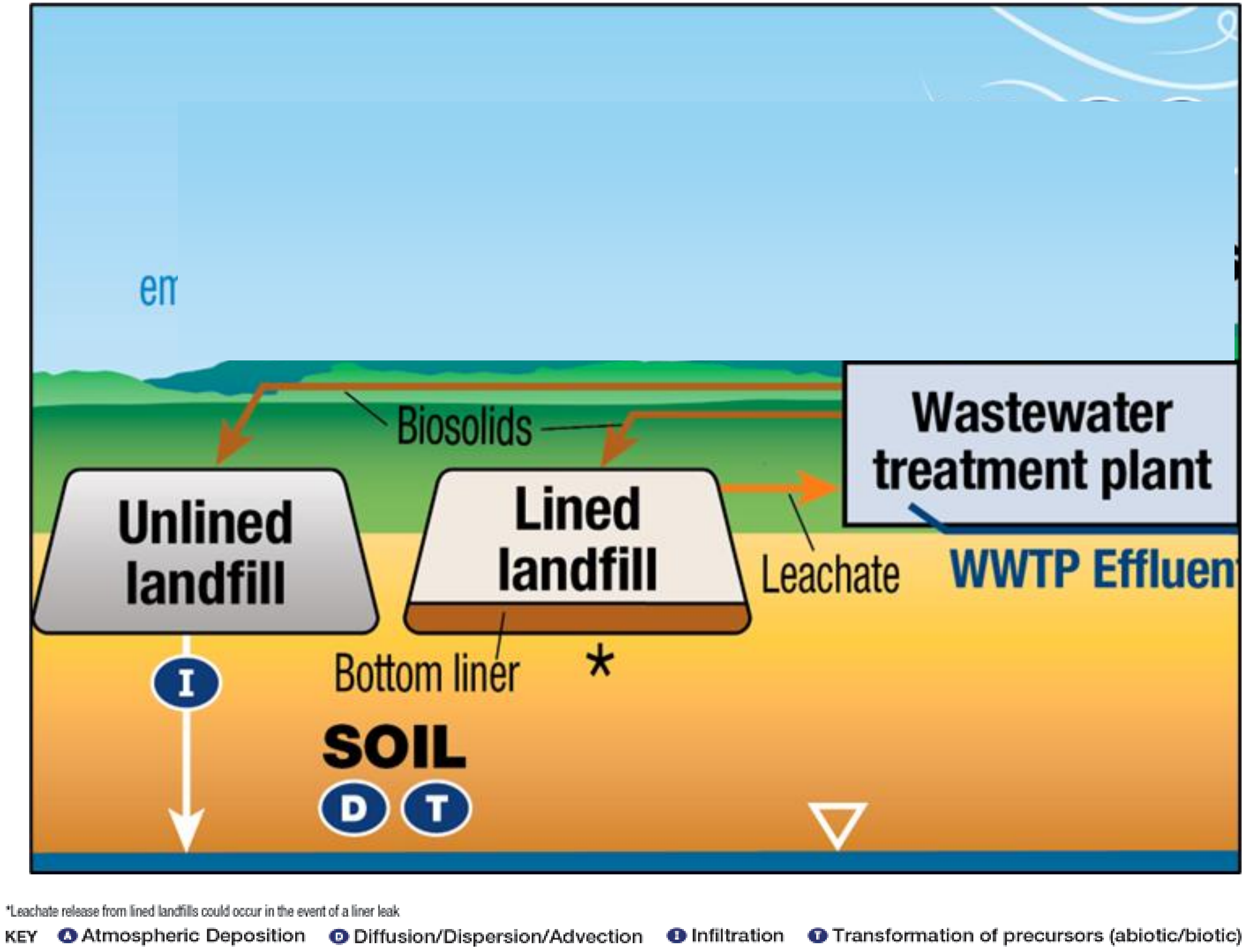


Cycling of PFAS Related to Biosolids

Wastewater treatment plants (WWTP) generating biosolids daily

- Residential
- Commercial/Industrial wastewater
- Leachate from lined landfills
- Inputs from pumping of residential septic tanks

WWTP sludge → Landfill → Leachate

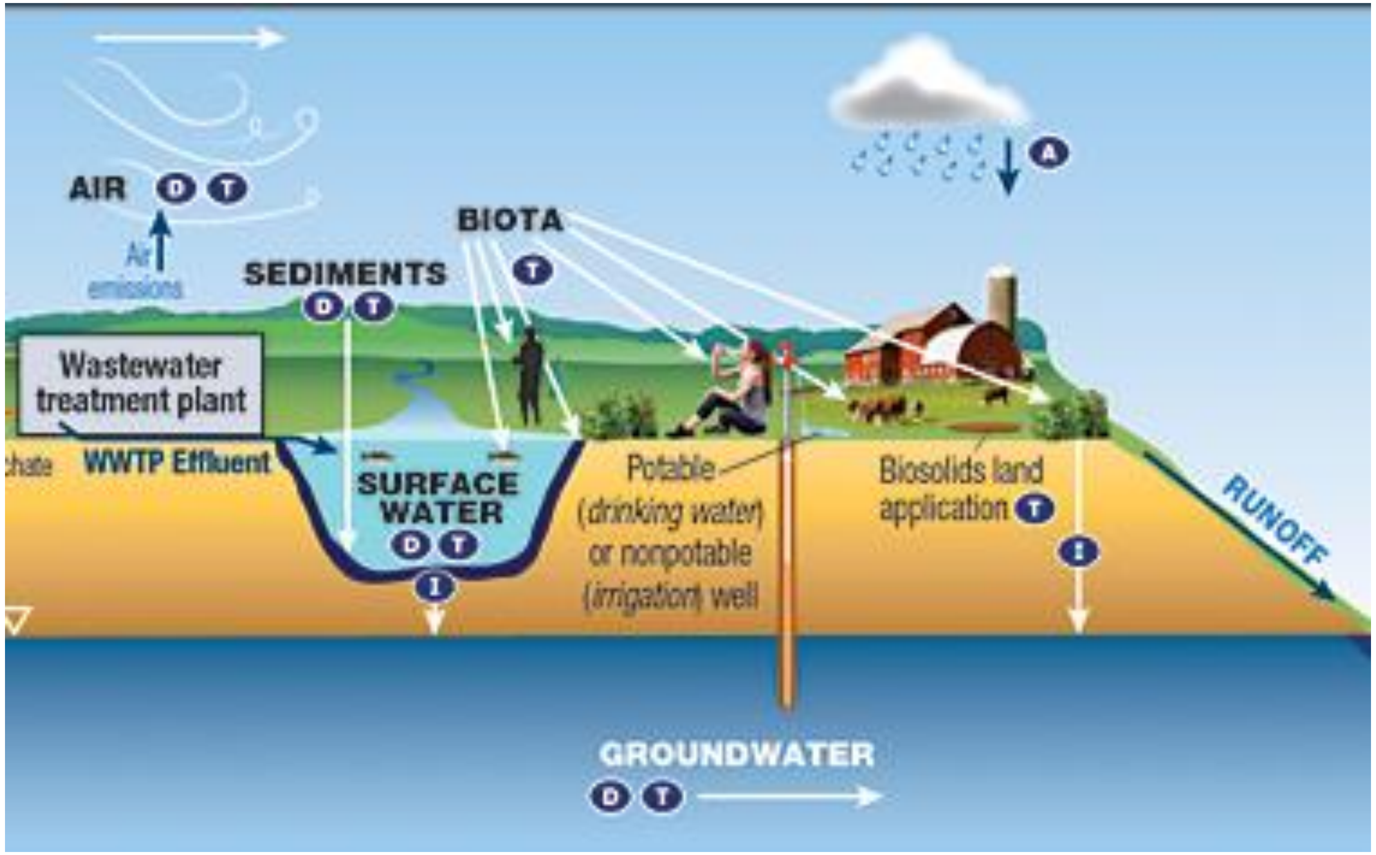


PFAS-1, Figure 2-22. CSM for landfills and WWTPs.
Source: Adapted from figure by L. Trozzolo, TRC, used with permission

Cycling of PFAS Related to Biosolids

Land application leaching may impact

- Crops
- Drinking water
- Dairy
- Meat
- Waterways and Fish



*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)

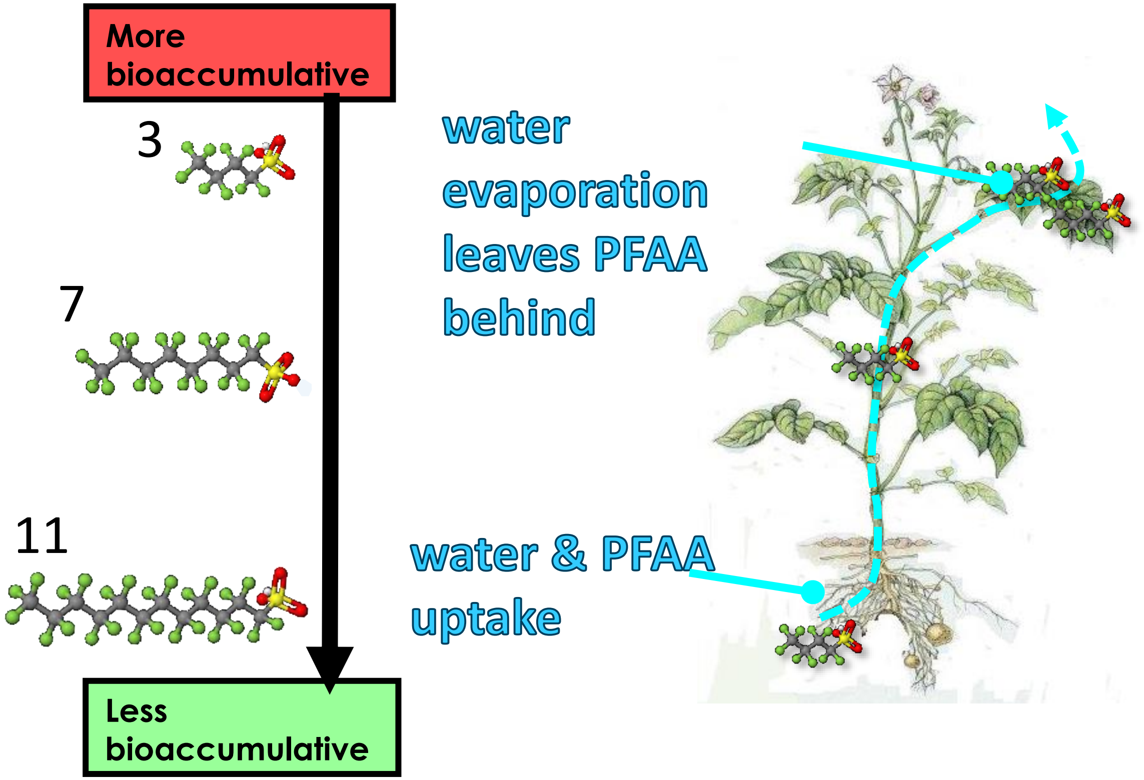
PFAS-1, Figure 2-22. CSM for landfills and WWTPs.
Source: Adapted from figure by L. Trozzolo, TRC, used with permission

PFAS Uptake in Plants

- High solubility of PFAS and hydrophilic functional group means plants can readily absorb PFAS in water or contaminated soil

- Bioconcentration factor (BCFs)
  - BCF = C(plant) / C(soil)
  - Values range from ~0.01 to 1000; but typically 0.1 to 10 (~70%)

- Greater concentrations in watery tissues (e.g., lettuce leaf, tomato fruit)



See Table 5-2 for list of bioconcentration factors

PFAS-1, Section 17.3 Figure 17-2 Bioaccumulation of PFAS in plants. Source: J. Conder, Geosyntec. Used with permission.

PFAS Uptake in Animals

- Dairy cows and other livestock may be exposed to PFAS from feed or water supply
- Aquatic animals exposed through runoff from fields
- Bind to proteins in blood, liver, and kidneys
- PFAS bioaccumulation
  - Long-chain PFAS generally accumulate more and have longer elimination half lives
  - PFSAs > PFCAs
  - Biomagnification up food chain
  - Precursor transformation

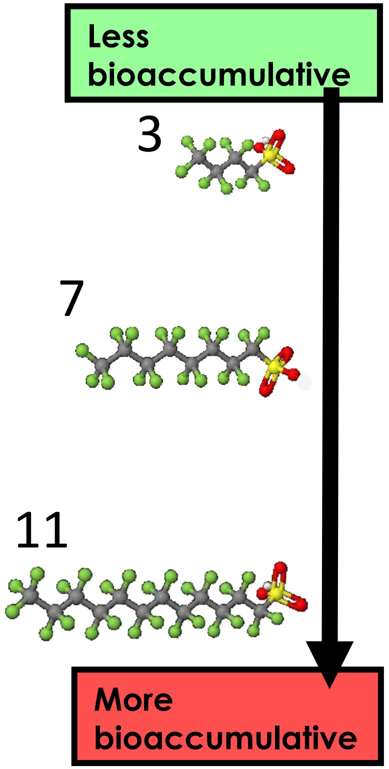
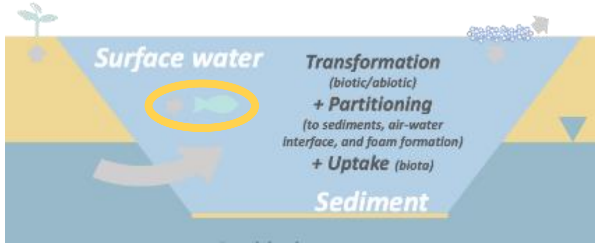


Photo by Frans de Wit licensed under https://creativecommons.org/licenses/by-nc-nd/2.0/#



PFAS-1, modified from Figure 5-1. Source: D. Adamson, GSI, used with permission.

PFAS-1, Section 17.3 Figure 17-2 Bioaccumulation of PFAS in plants. Source: J. Conder, Geosyntec. Used with permission.
Table 5-1 includes BAF, BCF and BMF values for various PFAS in aquatic organisms.

Biosolids and PFAS Fate and Transport in the Vadose Zone

- Source Zone Characteristics
- Vadose Zone Controls on Mobility
- Field Scale Fate, Transport, Uptake
- **Characterization and Treatment**

Additional Biosolids Considerations & Summary

Biosolids

- **Source Zones**
- **Fate and Transport**
- **Characterization and Treatment**

Site Investigations – Land-Applied Biosolids

General considerations

- Historical records
  - Record keeping varies; potential unidentified sources?
- Large application areas
- Transport potential
  - Receptors/pathways
- Other nearby sources
- Risk communication

Photo Source: C. Evans, ME DEP. Used with permission

PFAS-1, Section 10. Site Characterization
Section 14. Risk Communication

Site Investigations – Land-Applied Biosolids

Site-sampling considerations

- Application
  - Liquid or solid; soils possibly tilled
- Potentially sampled media
  - Source biosolids, soils, groundwater, pore water, surface water
- Transport potential
  - Surface runoff or infiltration
  - Pooling in low areas - PFAS accumulation?
- General PFAS-sampling protocols
- Appropriate analytical methods
  - 1633 appropriate for biosolids & soils
  - Fingerprinting/source ID; Would "total" PFAS data be useful?

Photo Source: C. Evans, ME DEP. Used with permission

PFAS-1, Section 10. Site Characterization; Section 11. Sampling and Analysis; Section 14. Risk Characterization

Biosolids Treatment-Disposal

Land Application
- Regulated/permit-limited process
- Application rates tied to nutrient management at farms
- Potential for leaching to groundwater or uptake

Landfilling
- Considerations include capacity of facilities
- Landfill leachate may be sent to WWTP

Incineration
- Recent studies document 99+% destruction effectiveness
- Potential concerns re: incomplete combustion
- *…other destructive methods in development: Supercritical Water Oxidation (SCWO), pyrolysis*

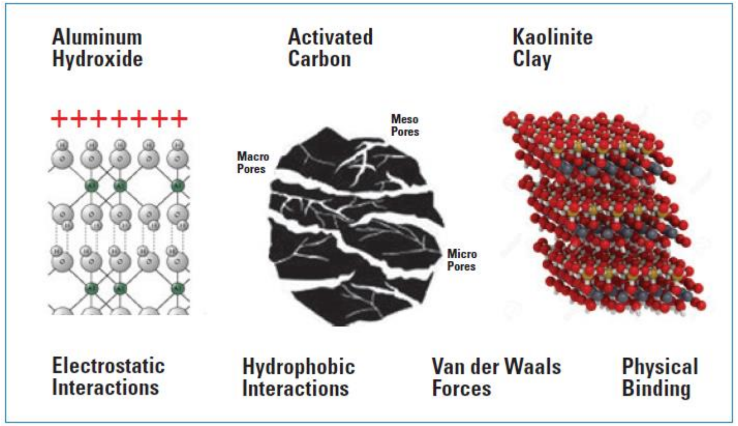
Photo from: http://clui.org/ludb/site/east-liverpool-hazardous-waste-incinerator.

PFAS-1, Section 2.6.3, Solid Waste Management Facilities; Section 2.6.4 Wastewater Treatment, Treatment Residuals and Biosolids; Section 12.4 Incineration; Section 12, Table 12-1, Treatment Technologies

Biosolids Treatment – Disposal

Soil stabilization/sorption

- Amendments to reduce PFAS release from solid media
- Established technology being adapted for PFAS
- Recent studies document reductions in PFAS leaching
- Scalable to biosolids and/or land-applied soils?
- Limitation: PFAS are not removed/destroyed



Images courtesy of Ziltek™ and AquaBlok Ltd. Used with permission.

Biosolids Treatment – Disposal

- Elimination of upstream sources to WWTP

- Treatment or reduction at WWTP prior to biosolids generation
  - GAC, ion exchange resin
  - Foam fractionation or other concentration methods
  - Pre-treatment for BOD, etc.

PFAS-1, Section 2.6.4 Wastewater Treatment, Treatment Residuals and Biosolids.
Table 12-1 Treatment Methods Table

Graphic used with permission, Scott Grieco, adapted from Stew Abrams and Purolite.
Photo used with permission, Francis Boodoo, Purolite.

Biosolids and PFAS Fate and Transport in the Vadose Zone

- Source Zone Characteristics
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Additional Biosolids Considerations & Summary

Biosolids

- **Source Zones**
- **Fate and Transport**
- **Characterization and Treatment**

PFAS Regulatory Environment

New & pending Federal regulations may affect management of biosolids

Inputs to WWTPs	Transportation
Disposal	Lower screening values

See the ITRC PFAS Regulatory Programs Table; Section 8.2

PFAS Regulatory Environment

USEPA Strategic Roadmap 2021-2024

- Includes future reductions in allowed PFAS in NPDES permitted discharges
  - EPA memo (December 2022) provides guidance for permit writers to include PFAS monitoring in discharge permits
- Risk Assessment for PFOA and PFOS in biosolids – winter 2024
- Maximum Contaminant Levels under the Safe Drinking Water Act (MCLs) for 6 PFAS
  - PFOS, PFOA at 4 ng/L (ppt)
  - PFHxS, PFNA, HFPO-DA (GenX) at 10 ng/L (ppt)
  - Hazard Index of 1.0 for 4 PFAS (PFNA, PFHxS, PFBS, GenX)

Biosolids Testing for PFAS

Standard Methods currently approved

- Most testing by a Modified 537.1 with some level isotope dilution
- Method 1633 completing multi-lab verification now final
- Others – ASTM D8421-22

Standard reporting lists limited; other techniques required to report additional precursors and "non-target" PFAS

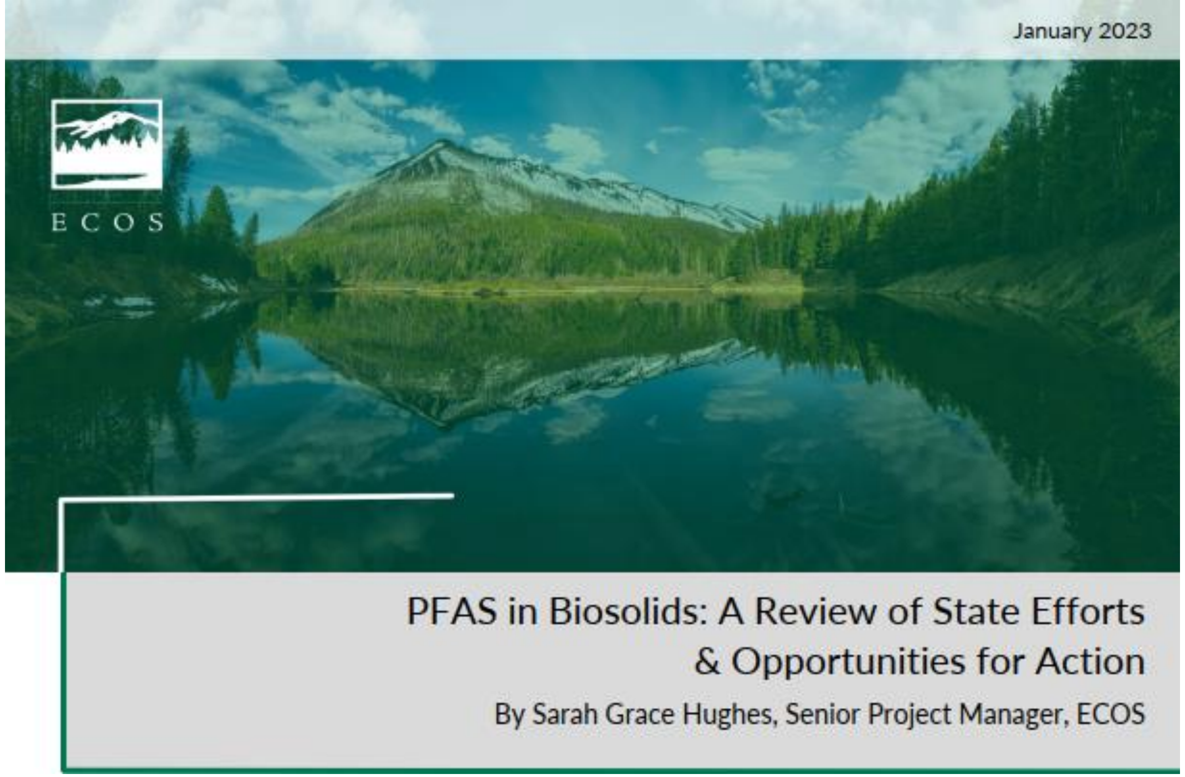
- TOP
- AOF
- High Res MS

State-Level Response to PFAS in Biosolids

Environmental Council of States (ECOS) study on PFAS in Biosolids

Published [January 2023]

Survey, 34 states responded



Joint Principles for Preventing and Managing PFAS in Biosolids

- Protect communities
- Reduce presence in wastewater
- Preserve flexibility and use, prioritize public health
- Ensure safety of food supply, support impacted farmers/ranchers
- Educate stakeholders/communicate risk
- Build capacity
- Embrace transparency and innovation

Published July 2023

Final Points

PFAS are associated with wastewater & biosolids due to decades of widespread production/use

After biosolids(or AFFF) land application PFAS tend to be retained in shallow soils

- May gradually leach to GW or be taken up by plants

Biosolids treatment involves destruction of biosolids or removal of PFAS before biosolids production

Biosolids have been regulated for decades; PFAS/biosolids regulations are evolving

ITRC PFAS Resources

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

Guidance Document

13 Fact Sheets

External Tables

PFAS Introductory Training

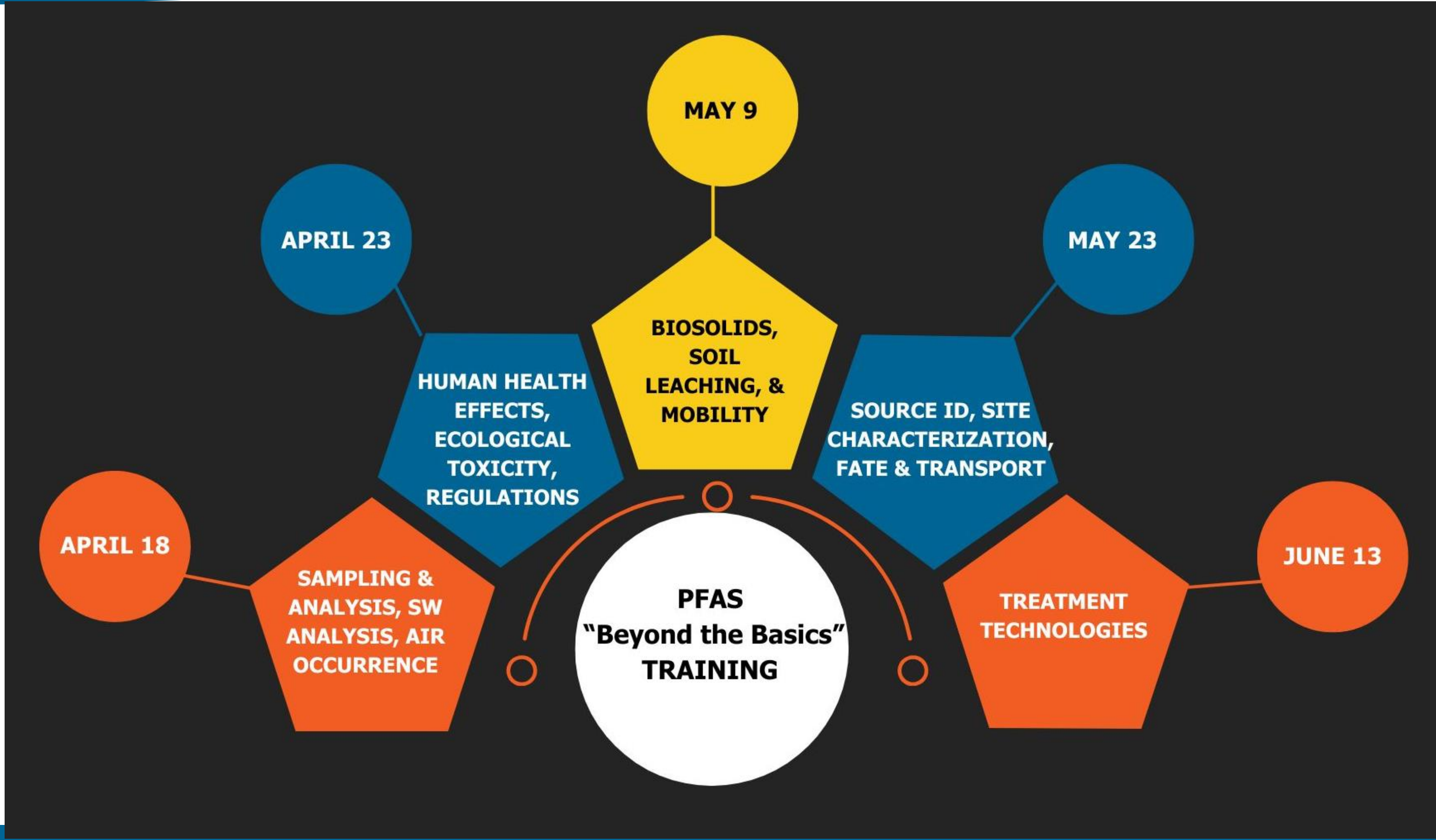
- Clu-In Archive: https://www.clu-in.org/conf/itrc/PFAS-Introductory/

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-Biosolids



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