Emerging technologies for an emerging contaminant: Practical Drivers for PFAS Remediation

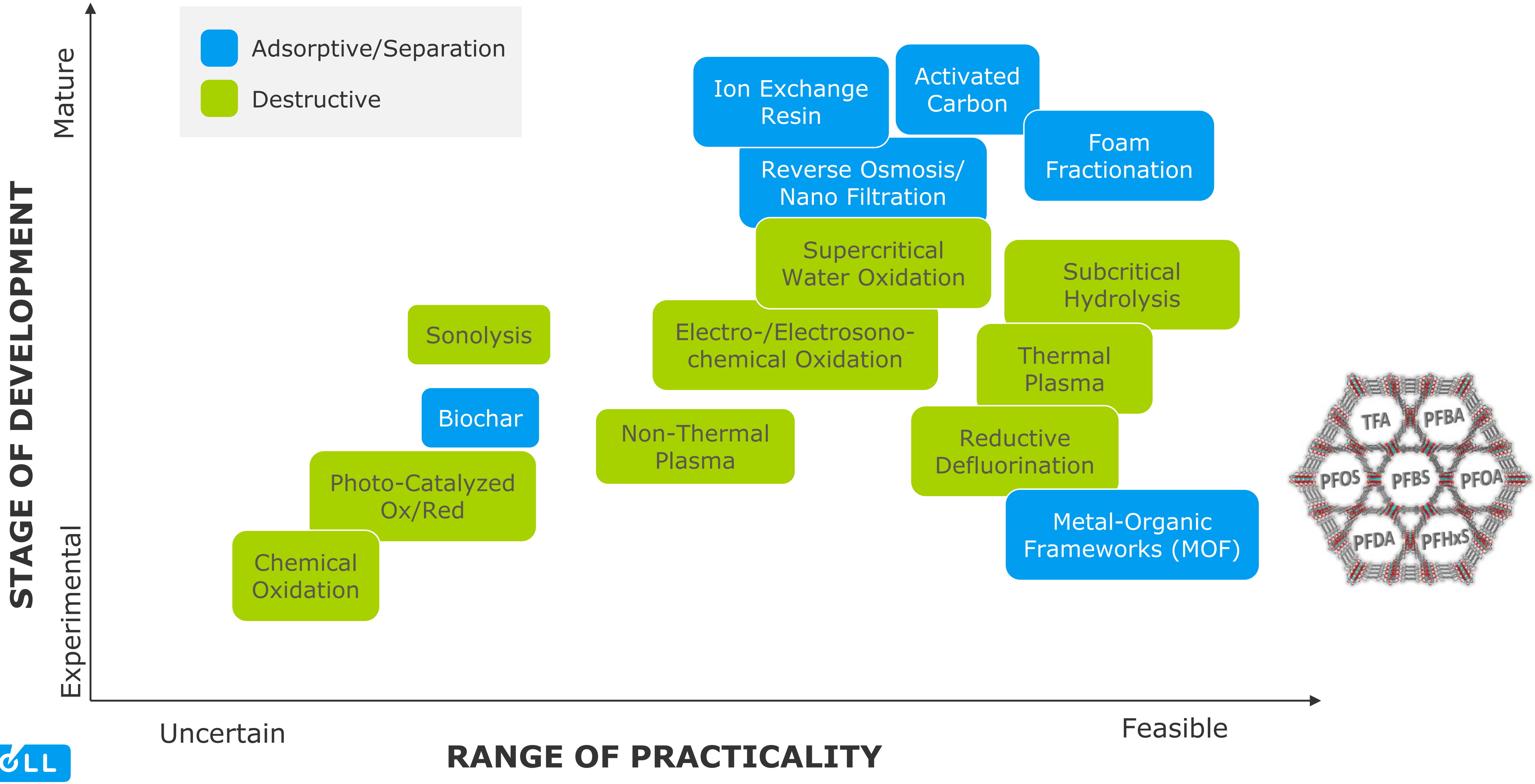
Jim Fenstermacher, PE
Ramboll, Blue Bell PA, USA

Photon Water
Photon Remediation
Albemarle
ALL THE ELEMENTS FOR A BETTER WORLD
CARUS®
Deltares
CZU Czech University of Life Sciences Prague

PFAS TECHNOLOGIES REPORTED BY MEDIA (2008-2022)

	Groundwater or Surface Water	Wastewater (municipal or industrial)	Leachates	AFFF Concentrate and Equipment	Soils	Bio-solids	Spent Media	Subtotals
Sorption and Ion Exchange	115	13	15				5	148
Chemical oxidation/ degradation	64	3			6			73
Membrane (RO/NF/electro membrane)	35	7	2					44
Microbial Bioremediation (anaerobic/aerobic)	1		1		27	9		38
Electrochemical oxidation (w/wo oxidant)	21	8	2		4			35
Photocatalytic oxidation/degradation	22	10	1					33
Concrete/Soil Fixation/solidification					30			30
Thermal destruction	7		1		5	4	3	20
Phytoremediation	4	1			15			20
Coagulation/Electro-coagulation	14	2		1	1			18
Reductive defluorination	13							13
Other, aqueous technologies	17	4	5	11				37
Other, solid media technologies					24	11	7	42
Subtotals:	313	48	27	12	112	24	15	551

STATE OF AQUEOUS TREATMENT TECHNOLOGIES

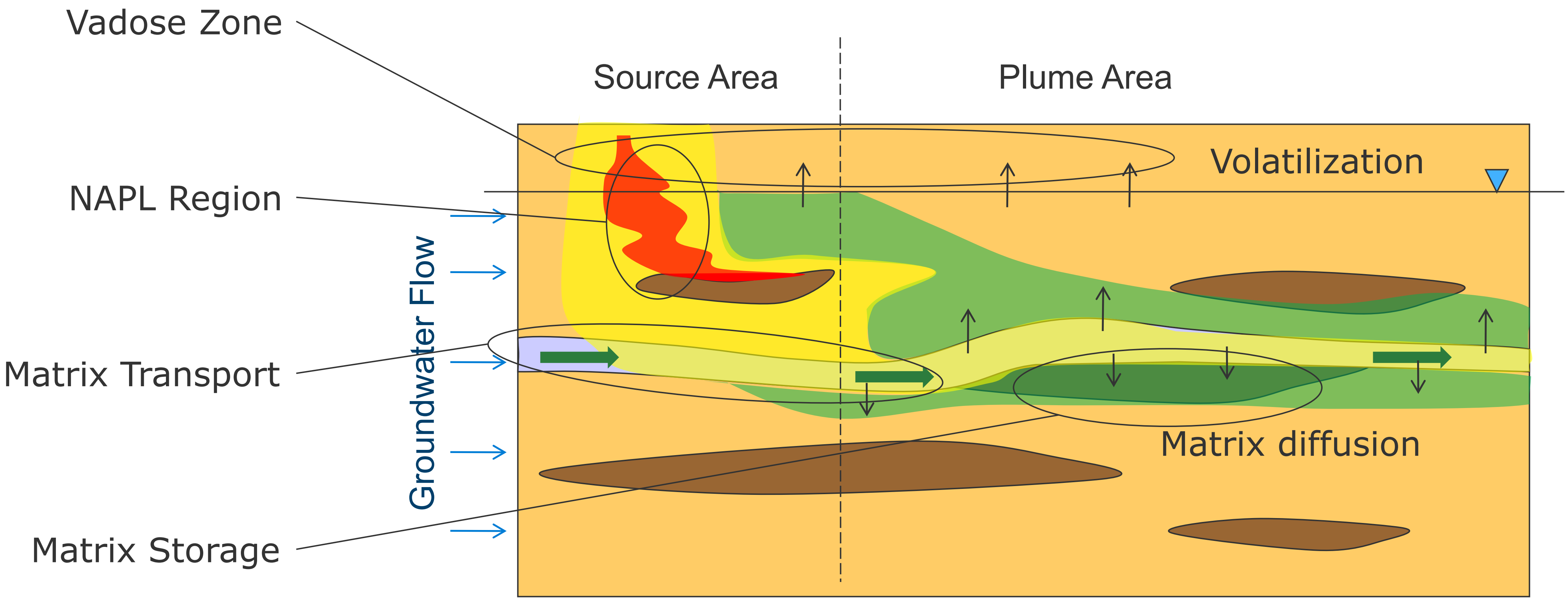


RAMBOLL

Modified from: Ross, et al., 2018. *Remediation* 28:101–126.

HOW ARE THESE TREATMENT TECHNOLOGIES APPLIED?

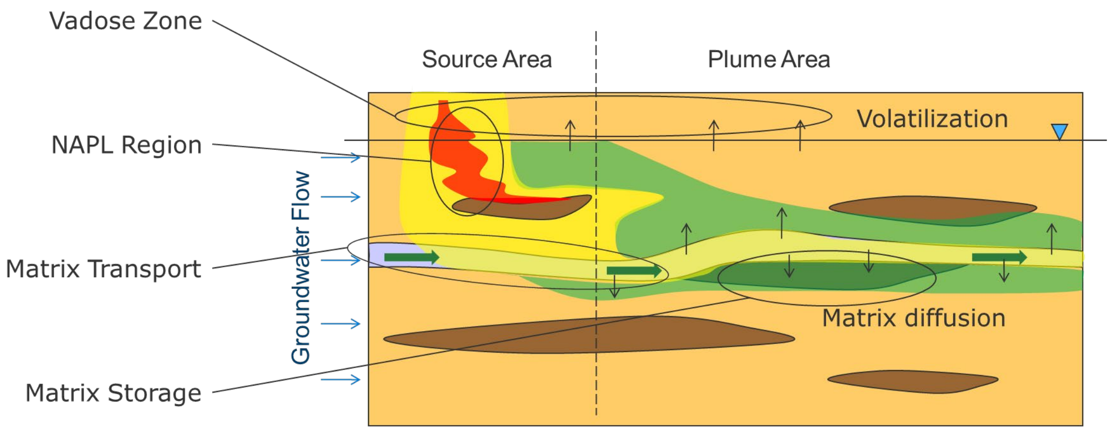
"CLASSICAL" CONTAMINANT BEHAVIOR…



Red, Yellow, Green = Decreasing Concentration

From: *Integrated DNAPL Site Strategy*, ITRC, 2011

THE "CLASSICAL" 14-COMPARTMENT MODEL…



Red, Yellow, Green = Decreasing Concentration

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

Reversible pathway
Irreversible pathway

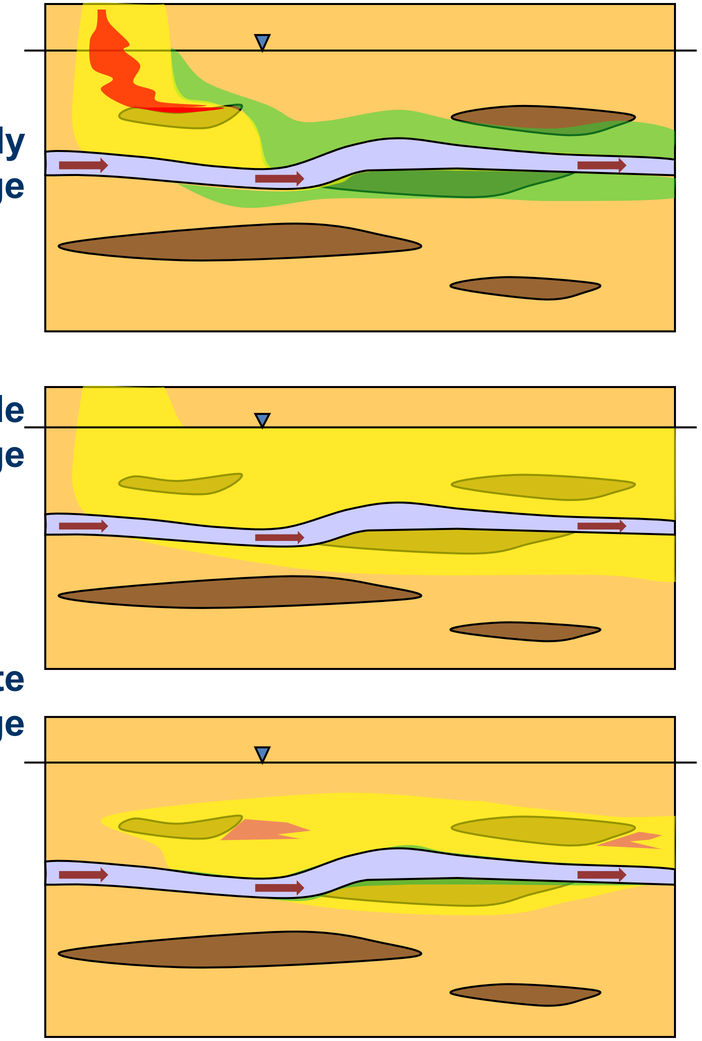
Integrated DNAPL Site Strategy, ITRC, 2011

DEPICTING MASS STORAGE WITH THE 14-C MODEL

Early Stage

Middle Stage

Late Stage



Early/middle stage

	Source Area		Plume Area	
	Low-Perm	Transport	Transport	Low-Perm
Vadose	2	2	2	1
NAPL	4	3		
Aqueous	3	3	3	2
Sorbed	3	3	3	2

Late/middle stage

	Source Area		Plume Area	
	Low-Perm	Transport	Transport	Low-Perm
Vadose	1	1	1	1
NAPL	2	2		
Aqueous	3	2	2	3
Sorbed	3	2	2	3

Relative mass distribution within compartments

4	>90%
3	>9%
2	1-5%
1	≤1%
0	~0%

Storage is dependent on contaminant properties and age of release

Forces practitioner to think through where contaminant mass is stored, and to think through the subsurface as a *system* that's seeking an *ever-evolving equilibrium*.

***Integrated DNAPL Site Strategy*, ITRC, 2011**

DEPICTING REMEDY EFFECTIVENESS WITH THE 14-C MODEL

Relative treatment within compartments

4	>90%
3	>9%
2	1-5%
1	≤1%
0	~0%

	Source Area		Plume Area	
	Low-Perm	Transport	Transport	Low-Perm
Vadose	2	2	2	1
NAPL	4	3		
Aqueous	3	3	3	2
Sorbed	3	3	3	2

Pump and Treat at source area

	Source Area		Plume Area	
	Low-Perm	Transport	Transport	Low-Perm
Vadose	0	0	0	0
NAPL	1	2		
Aqueous	1	2	1	0
Sorbed	0	1	1	0

	Source Area		Plume Area	
	Low-Perm	Transport	Transport	Low-Perm
Vadose	2	2	2	1
NAPL	3	1		
Aqueous	2	1	2	2
Sorbed	3	2	2	2

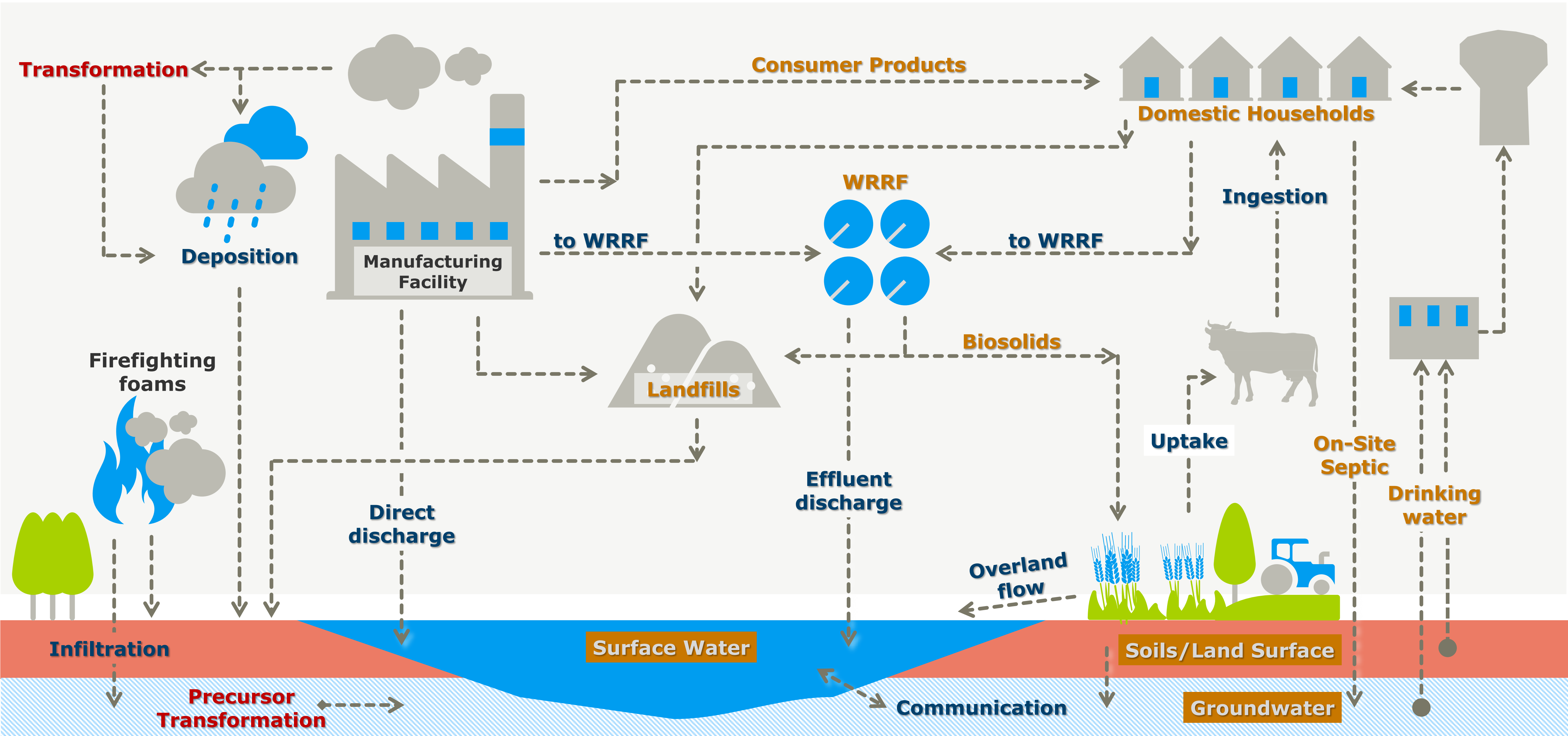
ISCO with soil mixing at source area

	Source Area		Plume Area	
	Low-Perm	Transport	Transport	Low-Perm
Vadose	0	0	0	0
NAPL	4	4		
Aqueous	3	3	1	0
Sorbed	3	3	0	0

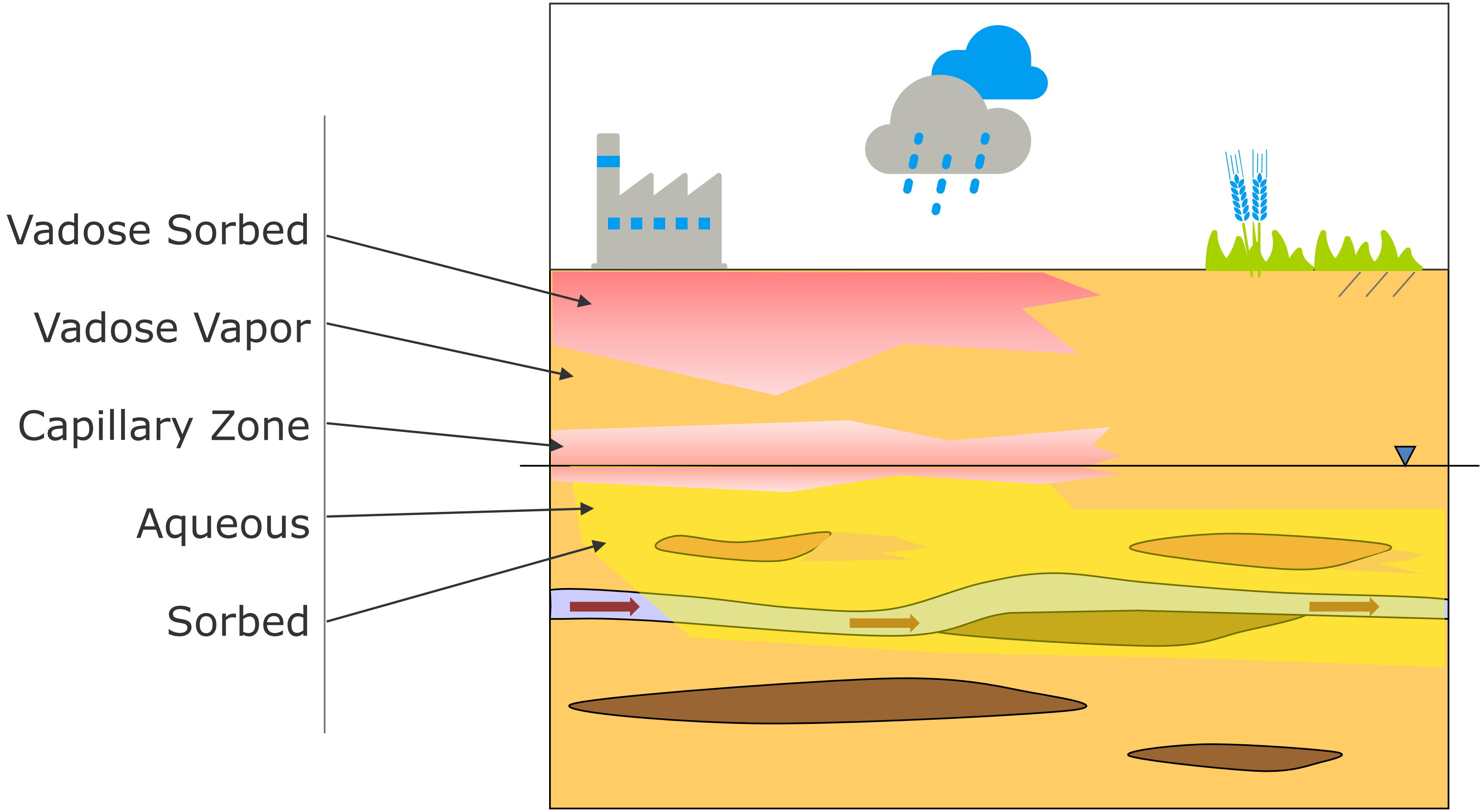
	Source Area		Plume Area	
	Low-Perm	Transport	Transport	Low-Perm
Vadose	2	2	2	1
NAPL	0	0		
Aqueous	0	0	2	2
Sorbed	0	0	3	2

PFAS DISTRIBUTION IN THE ENVIRONMENT

Receptors/Media
Fate/Transformation Phenomena
Transport/Exposure Phenomena



GENERALIZED COMPARTMENTS TO A CONCEPTUAL PFAS RELEASE



UNDERSTANDING VADOSE STORAGE AND TRANSPORT

Retardation increases with:

- Hydrophobicity of PFAS constituent
- Air-water interfacial area (soil type, clays)
- Salinity
- Organic carbon content (soil type)
- Mineral phases
- Time!
- Heterogeneity

Observation and models show storage is often on the order of decades

Dotted line of figure indicates transition from air-water to solid-phase adsorption dominated retardation due to decreasing moisture content

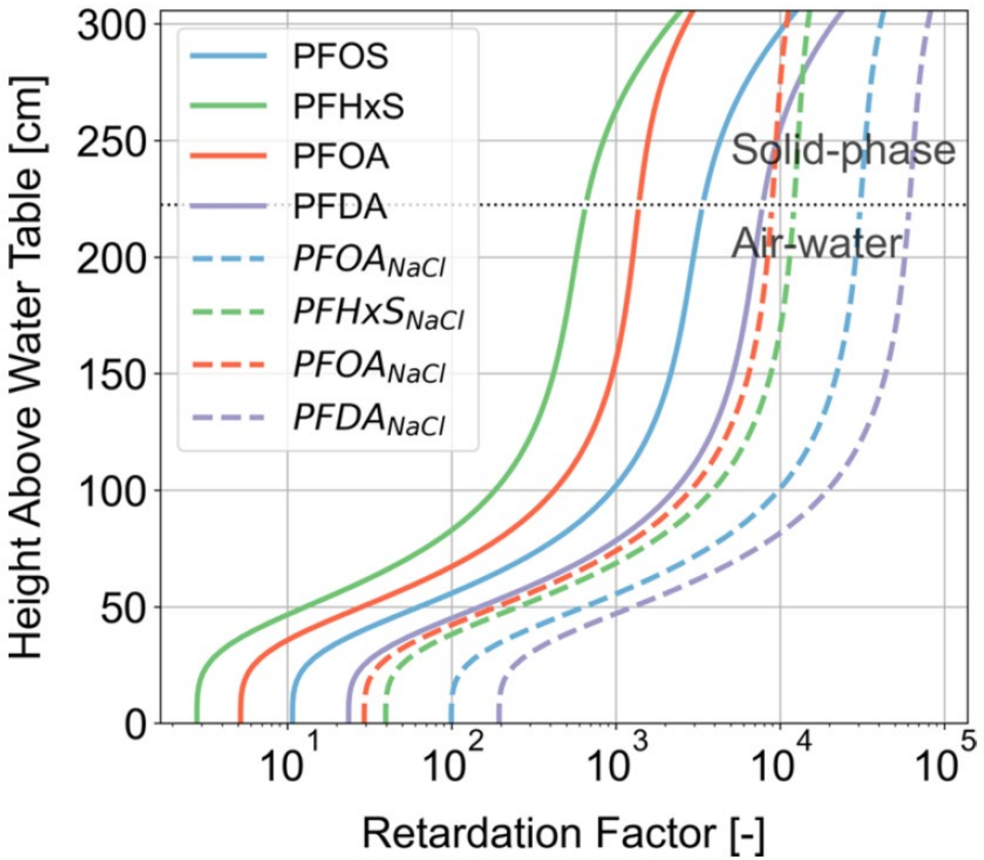


Figure 3 of "Adsorption of PFAAs in the Vadose Zone and Implications for Long-Term Groundwater Contamination," Gnesda et al. *Env Sci & Technol*, 2022 56 (23), DOI: 10.1021/acs.est.2c03962

THE PFAS 18-COMPARTMENT MODEL

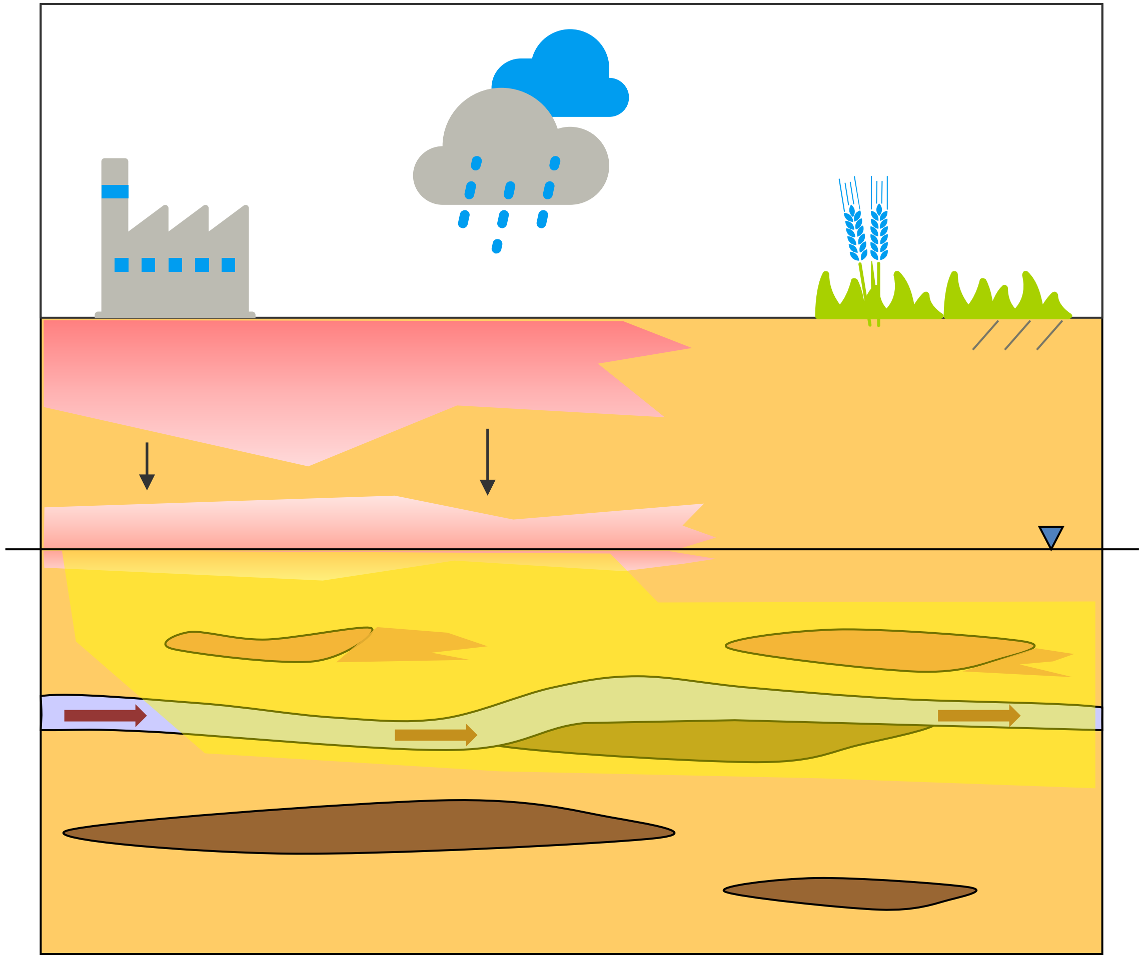
Early/middle stage

PFAS 18-C Model	Source Area		Plume Area		Former 14-C
	Low-Perm	Transport	Transport	Low-Perm	
Vadose	1	2	2	1	Vadose
Vadose Sorbed	4	4			NAPL
Capillary Zone	3	4	1	0	---
Aqueous	2	3	2	1	Aqueous
Sorbed	1	2	2	0	Sorbed

Late/middle stage

PFAS 18-C Model	Source Area		Plume Area		Former 14-C
	Low-Perm	Transport	Transport	Low-Perm	
Vadose	1	1	1	1	Vapor
Vadose Sorbed	3	3			NAPL
Capillary Zone	3	3	1	1	---
Aqueous	2	2	1	2	Aqueous
Sorbed	2	1	1	2	Sorbed

… And different PFAS compounds will transport at different rates, and will equilibrate and store differently



REMEDIAL EFFICACY IN SOURCE AREAS

Plume behavior

Early/middle stage

PFAS 18-C Model	Source Zone	
	Low Perm	Transmissive
Vadose Vapor	1	2
Vadose Sorbed	4	4
Capillary Zone	3	4
Aqueous	2	3
Sorbed	1	2

Late/middle stage

PFAS 18-C Model	Source Zone	
	Low Perm	Transmissive
Vadose Vapor	1	1
Vadose Sorbed	3	3
Capillary Zone	3	3
Aqueous	2	2
Sorbed	2	1

Treatment technology

Pump & Treat/Funnel and gate

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	0	1

Thermal desorption and recovery

	Low Perm	Transmissive
Vadose Vapor	3	4
Vadose Sorbed	3	4
Capillary	3	4
Aqueous	3	4
Sorbed	3	4

Excavation/Soil washing

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Injectable activated carbons

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	1	2

Soil mixing/In-situ stabilization/solidification

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Values for illustrative purposes only

REMEDIAL EFFICACY IN SOURCE AREAS

Plume behavior

Early/middle stage

PFAS 18-C Model	Source Zone	
	Low Perm	Transmissive
Vadose Vapor	1	2
Vadose Sorbed	4	4
Capillary Zone	3	4
Aqueous	2	3
Sorbed	1	2

Late/middle stage

PFAS 18-C Model	Source Zone	
	Low Perm	Transmissive
Vadose Vapor	1	1
Vadose Sorbed	3	3
Capillary Zone	3	3
Aqueous	2	2
Sorbed	2	1

Treatment technology

Pump & Treat/Funnel and gate

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	0	1

Thermal desorption and recovery

	Low Perm	Transmissive
Vadose Vapor	3	4
Vadose Sorbed	3	4
Capillary	3	4
Aqueous	3	4
Sorbed	3	4

Excavation/Soil washing

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Injectable activated carbons

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	1	2

Soil mixing/In-situ stabilization/solidification

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Values for illustrative purposes only

REMEDIAL EFFICACY IN DOWNGRADIENT AREAS

Plume behavior

Early/middle stage

PFAS 18-C Model	Plume	
	Low Perm	Transmissive
Vadose Vapor	1	2
Vadose Sorbed		
Capillary Zone	0	1
Aqueous	1	2
Sorbed	0	2

Late/middle stage

PFAS 18-C Model	Plume	
	Low Perm	Transmissive
Vadose Vapor	1	1
Vadose Sorbed		
Capillary Zone	1	1
Aqueous	2	1
Sorbed	2	1

Treatment technology

Pump & Treat/Funnel and gate

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	0	1

Thermal desorption and recovery

	Low Perm	Transmissive
Vadose Vapor	3	4
Vadose Sorbed	3	4
Capillary	3	4
Aqueous	3	4
Sorbed	3	4

Excavation/Soil washing

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Injectable activated carbons

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	1	2

Soil mixing/In-situ stabilization/solidification

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Values for illustrative purposes only

REMEDIAL EFFICACY IN DOWNGRADIENT AREAS

Plume behavior

Early/middle stage

PFAS 18-C Model	Plume	
	Low Perm	Transmissive
Vadose Vapor	1	2
Vadose Sorbed		
Capillary Zone	0	1
Aqueous	1	2
Sorbed	0	2

Late/middle stage

PFAS 18-C Model	Plume	
	Low Perm	Transmissive
Vadose Vapor	1	1
Vadose Sorbed		
Capillary Zone	1	1
Aqueous	2	1
Sorbed	2	1

Treatment technology

Pump & Treat/Funnel and gate

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	0	1

Thermal desorption and recovery

	Low Perm	Transmissive
Vadose Vapor	3	4
Vadose Sorbed	3	4
Capillary	3	4
Aqueous	3	4
Sorbed	3	4

Excavation/Soil washing

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Injectable activated carbons

	Low Perm	Transmissive
Vadose Vapor	0	0
Vadose Sorbed	0	0
Capillary	0	1
Aqueous	1	3
Sorbed	1	2

Soil mixing/In-situ stabilization/solidification

	Low Perm	Transmissive
Vadose Vapor	3	3
Vadose Sorbed	3	3
Capillary	3	3
Aqueous	3	3
Sorbed	3	3

Values for illustrative purposes only

KEY TAKE-AWAYS

What is the current state of the remediation practice and where does this leave us?

1. PFAS transport is different than that of traditional contaminants – less sensitivity to classic K_{ow}/f_{oc} relationships; adsorption, diffusion and storage at air/water interfaces
2. Understanding these differences is key to implementation of effective remedies
3. The 14-compartment model proved useful for classical contaminants; an 18-compartment model might be a more useful evaluation tool for PFAS sites
4. Vadose and capillary PFAS storage need to be considered in remedy evaluation and implementation
5. Without that consideration vadose storage can contribute mass to a groundwater system for decades
6. If part of the release history, impacts to vadose soils will serve as a source term, extending groundwater remediation at PFAS sites to decadal timeframes
7. A number of concentration methods are available at scale; destruction methods remain an active area of research

RAMBOLL

PFAS KEYWORD HITS IN LITERATURE, 2008-2022

Over 2,470 Literature Papers and Patents Included

Inner ring – reported media

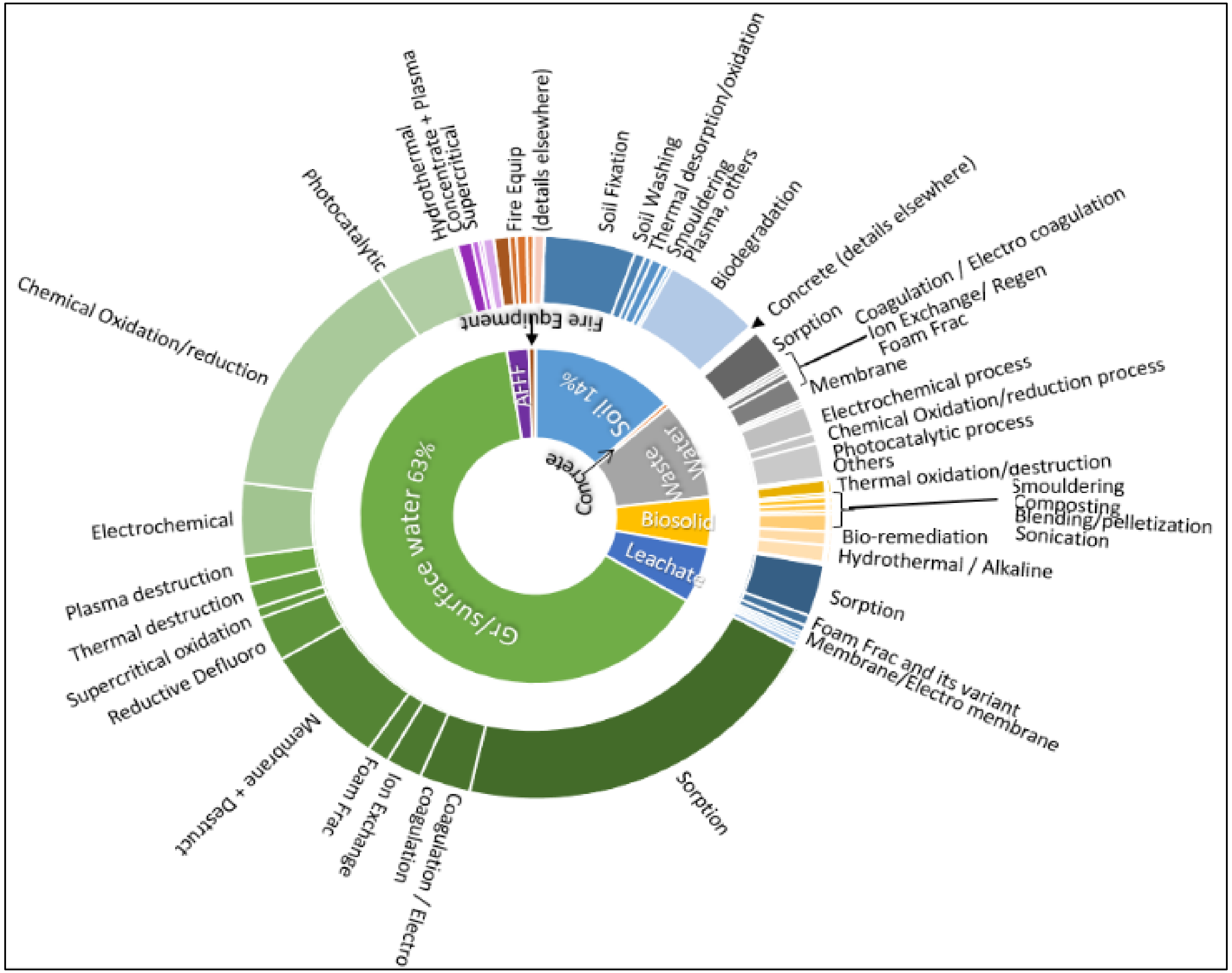
Water/groundwater represented 63% of the returns in the literature search

Soils represented 14%

All other media combined represented 23% of returned results

Outer ring – reported technology

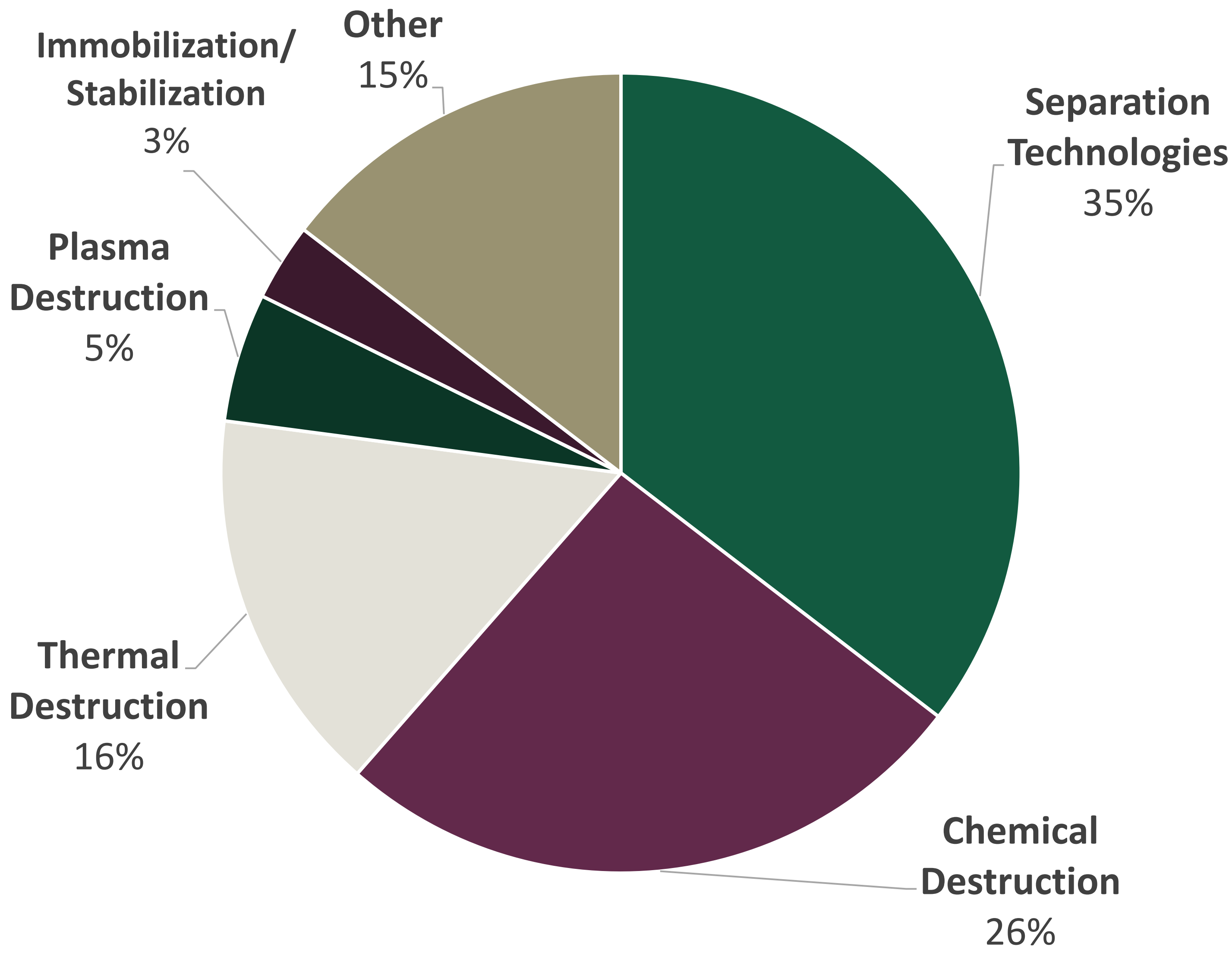
- Sorption
- Chemical oxidation
- Membrane separation
- Electrochemical



RAMBOLL

NUMBER OF U.S. PROJECTS CURRENTLY IN FUNDING

- **GAC, ion exchange, and membrane separation** remain as the default technologies; new separation methods (i.e., foam fractionation) are rapidly appearing
- **Lab-scale** PFAS destruction technologies appear in the scientific literature as early as **2003**
- **Field-scale** remediation activities begin appearing in literature around **2017**
- Early work began with chemical and electrochemical destruction; however, hydrothermal, supercritical water oxidation, and plasma processes have more recently entered the market



Thank you for your attention

Jim Fenstermacher, PE
D (+1) 484-804-7203
M (+1) 267-664-4748
jim.fenstermacher@ramboll.com

Ramboll
Blue Bell, PA, USA 19422
https://ramboll.com

Photon Water
Photon Remediation
Albemarle
ALL THE ELEMENTS FOR A BETTER WORLD
CARUS®
Deltares
CZU
Czech University of Life Sciences Prague