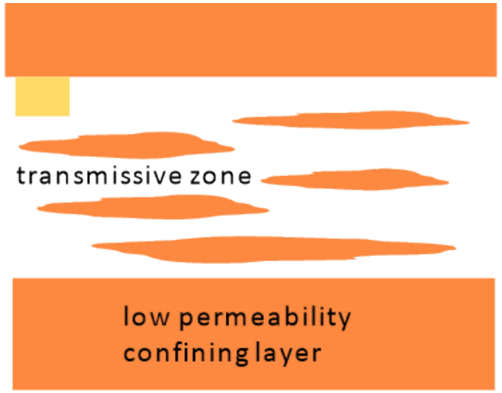
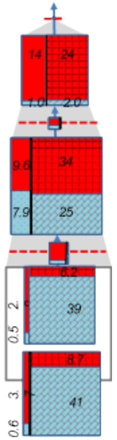
Matrix Diffusion as a Key Retention Process for PFAS in Groundwater





May 2023

Charles Newell, Poonam Kulkarni, Shahla Farhat, Dave Adamson
GSI Environmental Inc.

Hans Stroo
Stroo Consulting

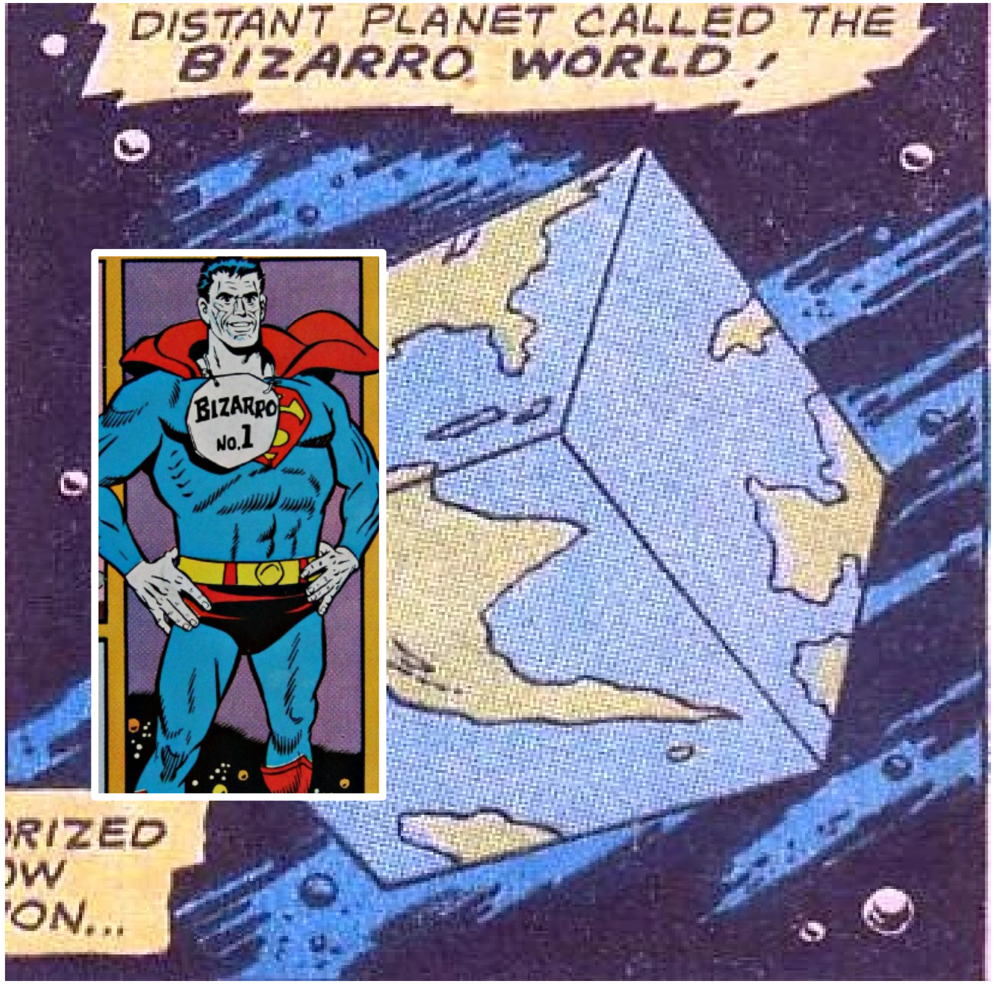
Battelle Bioremediation Symposium

Roadmap

- The PFAS Challenge
- Immobilization vs. Retention Processes in Groundwater
- Curse and Blessing of Matrix Diffusion (Shapiro, 2019)
- Modeling Matrix Diffusion
- Potential Framework to Manage PFAS Sites

PFAS = Bizarro World For Groundwater People?

- No current evidence of in-situ degradation of PFAAs!
- Biodegradation doesn’t help, it hurts!
- Front-line technology is Pump and Treat?
- Concentrations: single digit nanogram per liter?
- Thousands of individual PFAS!
- ~60,000 sites in US? (EBJ, 2022) (Salvatore et al., 2022)
- More expanding plumes than other COCs?

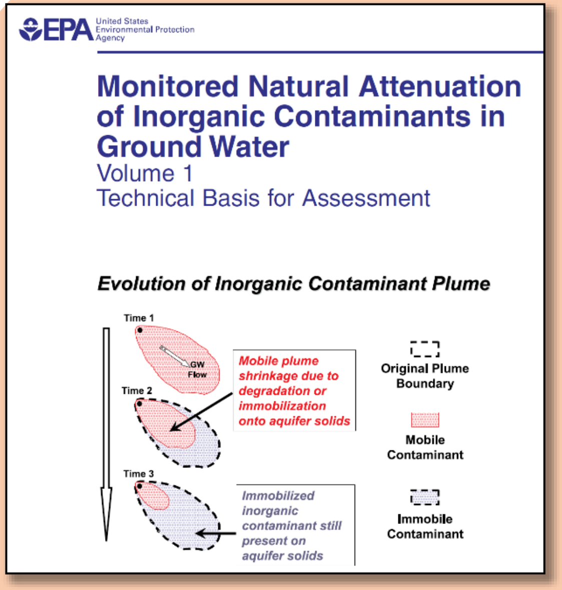


KEY POINT: “Business as Usual” won’t work for PFAS Groundwater Cleanup

Monitored Natural Attenuation (MNA) For PFAS?

MNA of metals, inorganics, radionuclides based on *immobilization* onto aquifer solids (no degradation)

Retention-Based MNA for PFAS?



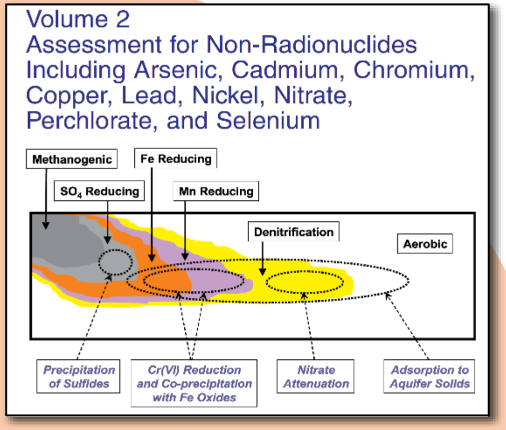
EPA United States Environmental Protection Agency

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1

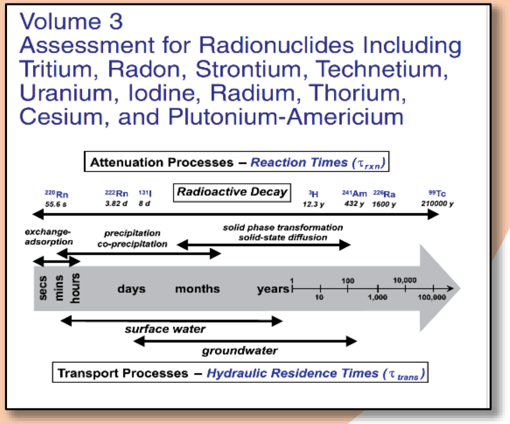
Technical Basis for Assessment

Evolution of Inorganic Contaminant Plume



Volume 2

Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium



Volume 3

Assessment for Radionuclides Including Tritium, Radon, Strontium, Technetium, Uranium, Iodine, Radium, Thorium, Cesium, and Plutonium-Americium

EPA Guidance Documents for MNA of Metals/Rads

Immobilization vs. Retention

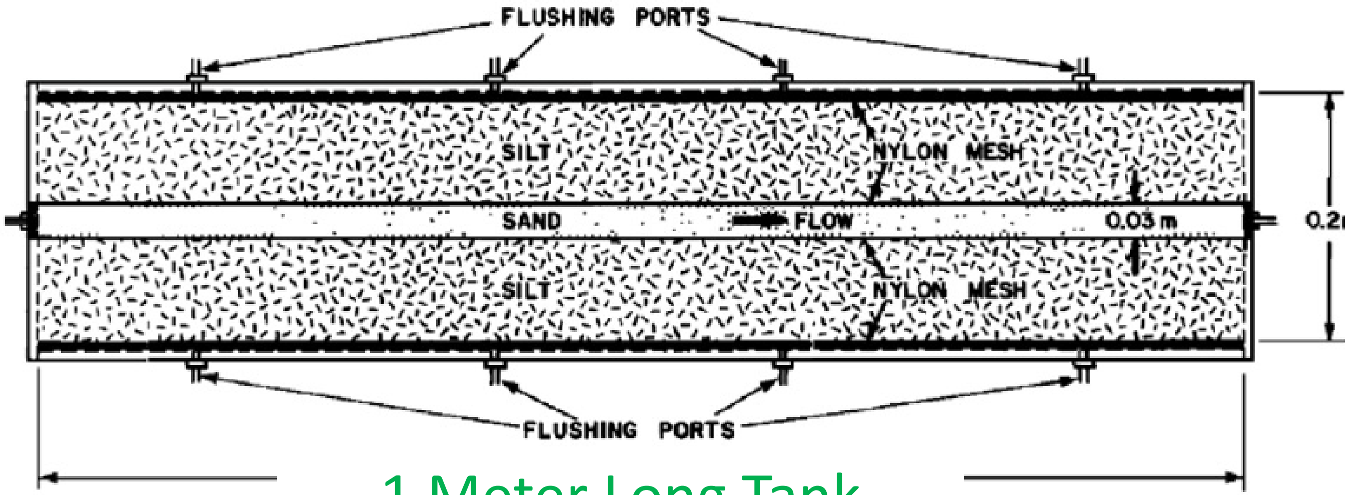
- *Immobilization:* The permanent trapping and isolation of a chemical in the environment.

- *Retention:* The storage of a chemical in the environment so that the chemical is isolated from potential receptors for a certain time.

Newell et al. 2022 Remediation

Matrix Diffusion Doesn't Immobilize, but it Can Retain and Slow Plume Expansion

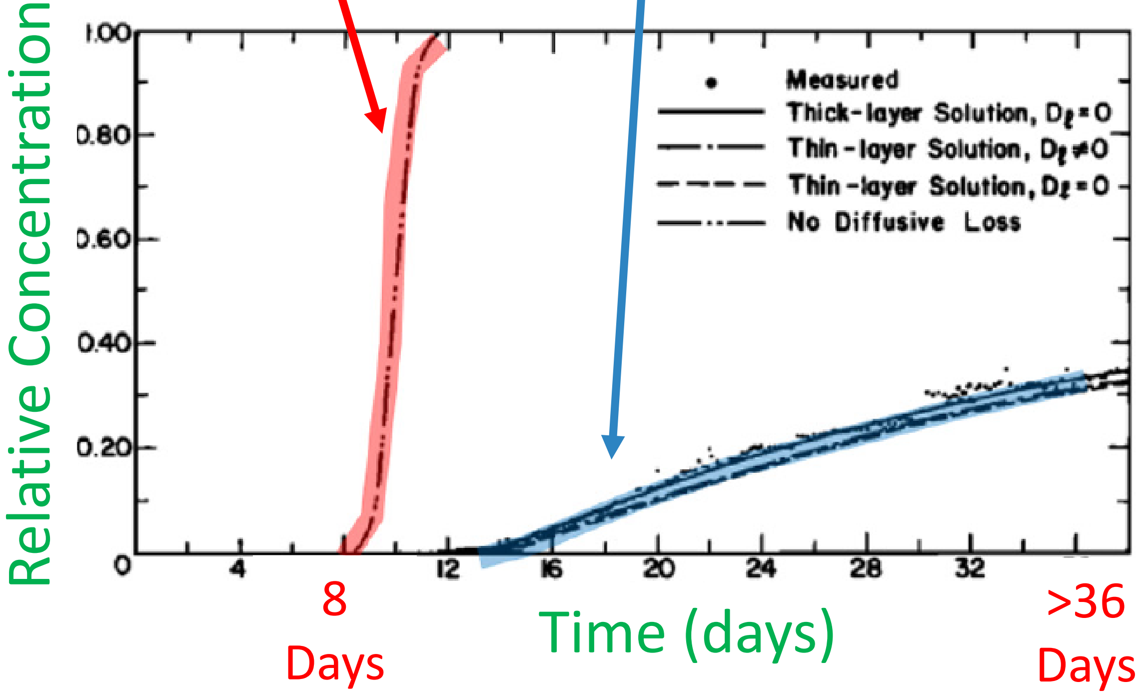
Sudicky et al., 1985 WRR



1 Meter Long Tank Experiment

Model No Diffusive Loss

Model and Lab Experiment With Diffusive Loss



"The experimental results show a delay in the breakthrough of the tracer…."

Dr. Allen Shapiro (2019)

Retention and Release of Groundwater in Fractured Rock and Other Dual-Porosity Media

Matrix Diffusion Curse or Blessing?

the curse. . .retention of contaminants in flow limited regions of the aquifer. .

limiting access to remediation amendments

slow release of contaminants to permeable pathways yields a long-term contaminant source

the blessing. . .retention of contaminants in flow limited regions of the aquifer. . .

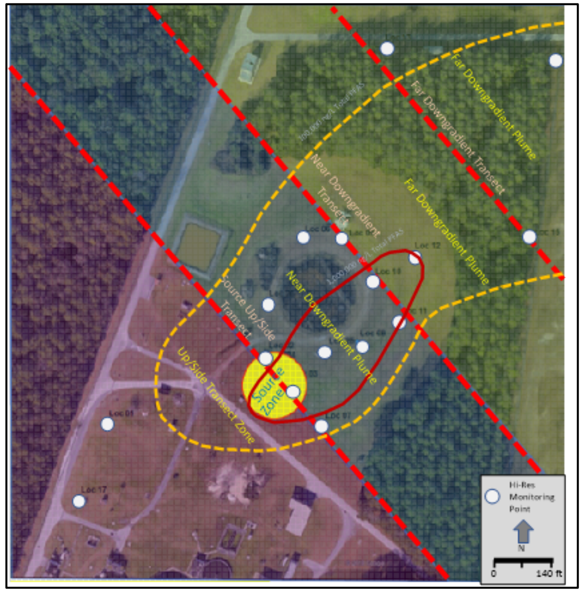
attenuating the downgradient concentrations. . .

delaying downgradient migration of contaminants. .

. . .matrix diffusion is the rationale for the licensing of selected geologic environments as sites for waste isolation (e.g., WIPP site, New Mexico, USA)

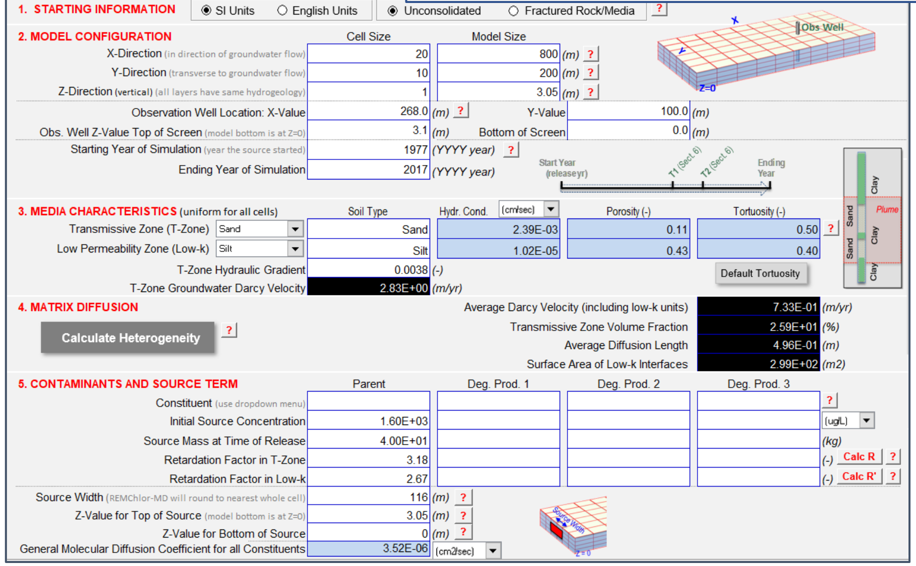
Influence of Matrix Diffusion on Plume Expansion

- Use REMCHLOR-MD as screening tool for understanding influence of matrix diffusion processes on PFOS plume extent



REMChlor-MD

Evaluating Matrix Diffusion for Chlorinated Solvents
Version 1.0



REMChlor-MD Data Input Screen

Site Location and ID: Model 2B: LowK=SM+ML+CL; K

1. STARTING INFORMATION ● SI Units ○ English Units ● Unconsolidated ○ Fractured Rock/Media

2. MODEL CONFIGURATION

	Cell Size	Model Size	
X-Direction (in direction of groundwater flow)	20	800	(m)
Y-Direction (transverse to groundwater flow)	10	200	(m)
Z-Direction (vertical) (all layers have same hydrogeology)	1	3.05	(m)

Observation Well Location: X-Value 268.0 (m) Y-Value 100.0 (m)
Obs. Well Z-Value Top of Screen (model bottom is at Z=0) 3.1 (m) Bottom of Screen 0.0 (m)
Starting Year of Simulation (year the source started) 1977 (YYYY year)
Ending Year of Simulation 2017 (YYYY year)

3. MEDIA CHARACTERISTICS (uniform for all cells)

		Soil Type	Hydr. Cond. (cm/sec)	Porosity (-)	Tortuosity (-)
Transmissive Zone (T-Zone)	Sand	Sand	2.39E-03	0.11	0.50
Low Permeability Zone (Low-k)	Silt	Silt	1.02E-05	0.43	0.40

T-Zone Hydraulic Gradient 0.0038 (-)
T-Zone Groundwater Darcy Velocity 2.83E+00 (m/yr)

4. MATRIX DIFFUSION

Average Darcy Velocity (including low-k units) 7.33E-01 (m/yr)
Transmissive Zone Volume Fraction 2.59E+01 (%)
Average Diffusion Length 4.96E-01 (m)
Surface Area of Low-k Interfaces 2.99E+02 (m2)

5. CONTAMINANTS AND SOURCE TERM

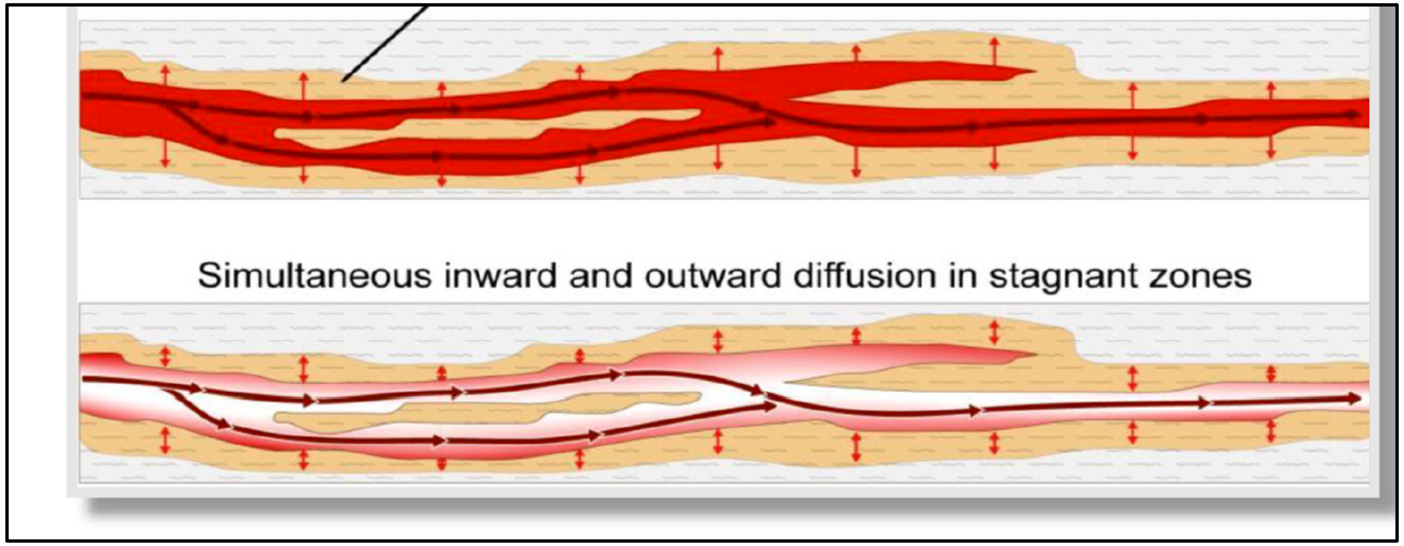
	Parent	Deg. Prod. 1	Deg. Prod. 2	Deg. Prod. 3	
Constituent (use dropdown menu)					
Initial Source Concentration	1.60E+03				(ug/L)
Source Mass at Time of Release	4.00E+01				(kg)
Retardation Factor in T-Zone	3.18				(-)
Retardation Factor in Low-k	2.67				(-)

Source Width (REMChlor-MD will round to nearest whole cell) 116 (m)
Z-Value for Top of Source (model bottom is at Z=0) 3.05 (m)
Z-Value for Bottom of Source 0 (m)
General Molecular Diffusion Coefficient for all Constituents 3.52E-06 (cm2/sec)

REMChlor-MD: Falta et al., 2018

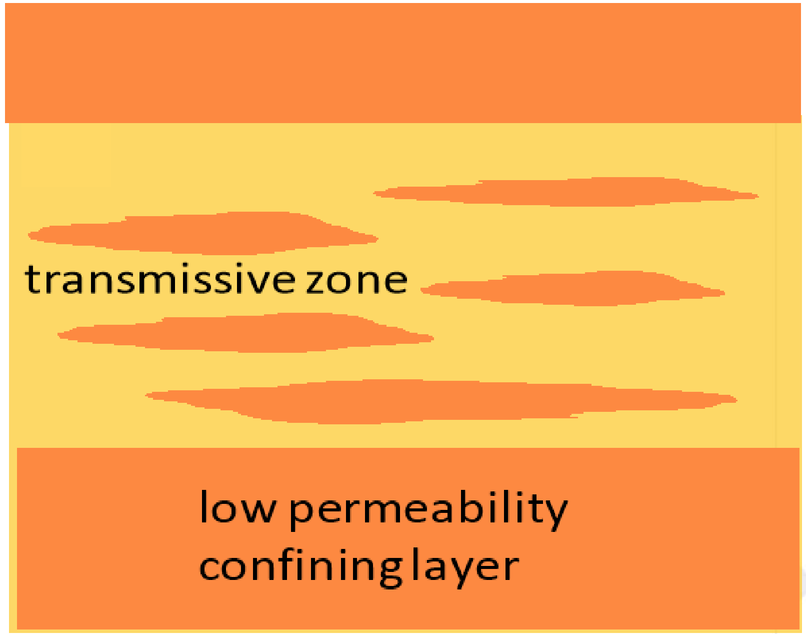
What is a Low Permeability (“Low-K”) Unit?

Image Fred Payne/ARCADIS

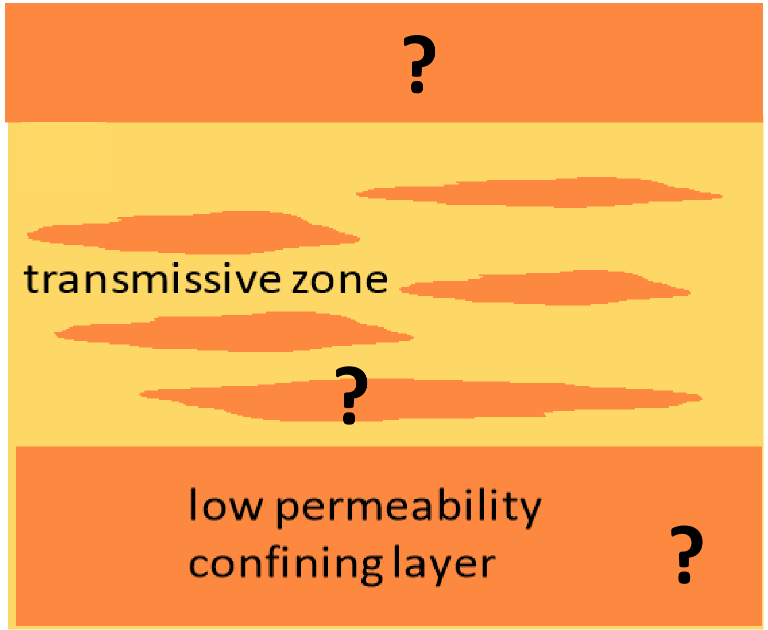


Simultaneous inward and outward diffusion in stagnant zones

Real-Life Geology to REMChlor-MD Conceptualization



What is a Low Permeability (Low-K) Unit When Using a Two-Compartment Conceptual Model?



- **<10^{-5} cm/sec** (Brooks et al. (2021) citing Walden (1997)
- **<10^{-4} cm/sec** (Horst et al., 2019)
- **100X contrast** (REMChlor-MD Manual)
- **Sand with 7-17% Silt is Low-K** **(**if in contact with Sand with 1-5% Silt) (Example from Payne, 2016)
- **10X contrast** (current thinking)

Kulkarni et al. 2022 JCH

What is Low-K Unit?
Lets Get Quantitative With the USCS (Sort of)

General Ratio of K for Different USCS Soils

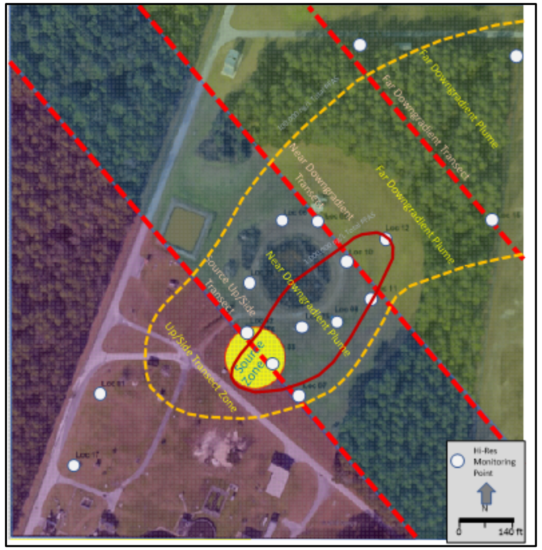
Ratio of Hydraulic Conductivity (K) of more Permeable Unit K divided by less permeable unit K								
Soil Type		GW GP	GM	SW SP	SM SC	GC	MH ML	CH CL
	K (ft/day)	**2,835**	**269**	**90**	**2.6**	**0.9**	**0.0090**	**9.0E-06**
GW GP	**2,835**							
GM	**269**	🟧 11						
SW SP	**90**	🟧 32	🟩 3					
SM SC	**2.6**	🟧 1,111	🟧 105	🟧 35				
GC	**0.9**	🟧 3,333	🟧 316	🟧 105	🟩 3			
MH ML	**0.0090**	🟧 316,228	🟧 30,000	🟧 10,000	🟧 285	🟧 95		
CH CL	**9.0E-06**	🟧 316,227,766	🟧 30,000,000	🟧 10,000,000	🟧 284,605	🟧 94,868	🟧 1,000	

RESULTS:
- 🟩 Matrix Diffusion Likely Less Important
- 🟧 Matrix Diffusion Likely Important

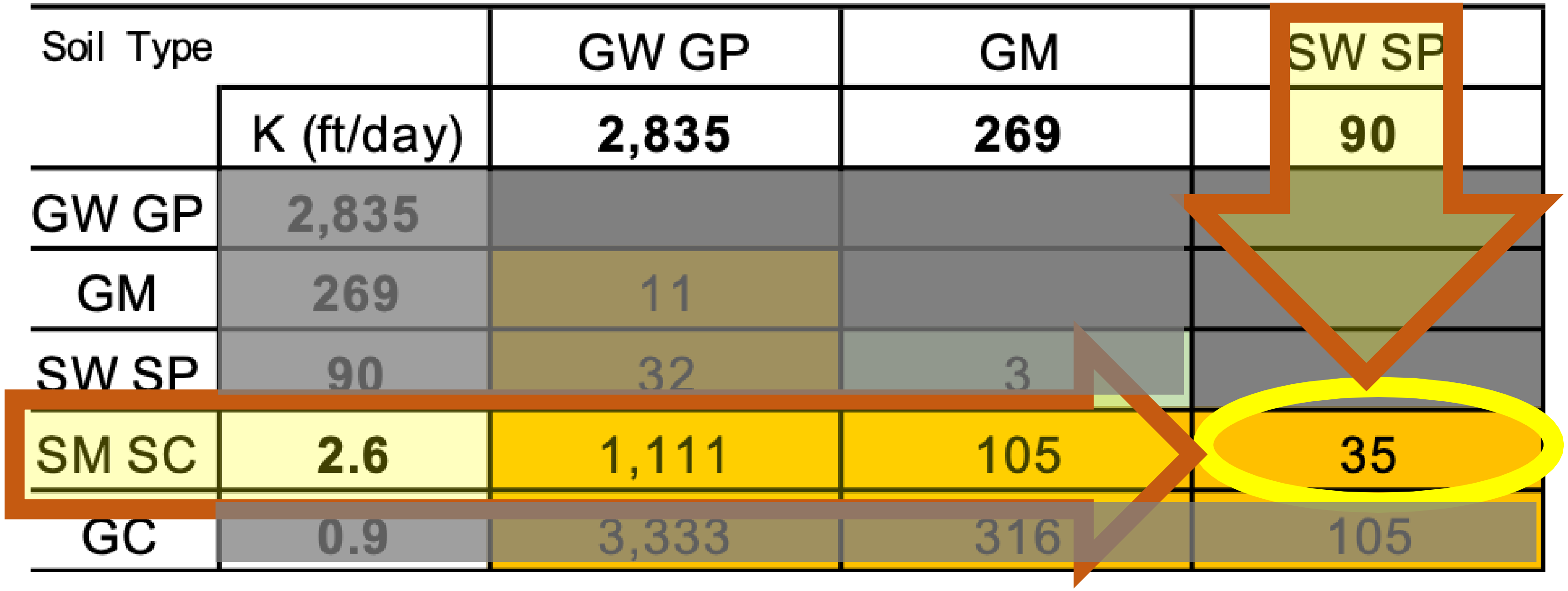
SERDP Project ER20-1429 TA^2 Web Tool

PI: Dr. Dave Adamson, GSI

Definition of Low-K Unit at PFAS Research Site



1. General Table Approach **K ratio = 35**



Soil Type		GW GP	GM	SW SP
	K (ft/day)	**2,835**	**269**	**90**
GW GP	2,835			
GM	269	11		
SW SP	90	32	3	
SM SC	**2.6**	1,111	105	35
GC	0.9	3,333	316	105

Kulkarni et al. 2022 JCH

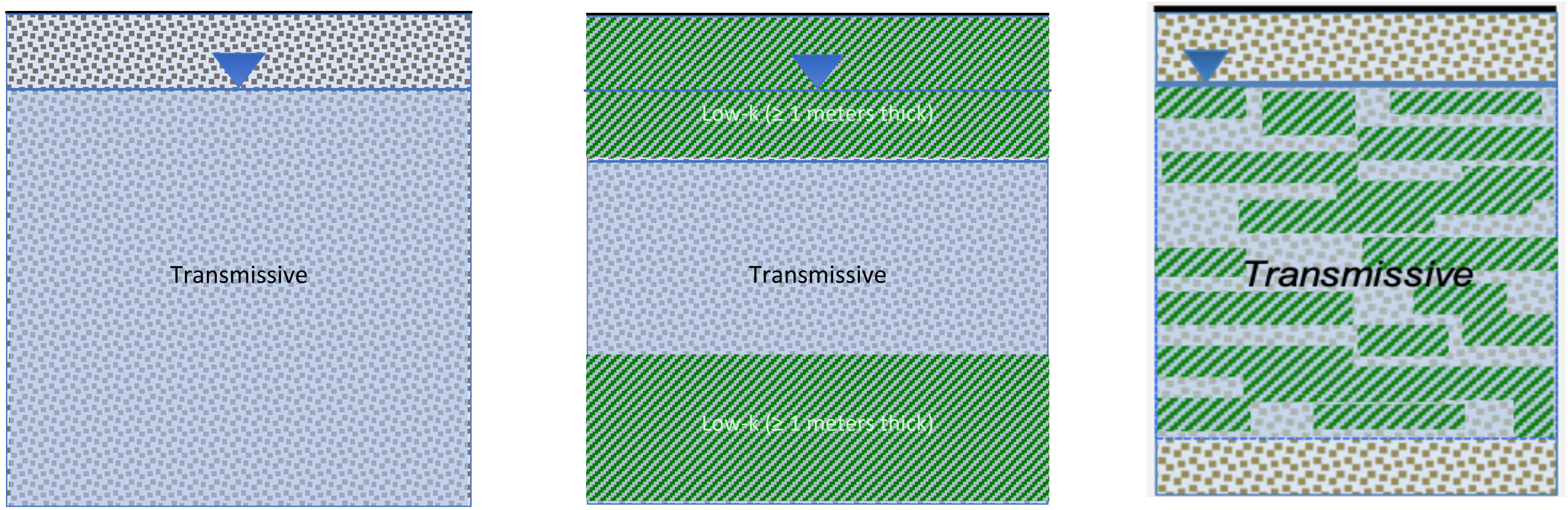
Adamson et al., 2020 ES&T

K ratio = 35

What Types of Geologic Heterogeneity Slow Down Plumes the Most?

Farhat et al., 2022 JCH

- REMChlor-MD Modeling Studies to Explore Retention-Based PFAS MNA
- Lenses slow plume down more than aquitards



Homogeneous Aquifer

Transmissive With Aquitards

Transmissive With 80% Lenses

PFOS Plume Length after 100 years:

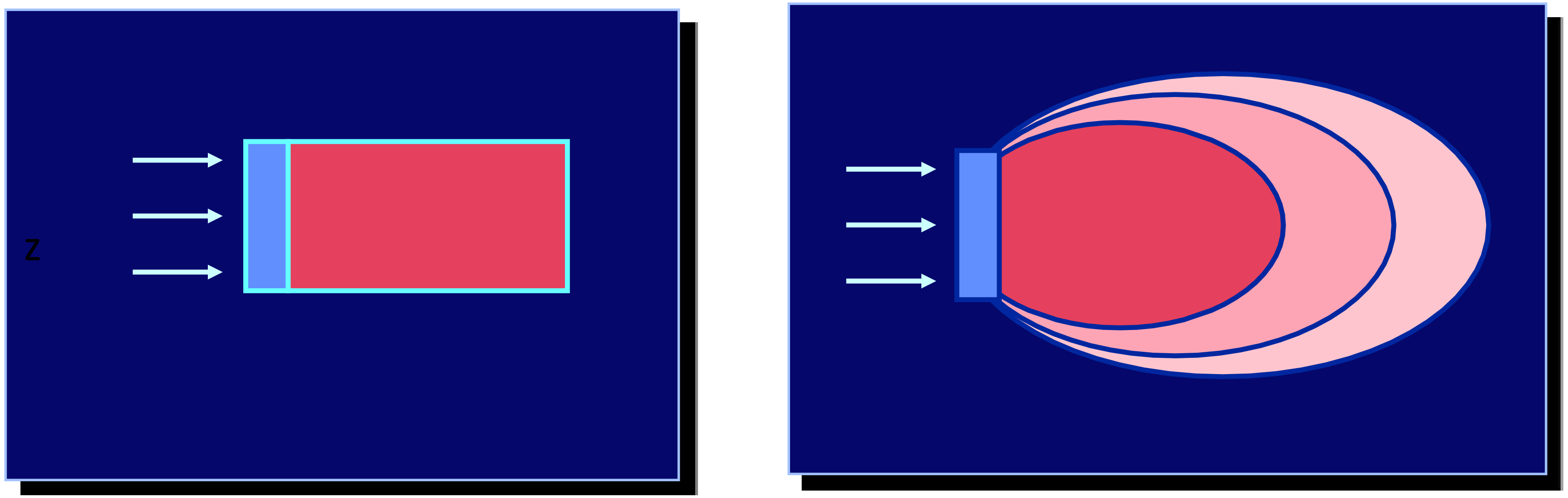
1310 meters

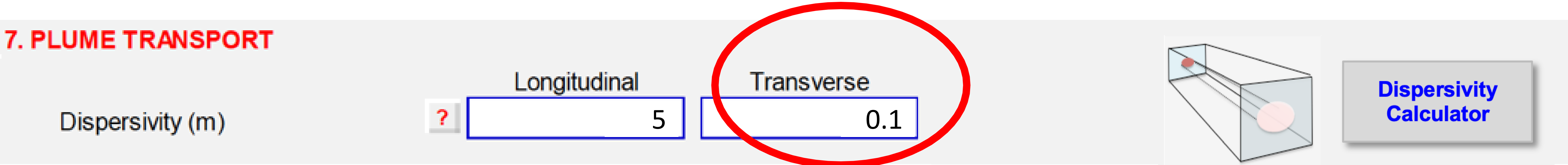
1040 meters

250 meters

How Much Dispersion is Really Out There?

To model plume expansion, need to estimate: ***transverse dispersivity (alpha-y)***



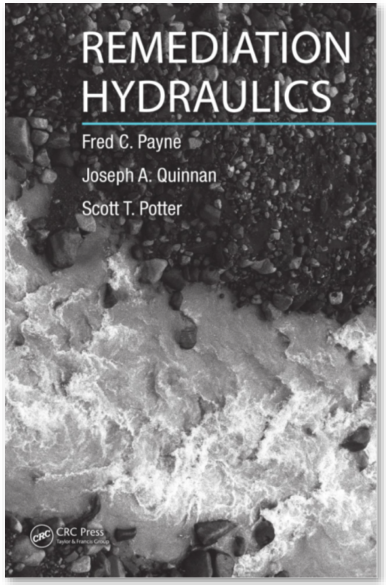


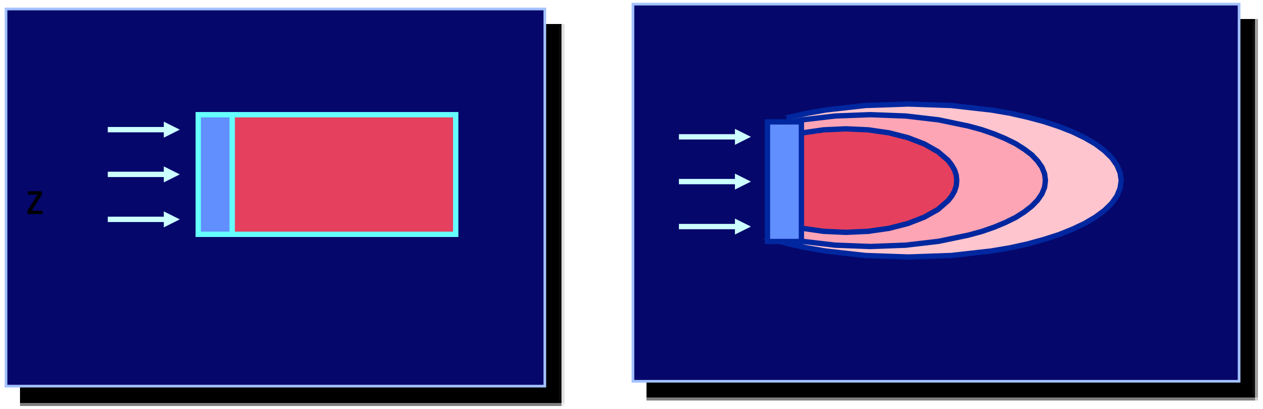
7. PLUME TRANSPORT

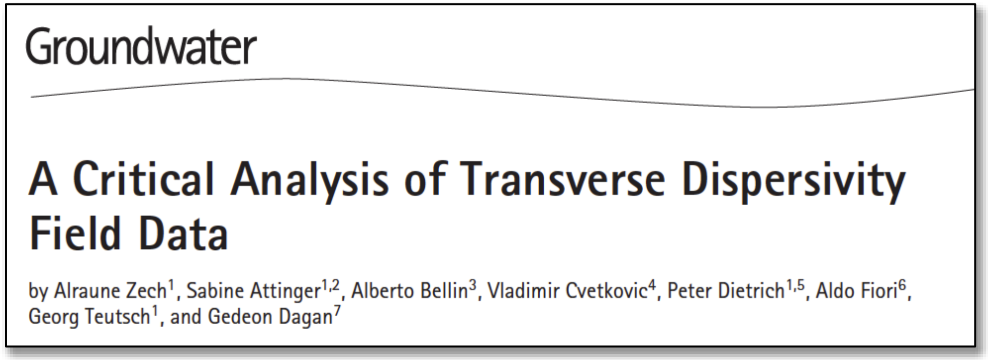
	Longitudinal	Transverse
Dispersivity (m)	5	0.1

Alpha-y for a 1000 Meter Long Plume Through the Ages

1980s: 10 meters (10% rule)
1990s: 1 meter (Xu-Eckstein, 1995)
2006: *“quite limited"* (Payne et al.)
2017: 0.1 meters (Zech et al., 2019)


REMEDIATION HYDRAULICS
Fred C. Payne
Joseph A. Quinnan
Scott T. Potter
CRC Press



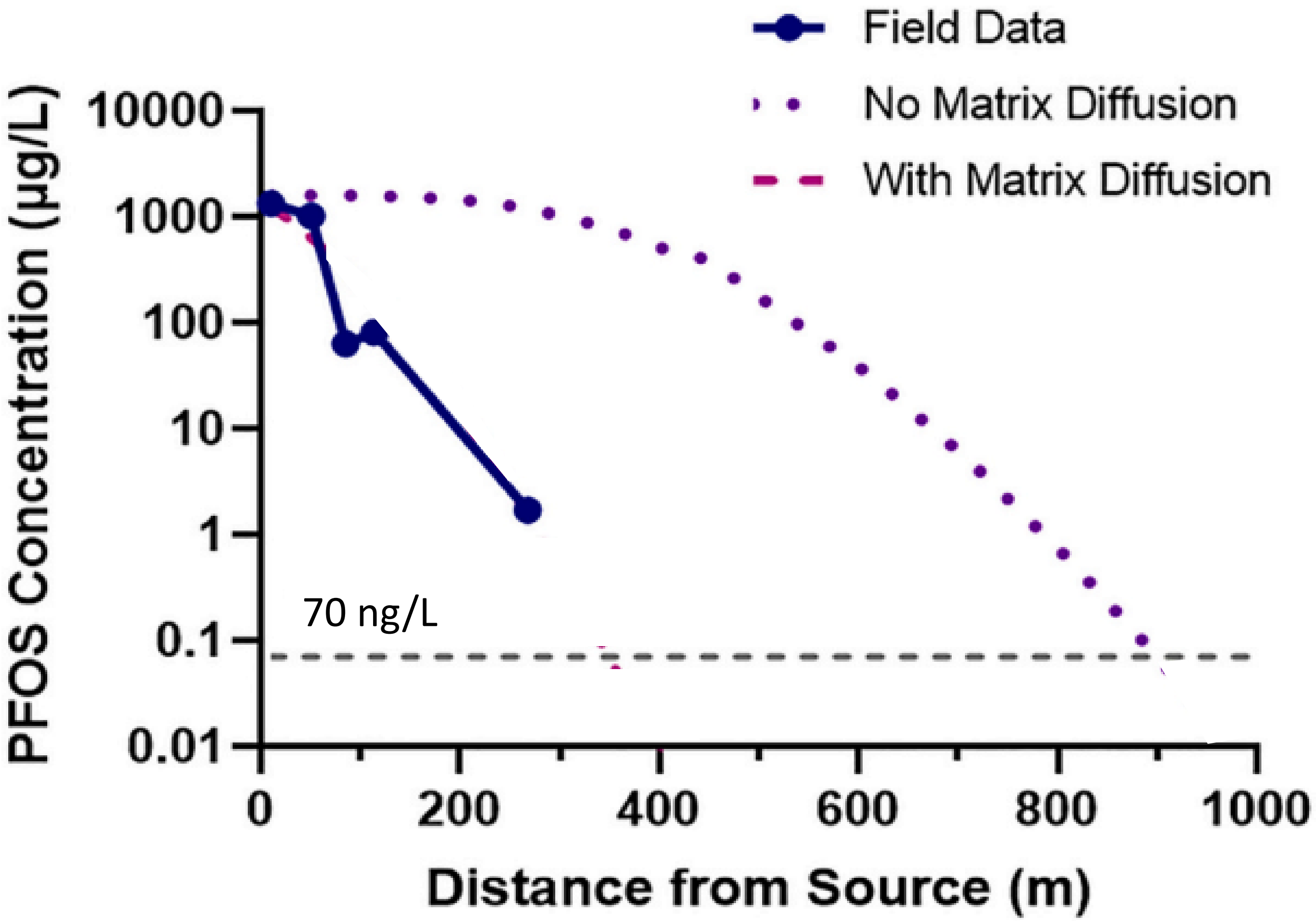

Groundwater

A Critical Analysis of Transverse Dispersivity Field Data

by Alraune Zech[1], Sabine Attinger[1,2], Alberto Bellin[3], Vladimir Cvetkovic[4], Peter Dietrich[1,5], Aldo Fiori[6], Georg Teutsch[1], and Gedeon Dagan[7]

Influence of Matrix Diffusion on Plume Length:
Site 1 Example

- Using REMChlor-MD Matrix Diffusion Model to Simulate the PFOS plume development
- Estimated actual plume length in year 2020: ~ 300-400 meters
- Ran best estimate for input parameters without matrix diffusion, but plume was \ longer.

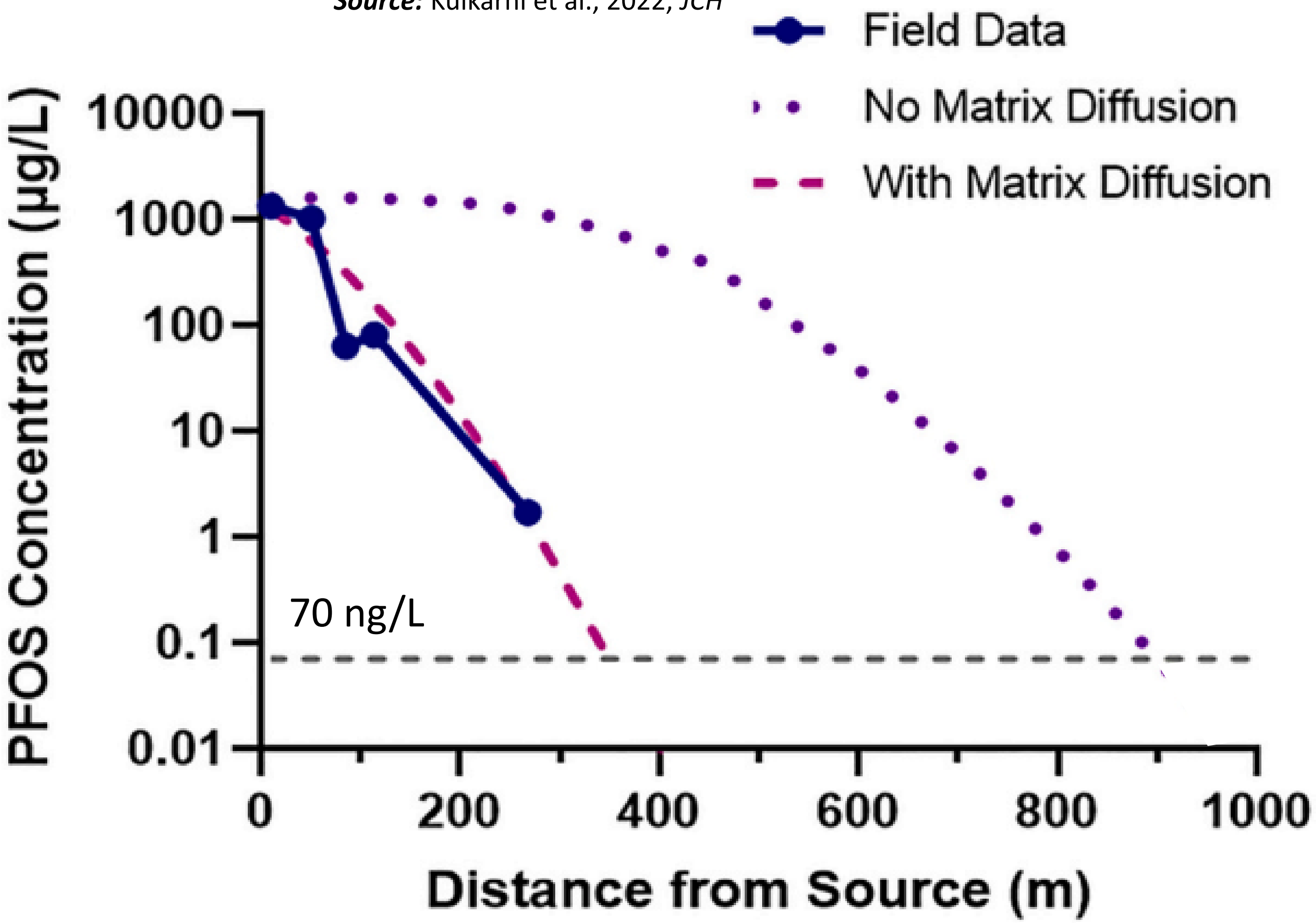


Kulkarni et al., 2022 JCH

Influence of Matrix Diffusion on Plume Length: *Site 1 Example*

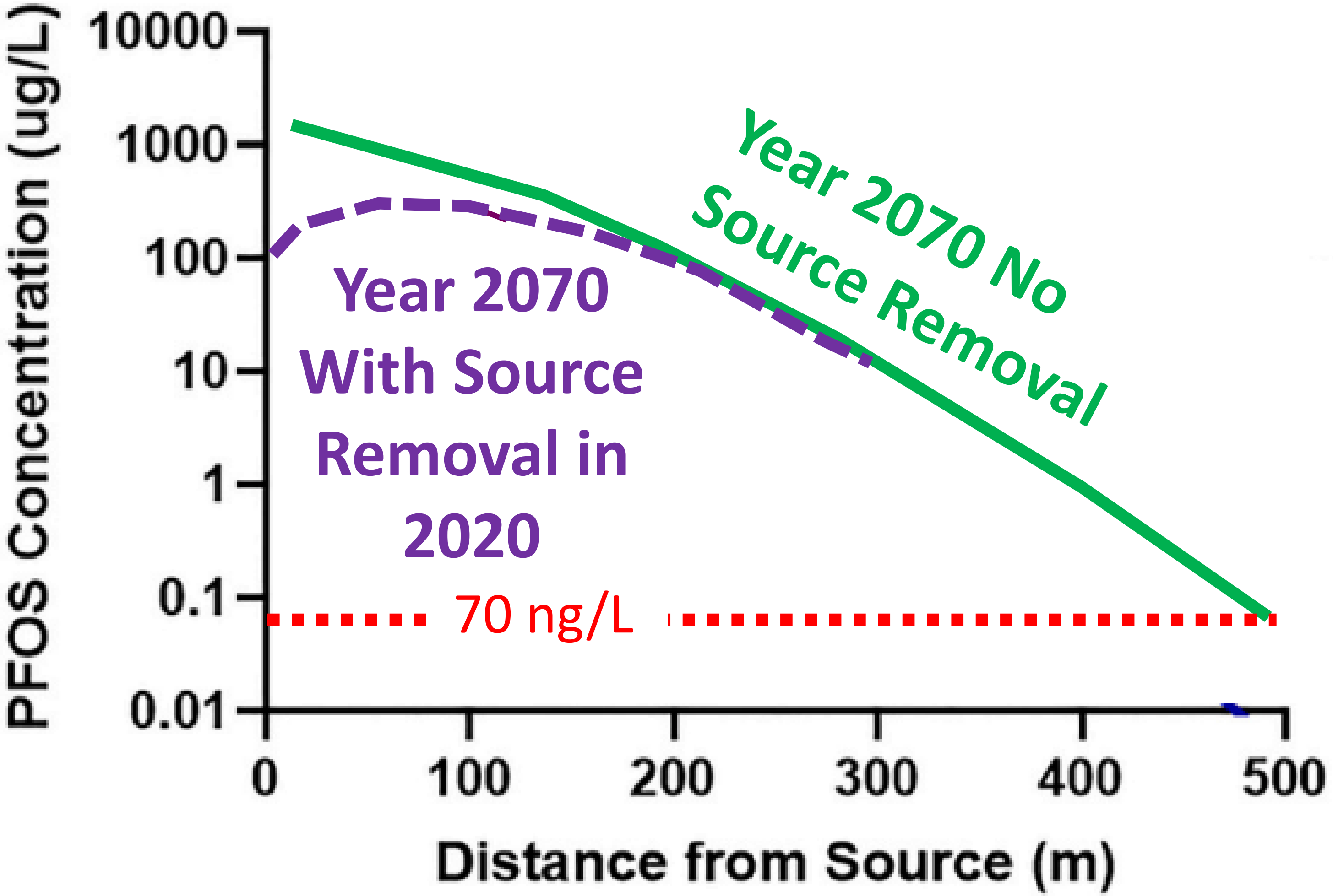
- Included matrix diffusion terms and model fit observed data muc
better!

Source: Kulkarni et al., 2022, *JCH*



Kulkarni et al., 2022 JCH

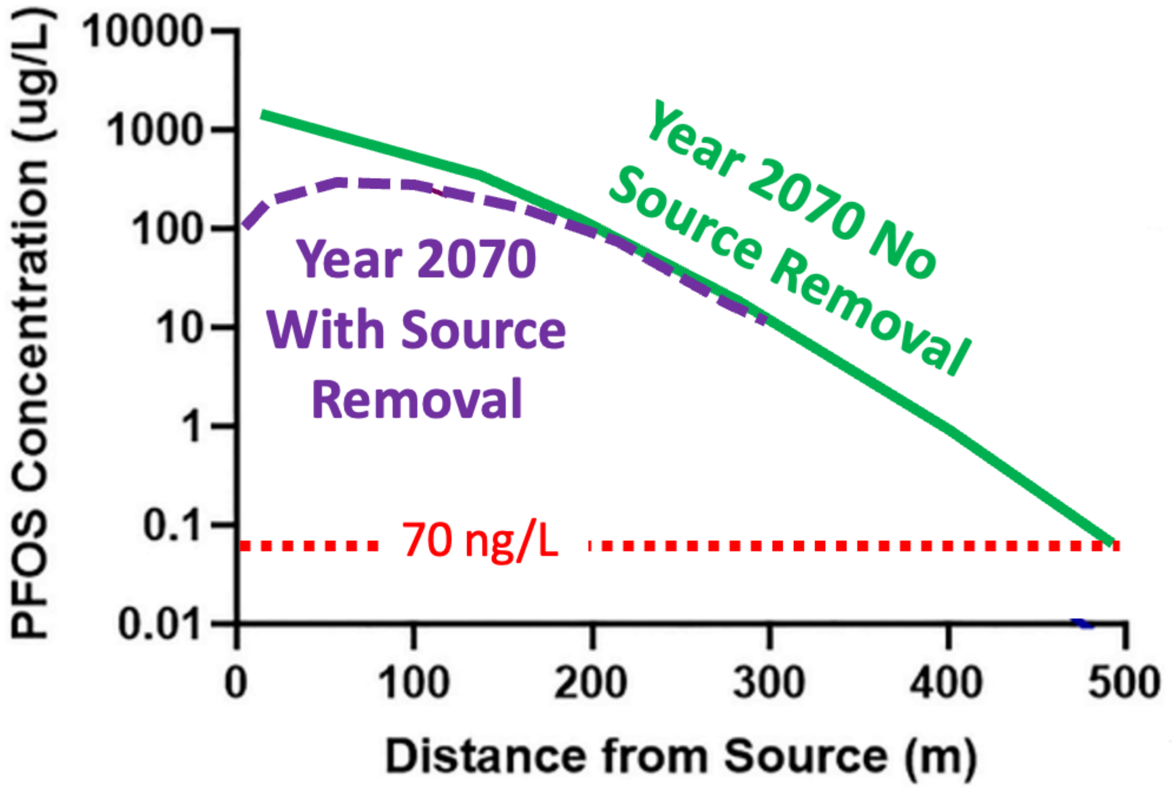
What Does Source Remediation Do?

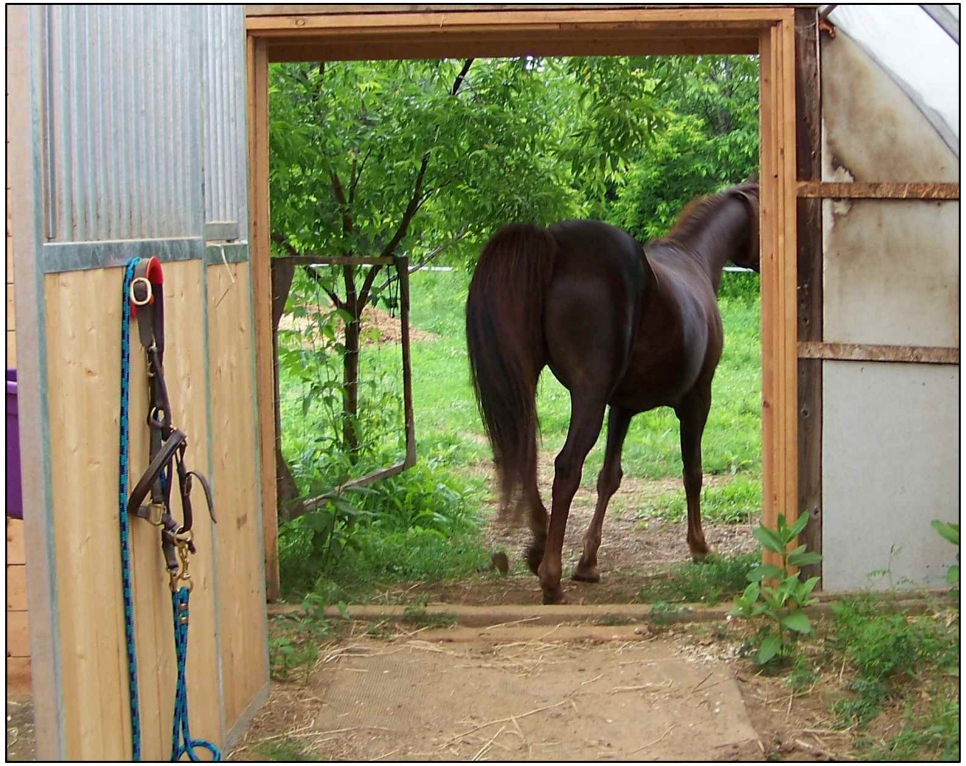


Kulkarni et al., 2022 JCH

the horse has (already) left the barn ??

It is too late to prevent, change, or rectify some problem or situation, as the ill effects have already been wrought. Likely derived from the phrase "close the barn door after the horse has bolted."





Kulkarni et al., 2022 JCH

Potential MNA / EA Framework

Why?

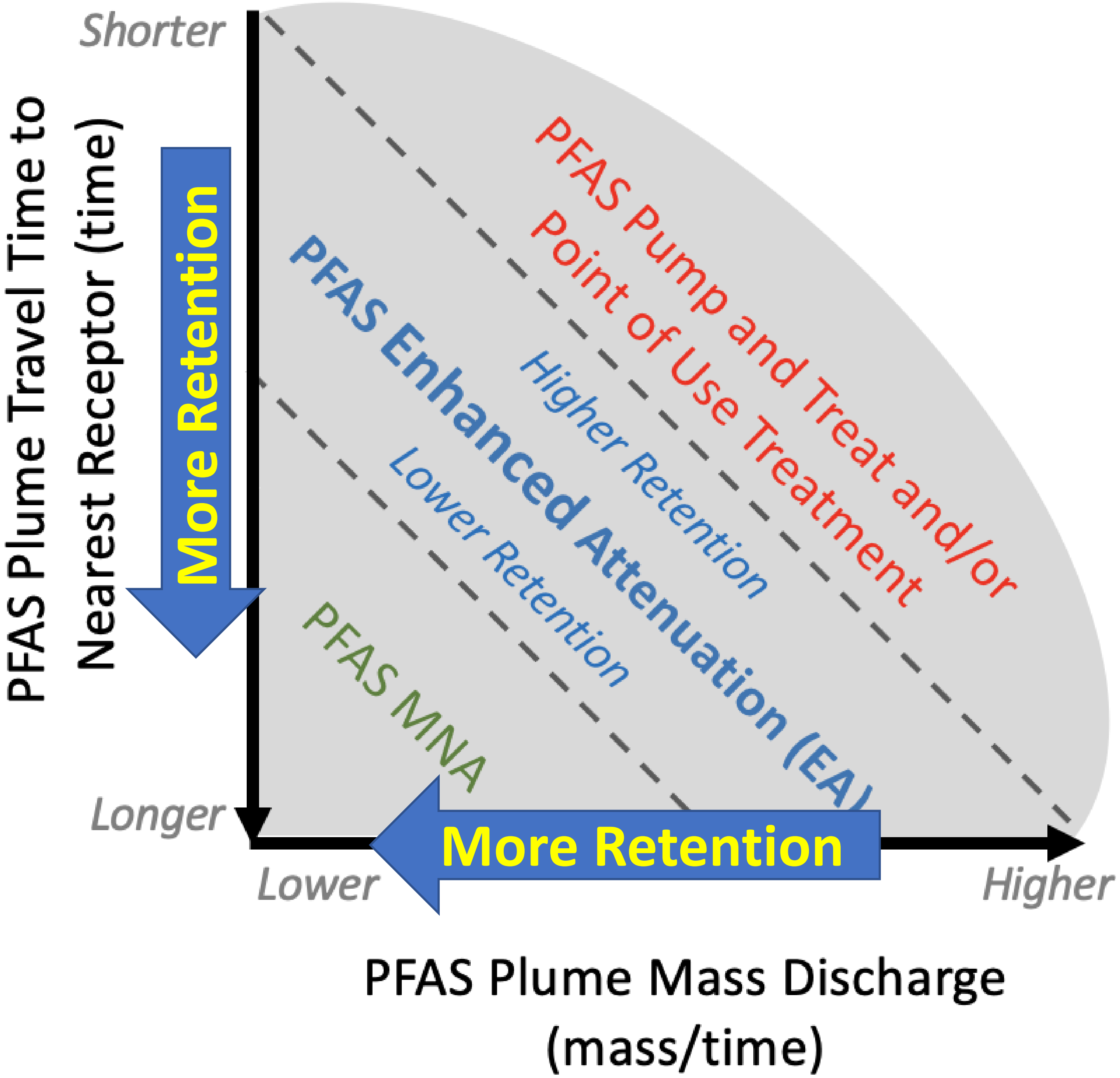
58,000 remediation sites?

$100 billion costs?

Potential decision drivers?

- Travel time to receptors
- Mass discharge

Enhanced Attenuation (EA) to Manage PFAS Plumes in Groundwater (Newell et al., 2022 Remediation)



What is the Best Name for This Thing?

- Retention-Based Monitored Natural Attenuation for PFAS
- PFAS Remediation Prioritization Framework
- Low Threat PFAS Plumes Identification System
- Decision Framework for PFAS Plume Control
- PFAS MNA Framework as an Interim Measure
- PFAS Monitored Retention

WRAP UP

- **Conventional destruction-based MNA not possible for PFAA plumes**
  - Immobilization of non-degrading COCs is accepted practice
  - But not clear any permanent immobilization of PFAS occurs in groundwater
- **But processes that retain PFAS in groundwater may be important**
- **Matrix diffusion can retain non-degrading plumes, slow them down**
- **Monitored Natural Attenuation/Retention may be useful:**
  - As a closure method for very low concentration plumes
  - As a site prioritization tool
  - As an interim measure

REFERENCES

(* Open Access)

Adamson, D. T., Nickerson, A., Kulkarni, P. R., Higgins, C. P., Popovic, J., Field, J., Rodowa, A., Newell, C., Deblanc, P., & Kornuc, J. J. (2020). Mass-Based, Field-Scale Demonstration of PFAS Retention within AFFF-Associated Source Areas. Environmental Science and Technology. https://doi.org/10.1021/acs.est.0c04472

Kulkarni, P. R., Adamson, D. T., Popovic, J., & Newell, C. J. (2022). Modeling a well-characterized perfluorooctane sulfonate (PFOS) source and plume using the REMChlor-MD model to account for matrix diffusion. Journal of Contaminant Hydrology, 247, 103986. https://doi.org/https://doi.org/10.1016/j.jconhyd.2022.103986

Newell, C. J., DiGuiseppi, W. H., Cassidy, D. P., Divine, C. E., Fenstermacher, J. M., Hagelin, N. W., Thomas, R. A., Tomiczek III, P., Warner, S. D., Xiong, Z. J., & Hatzinger, P. B. (2022a). PFAS Experts Symposium 2. PFAS Research: Evolution from past to present, current efforts, and potential futures. Remediation Journal, https://doi.org/https://doi.org/10.1002/rem.21705

*Newell, C. J., Adamson, D. T., Kulkarni, P. R., Nzeribe, B. N., & Stroo, H. (2020). Comparing PFAS to other groundwater contaminants: Implications for remediation. Remediation, 30(3), 7–26. https://doi.org/10.1002/rem.21645

*Newell, C. J., Adamson, D. T., Kulkarni, P. R., Nzeribe, B. N., Connor, J, A., Popovic, J., & Stroo, H. F. (2021). Monitored Natural Attenuation to Manage PFAS Impacts to Groundwater: Scientific Basis. Groundwater Monitoring \& Remediation. https://doi.org/10.1111/gwmr.12486

*Newell, C. J., Adamson, D. T., Kulkarni, P. R., Nzeribe, B. N., Connor, J. A., Popovic, J., & Stroo, H. F. (2021). Monitored natural attenuation to manage PFAS impacts to groundwater: Potential guidelines. Remediation Journal, n/a(n/a). https://doi.org/https://doi.org/10.1002/rem.21697

*Newell, C.J., H. Javed, Y. Li, N.J. Johnson, S.D. Richardson, J.A. Connor, and D.T. Adamson, (2022b). Enhanced Attenuation (EA) to Manage PFAS Plumes in Groundwater. Remediation Journal. https://doi.org/10.1002/rem.21731

Farhat, S. K., Newell, C. J., Lee, S. A., Looney, B. B., & Falta, R. W. (2022). Impact of matrix diffusion on the migration of groundwater plumes for Perfluoroalkyl acids (PFAAs) and other non-degradable compounds. Journal of Contaminant Hydrology, 247, 103987. https://doi.org/https://doi.org/10.1016/j.jconhyd.2022.103987

Simon, J. A., Abrams, S., Bradburne, T., Bryant, D., Burns, M., Cassidy, D., Cherry, J., Chiang, S. Y., Cox, D., Crimi, M., Denly, E., DiGuiseppi, B., Fenstermacher, J., Fiorenza, S., Guarnaccia, J., Hagelin, N., Hall, L., Hesemann, J., Houtz, E., … Wice, R. (2019). PFAS Experts Symposium: Statements on regulatory policy, chemistry and analytics, toxicology, transport/fate, and remediation for per- and polyfluoroalkyl substances (PFAS) contamination issues. Remediation, 29(4), 31–48. https://doi.org/10.1002/rem.21624

QUESTIONS

GSI
ENVIRONMENTAL

R&D Projects Related to PFAS Matrix Diffusion

2019: ESTCP Project ER19-5028
Incorporating Matrix Diffusion in MODFLOW USG

2021: ESTCP Project ER21-5198
Developing a Framework for MNA at PFAS Sites (Monitored Retention?)

2022: Air Force PFAS REMChlor-MD Project (GSI - AFCEC)

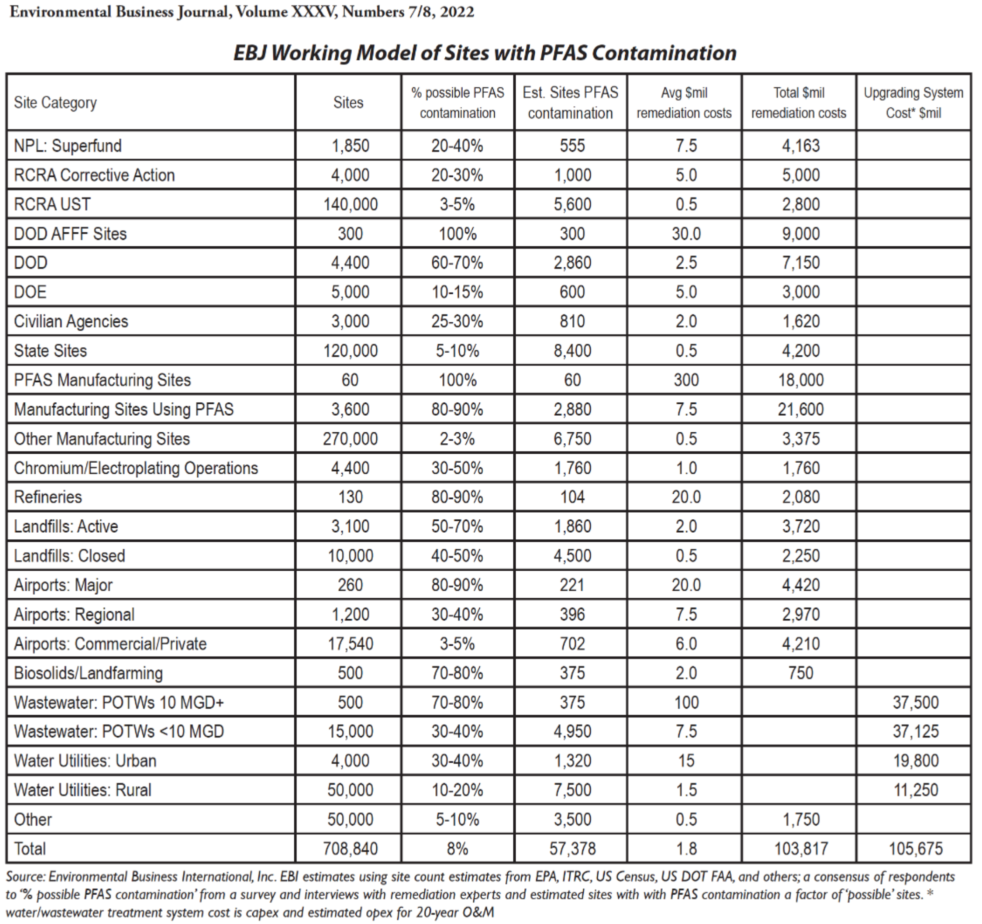
2022: Navy EXWC Guidance for PFAS RI Studies (GSI – EXWC)


ENVIRONMENTAL BUSINESS JOURNAL®
Strategic Information for a Changing Industry
Vol. XXXV, Numbers 7/8, 2022 *Markets & Technology in Remediation & PFAS* Environmental Business International Inc.

Estimated Number of Sites With PFAS Contamination in U.S

Regulated sites	15,555
Dept. Defense	3,160
DOE/Agencies Other	4,910
Manufacturing	11,450
Refineries	104
Landfills	6,360
Airports	1,319
Water/Wastewater	14,520
TOTAL	**57,378**

Recent paper: Salvatore et al. 2022: 57,000 sites


Environmental Business Journal, Volume XXXV, Numbers 7/8, 2022

EBJ Working Model of Sites with PFAS Contamination

Site Category	Sites	% possible PFAS contamination	Est. Sites PFAS contamination	Avg $mil remediation costs	Total $mil remediation costs	Upgrading System Cost* $mil
NPL: Superfund	1,850	20-40%	555	7.5	4,163	
RCRA Corrective Action	4,000	20-30%	1,000	5.0	5,000	
RCRA UST	140,000	3-5%	5,600	0.5	2,800	
DOD AFFF Sites	300	100%	300	30.0	9,000	
DOD	4,400	60-70%	2,860	2.5	7,150	
DOE	5,000	10-15%	600	5.0	3,000	
Civilian Agencies	3,000	25-30%	810	2.0	1,620	
State Sites	120,000	5-10%	8,400	0.5	4,200	
PFAS Manufacturing Sites	60	100%	60	300	18,000	
Manufacturing Sites Using PFAS	3,600	80-90%	2,880	7.5	21,600	
Other Manufacturing Sites	270,000	2-3%	6,750	0.5	3,375	
Chromium/Electroplating Operations	4,400	30-50%	1,760	1.0	1,760	
Refineries	130	80-90%	104	20.0	2,080	
Landfills: Active	3,100	50-70%	1,860	2.0	3,720	
Landfills: Closed	10,000	40-50%	4,500	0.5	2,250	
Airports: Major	260	80-90%	221	20.0	4,420	
Airports: Regional	1,200	30-40%	396	7.5	2,970	
Airports: Commercial/Private	17,540	3-5%	702	6.0	4,210	
Biosolids/Landfarming	500	70-80%	375	2.0	750	
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Other	50,000	5-10%	3,500	0.5	1,750	
Total	708,840	8%	57,378	1.8	103,817	105,675

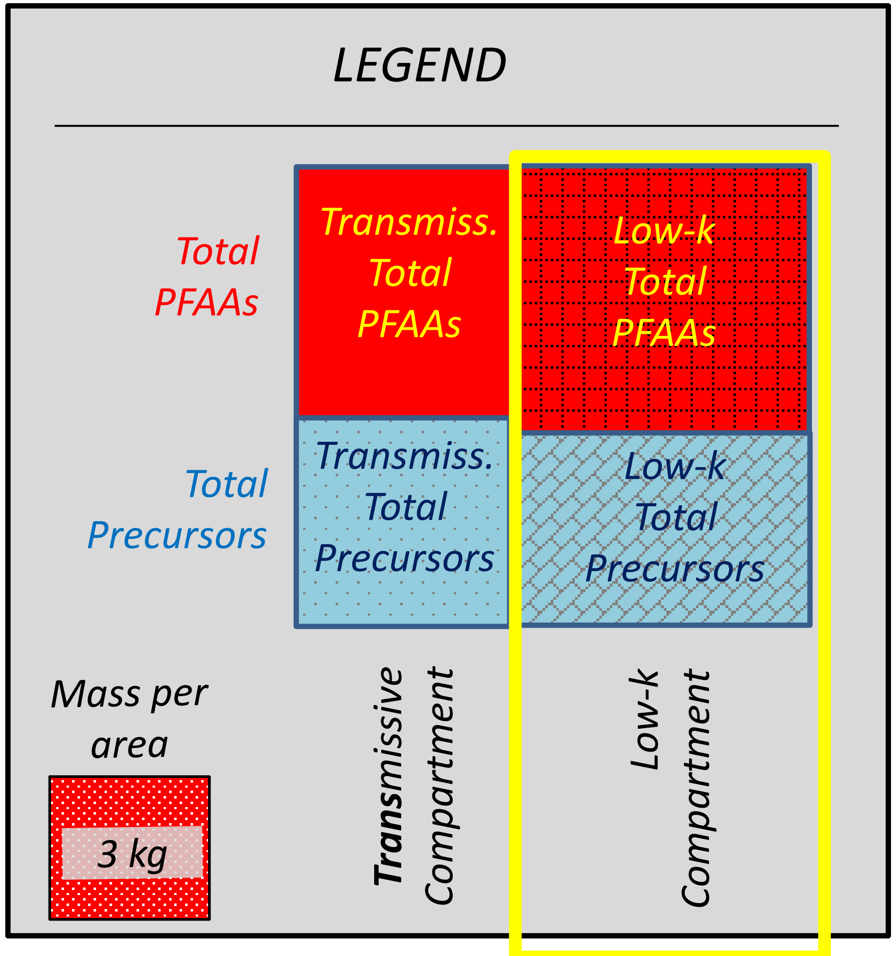
*Source: Environmental Business International, Inc. EBI estimates using site count estimates from EPA, ITRC, US Census, US DOT FAA, and others; a consensus of respondents to '% possible PFAS contamination' from a survey and interviews with remediation experts and estimated sites with with PFAS contamination a factor of 'possible' sites. * water/wastewater treatment system cost is capex and estimated opex for 20-year O&M*

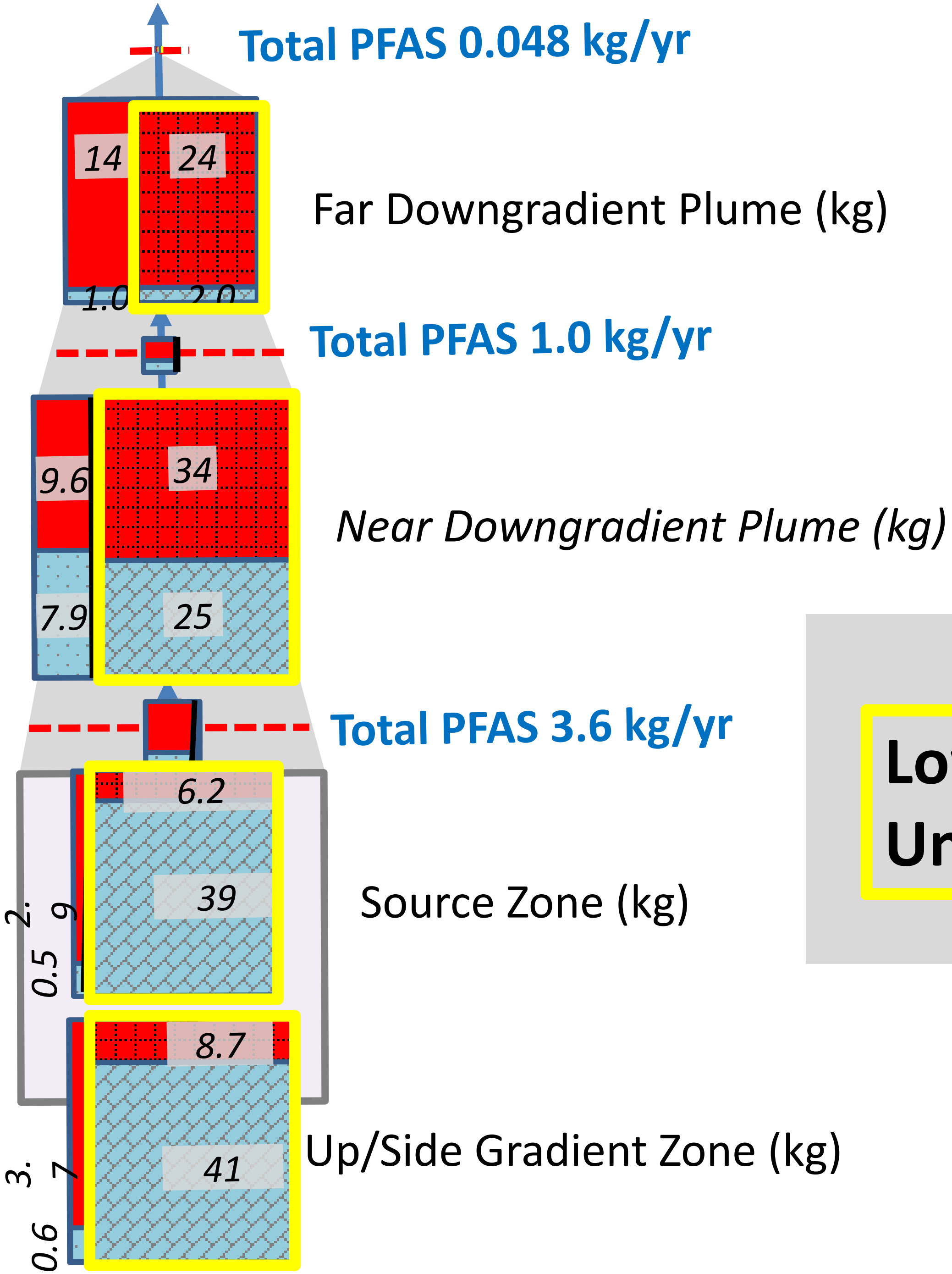
Estimated Remediation Cost:
$104 Billion

Mass Distribution at PFAS Research Site

82% of Mass in Low-K Soils

Adamson et al., 2020 ES&T

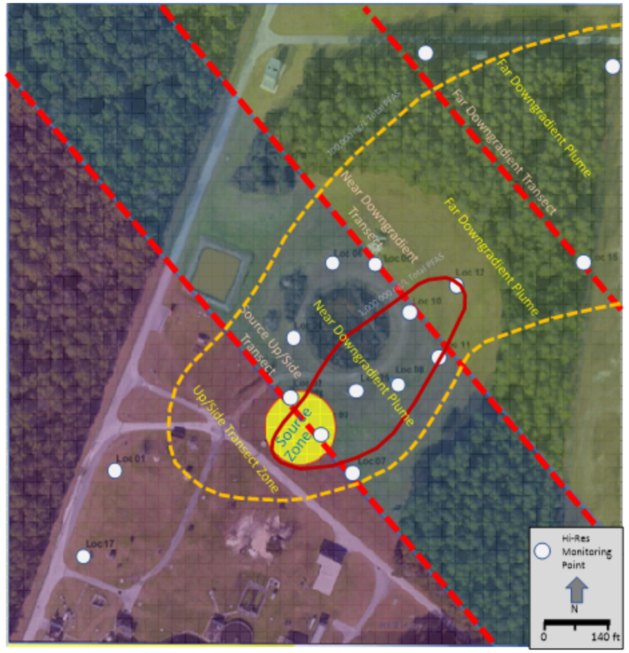




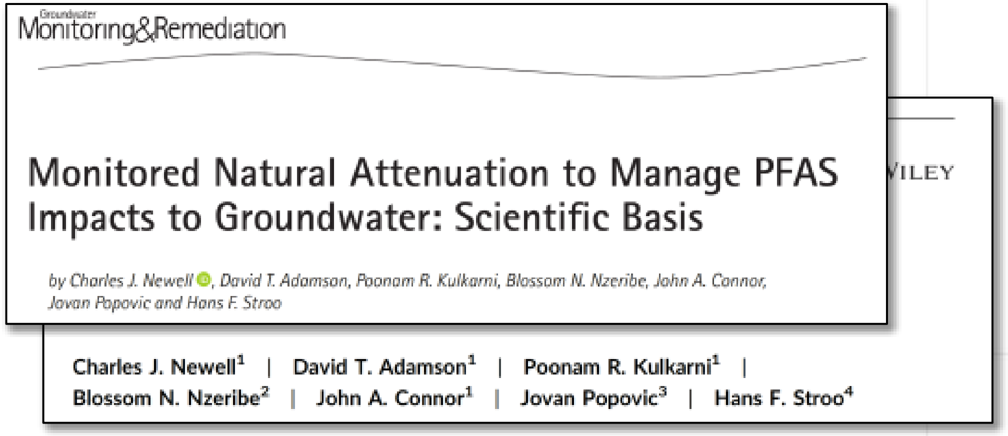
Low-K Units

Monitored Natural *Attenuation* for PFAS?

- **Key Inspiration**:
  - High-res sampling/analysis and matrix diffusion modeling for ESTCP ER-201633 and Navy projects (GSI, Oregon State, CSM, EXWC)
- **Key Result:**
  - Over 80% of PFAS mass in saturated zone is retained in low-k units (Adamson et al., 2020)
- **Key Implication:**
  - PFAS attenuation may be occurring at some sites where PFAS is not *immobilized*, but *retained*



Adamson et al., 2020 ES&T


Groundwater Monitoring&Remediation

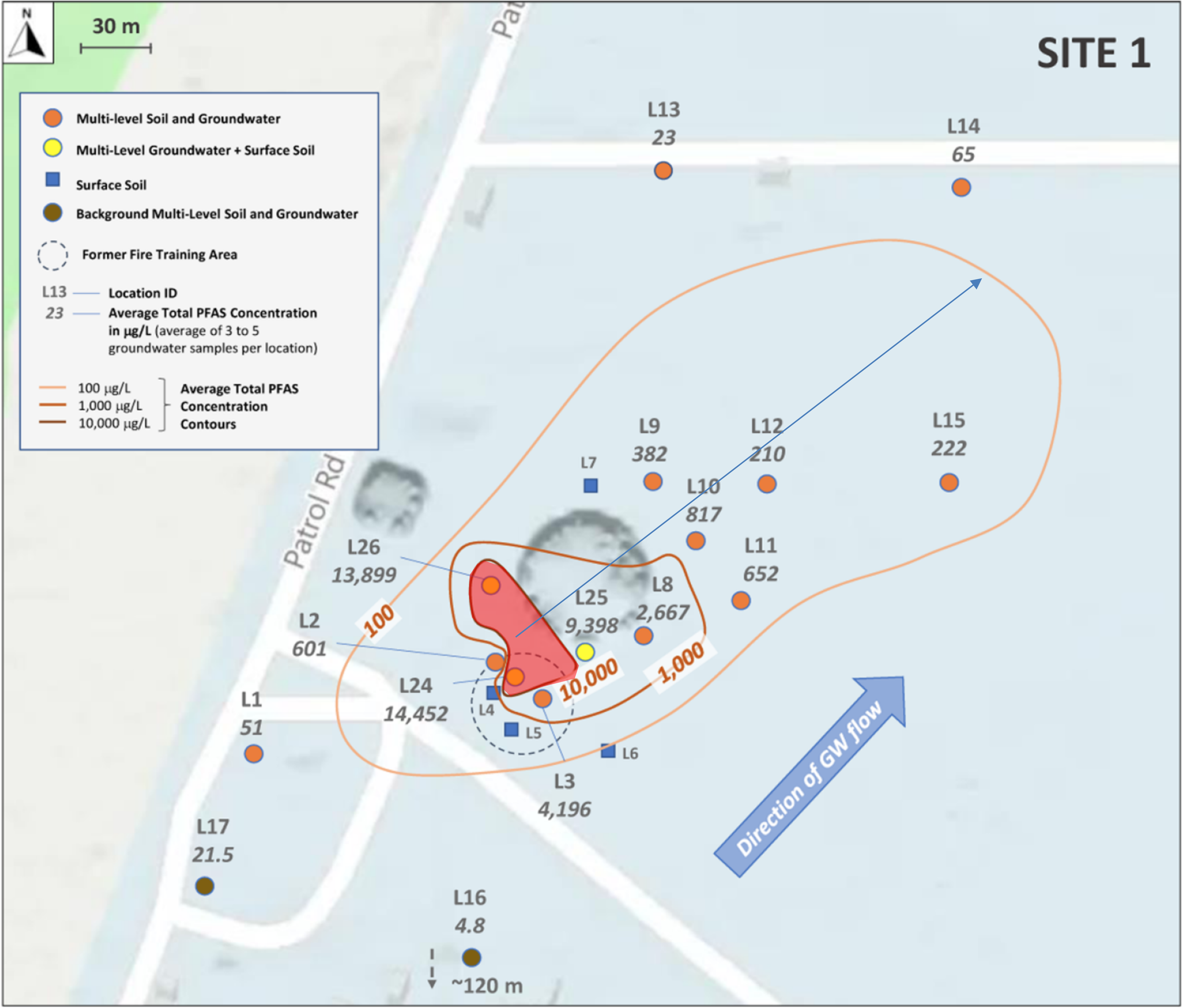
Monitored Natural Attenuation to Manage PFAS Impacts to Groundwater: Scientific Basis

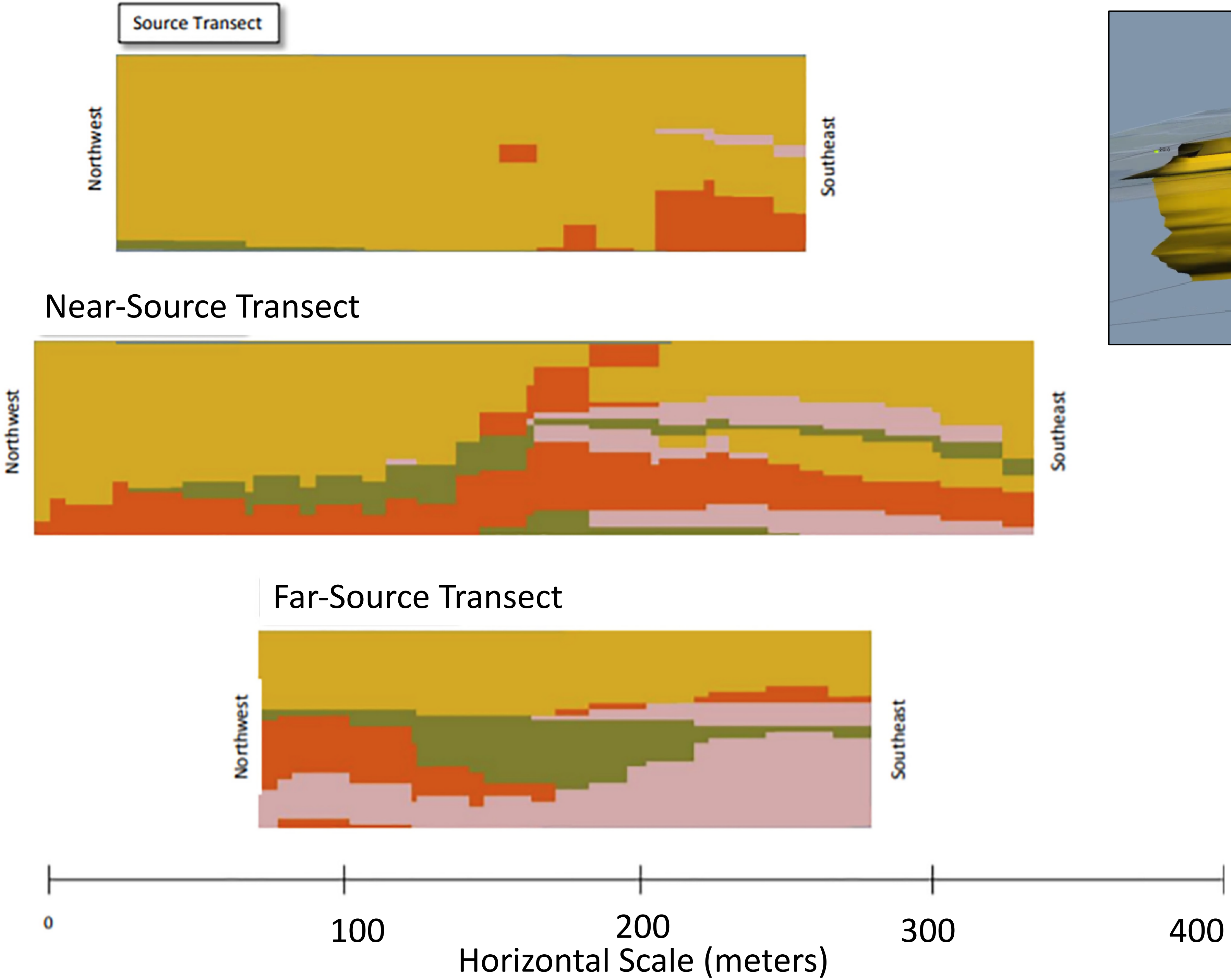
by Charles J. Newell, David T. Adamson, Poonam R. Kulkarni, Blossom N. Nzeribe, John A. Connor, Jovan Popovic and Hans F. Stroo

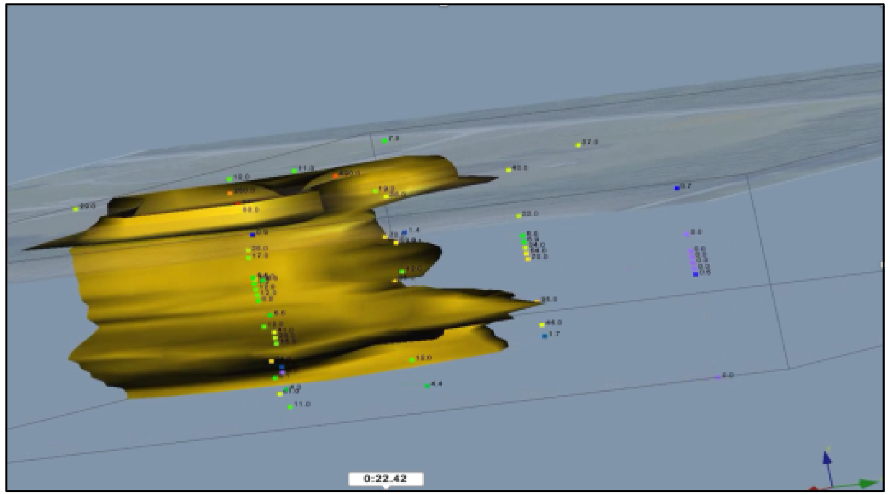
WILEY

Charles J. Newell[1] | David T. Adamson[1] | Poonam R. Kulkarni[1] | Blossom N. Nzeribe[2] | John A. Connor[1] | Jovan Popovic[3] | Hans F. Stroo[4]

Site 1 Source Zone







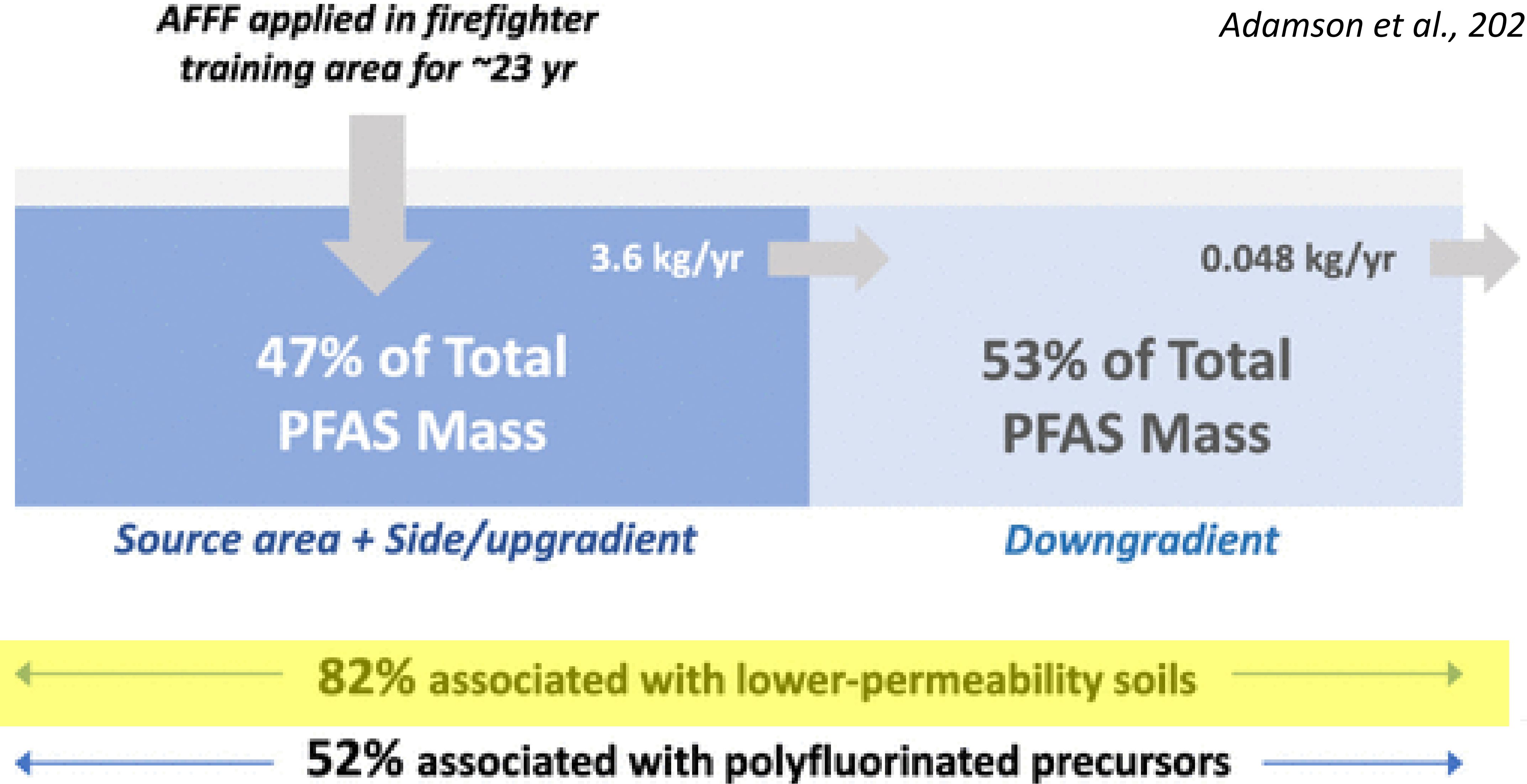
Soil Types

🟥 SP
🟨 SM
🟪 ML
🟩 CL

Adamson et al., 2020 ES&T
Kulkarni et al. 2022 JCH

Mass-Based, Field-Scale Demonstration of PFAS Retention within AFFF-Associated Source Areas

Adamson et al., 2020 ES&T



AFFF applied in firefighter training area for ~23 yr

3.6 kg/yr

0.048 kg/yr

47% of Total PFAS Mass

53% of Total PFAS Mass

Source area + Side/upgradient

Downgradient

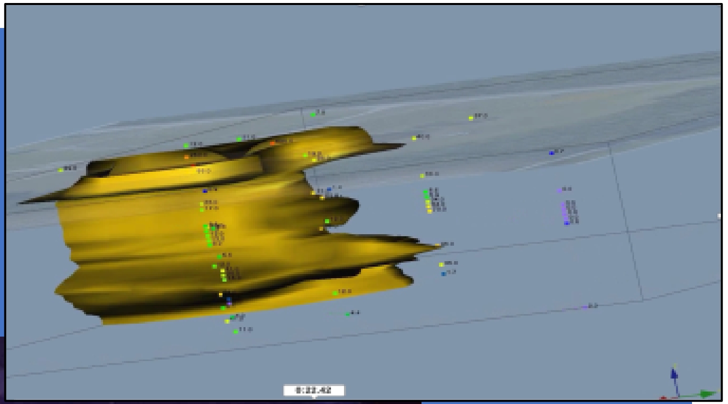
82% associated with lower-permeability soils

52% associated with polyfluorinated precursors

Final Thoughts about Human Ingenuity

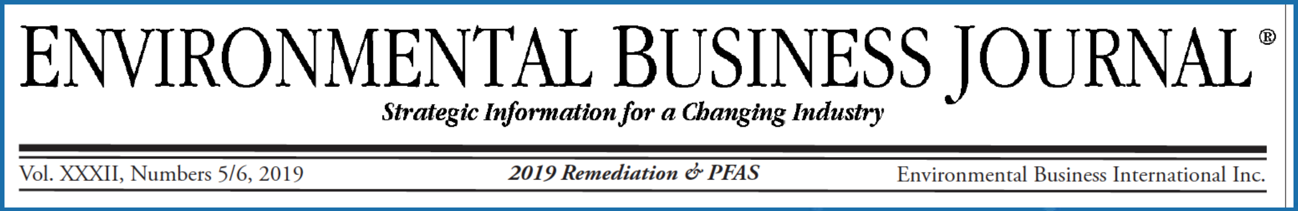
"Although the problem of PFAS in groundwater appears to be a daunting one, we feel confident that a similar level of ingenuity (invented for previous contaminants) will lead to surprising technical developments in remediating PFAS sites in the future as well"

"Comparing PFAS to other groundwater contaminants: Implications for remediation" Newell et al., 2020



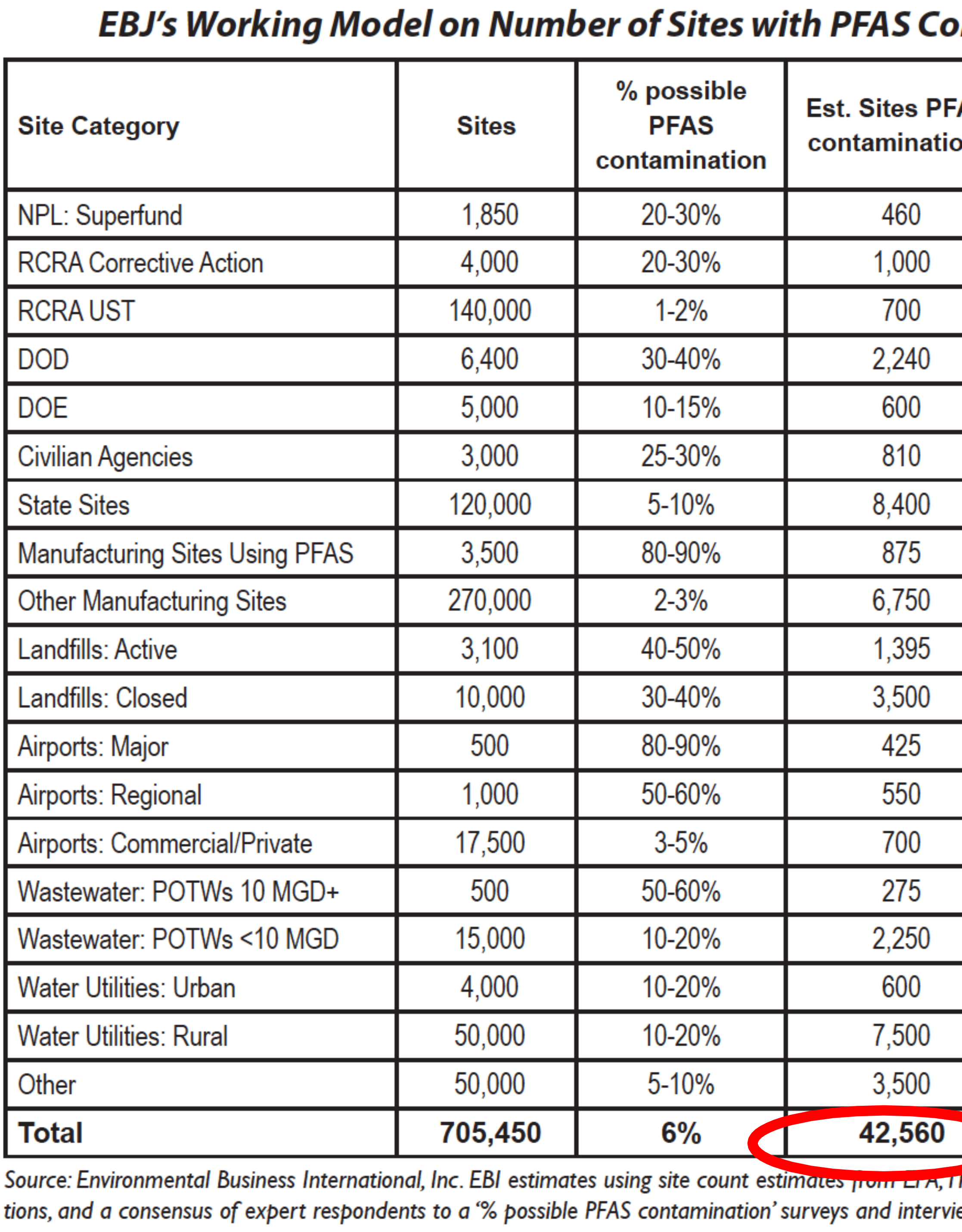
Source: GSI Environmental

Source: Clarkson University


ENVIRONMENTAL BUSINESS JOURNAL®
Strategic Information for a Changing Industry
Vol. XXXII, Numbers 5/6, 2019 *2019 Remediation & PFAS* Environmental Business International Inc.

Estimated Number of Sites With PFAS Contamination in U.S>

Regulated sites:	10,560
Dept. Defense:	2,240
Manufacturing:	7,625
Landfills:	4,895
Airports:	1,675
Water/Wastewater:	10,625
DOE/Agencies Other:	4,910
TOTAL	**42,530 Sites**

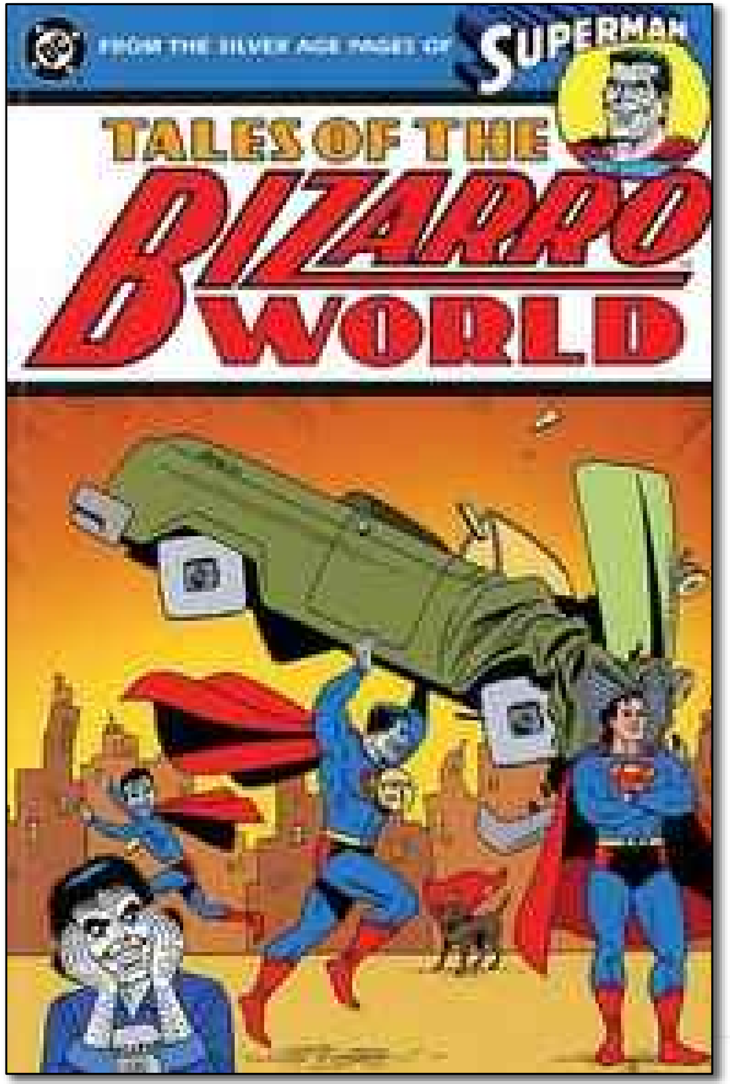

EBJ's Working Model on Number of Sites with PFAS Co

Site Category	**Sites**	**% possible PFAS contamination**	**Est. Sites PF contaminatio**
NPL: Superfund	1,850	20-30%	460
RCRA Corrective Action	4,000	20-30%	1,000
RCRA UST	140,000	1-2%	700
DOD	6,400	30-40%	2,240
DOE	5,000	10-15%	600
Civilian Agencies	3,000	25-30%	810
State Sites	120,000	5-10%	8,400
Manufacturing Sites Using PFAS	3,500	80-90%	875
Other Manufacturing Sites	270,000	2-3%	6,750
Landfills: Active	3,100	40-50%	1,395
Landfills: Closed	10,000	30-40%	3,500
Airports: Major	500	80-90%	425
Airports: Regional	1,000	50-60%	550
Airports: Commercial/Private	17,500	3-5%	700
Wastewater: POTWs 10 MGD+	500	50-60%	275
Wastewater: POTWs <10 MGD	15,000	10-20%	2,250
Water Utilities: Urban	4,000	10-20%	600
Water Utilities: Rural	50,000	10-20%	7,500
Other	50,000	5-10%	3,500
Total	**705,450**	**6%**	**42,560**

Source: Environmental Business International, Inc. EBI estimates using site count estimates from EPA,
tions, and a consensus of expert respondents to a '% possible PFAS contamination' surveys and intervie

Bizarro World

- “The Bizarro World (also known as Htrae, which is "Earth" spelled backwards) is a fictional planet appearing in American DC comic books.
- Htrae is a cube-shaped planet, home to Bizarro and companions, all of whom were initially Bizarro versions of Superman, Lois Lane, others
- In popular culture, "Bizarro World" has come to mean a situation or setting which is weirdly inverted or opposite to expectations.”



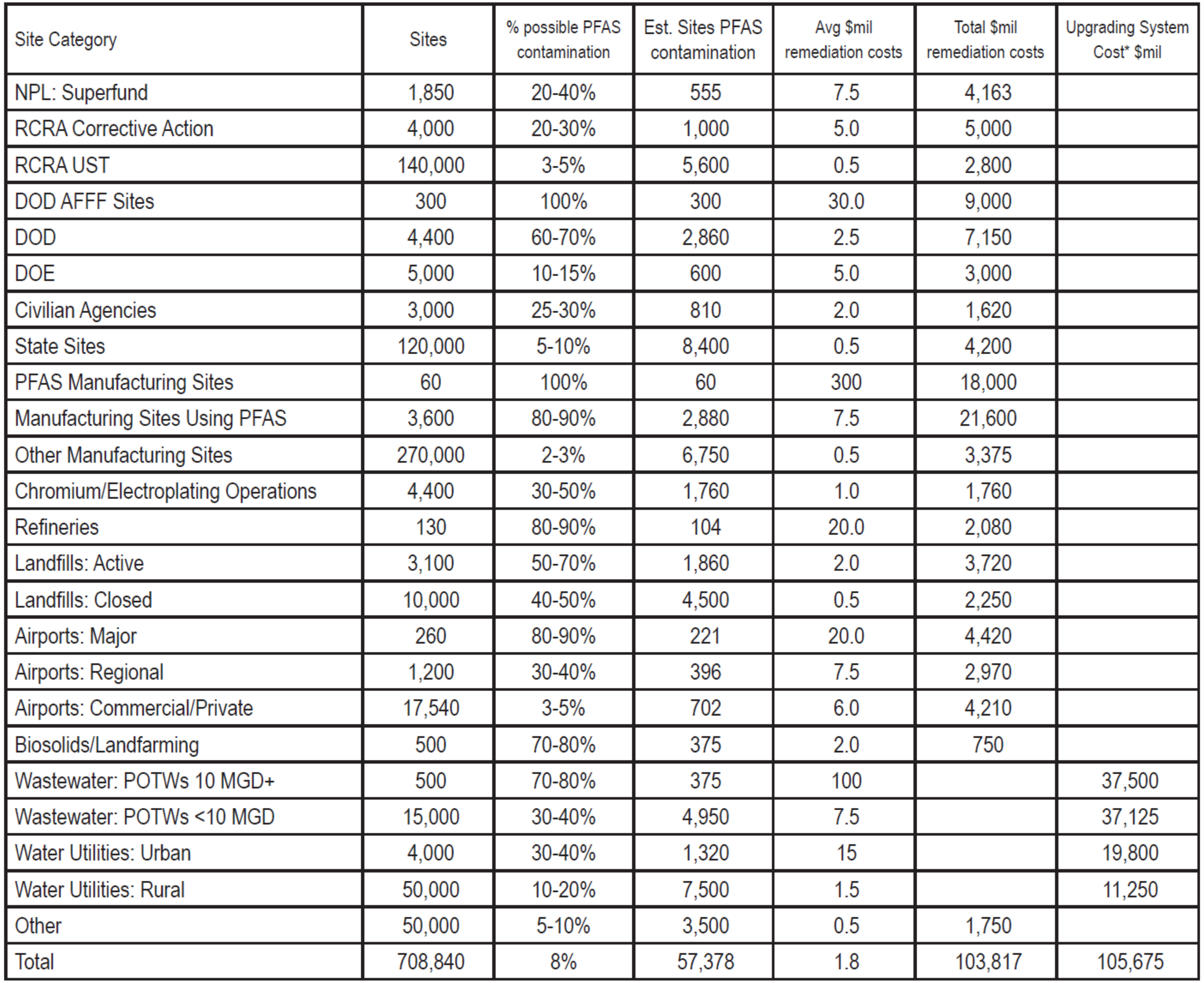
Wikipedia, 2022

Target End Users and Expected PFAS Remediation Costs

- DoD Sites: $9 Billion
- Wastewater: $37 Billion
- Water Utilities: $31 Billion
- Refineries: $2 Billion

GSI
ENVIRONMENTAL

EBJ Working Model of Sites with PFAS Contamination



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RCRA Corrective Action	4,000	20-30%	1,000	5.0	5,000	
RCRA UST	140,000	3-5%	5,600	0.5	2,800	
DOD AFFF Sites	300	100%	300	30.0	9,000	
DOD	4,400	60-70%	2,860	2.5	7,150	
DOE	5,000	10-15%	600	5.0	3,000	
Civilian Agencies	3,000	25-30%	810	2.0	1,620	
State Sites	120,000	5-10%	8,400	0.5	4,200	
PFAS Manufacturing Sites	60	100%	60	300	18,000	
Manufacturing Sites Using PFAS	3,600	80-90%	2,880	7.5	21,600	
Other Manufacturing Sites	270,000	2-3%	6,750	0.5	3,375	
Chromium/Electroplating Operations	4,400	30-50%	1,760	1.0	1,760	
Refineries	130	80-90%	104	20.0	2,080	
Landfills: Active	3,100	50-70%	1,860	2.0	3,720	
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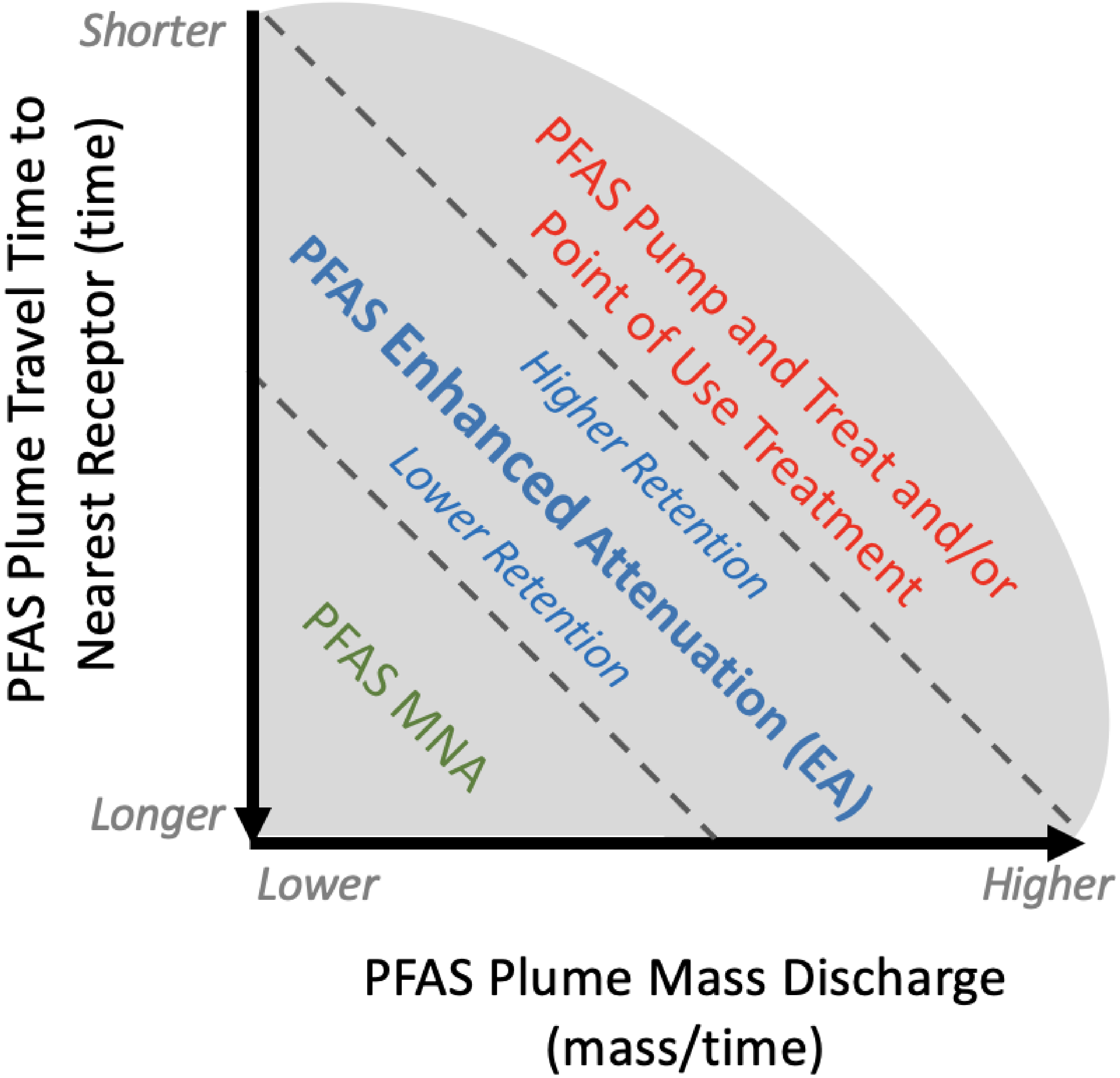
When EA?

Potential decision drivers?

- Travel time to receptors
- Mass discharge

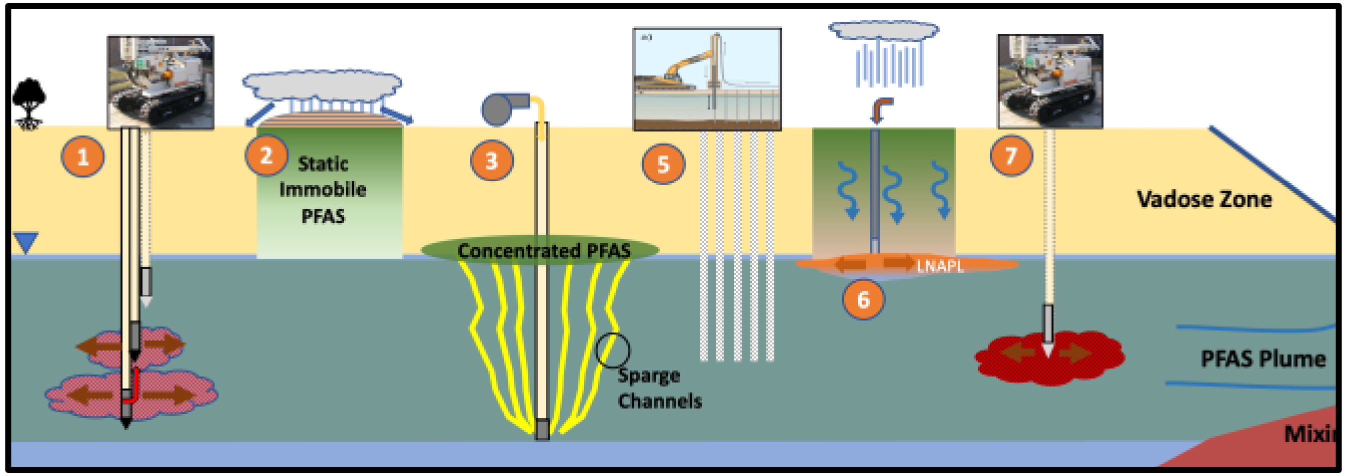
Enhanced Attenuation (EA) to Manage PFAS Plumes in Groundwater
(Newell et al., 2022b)



Potential Enhanced Attenuation (EA) Processes to Manage PFAS Plumes in Groundwater

CleanUp 2022 Conference

Adelaide, South Australia

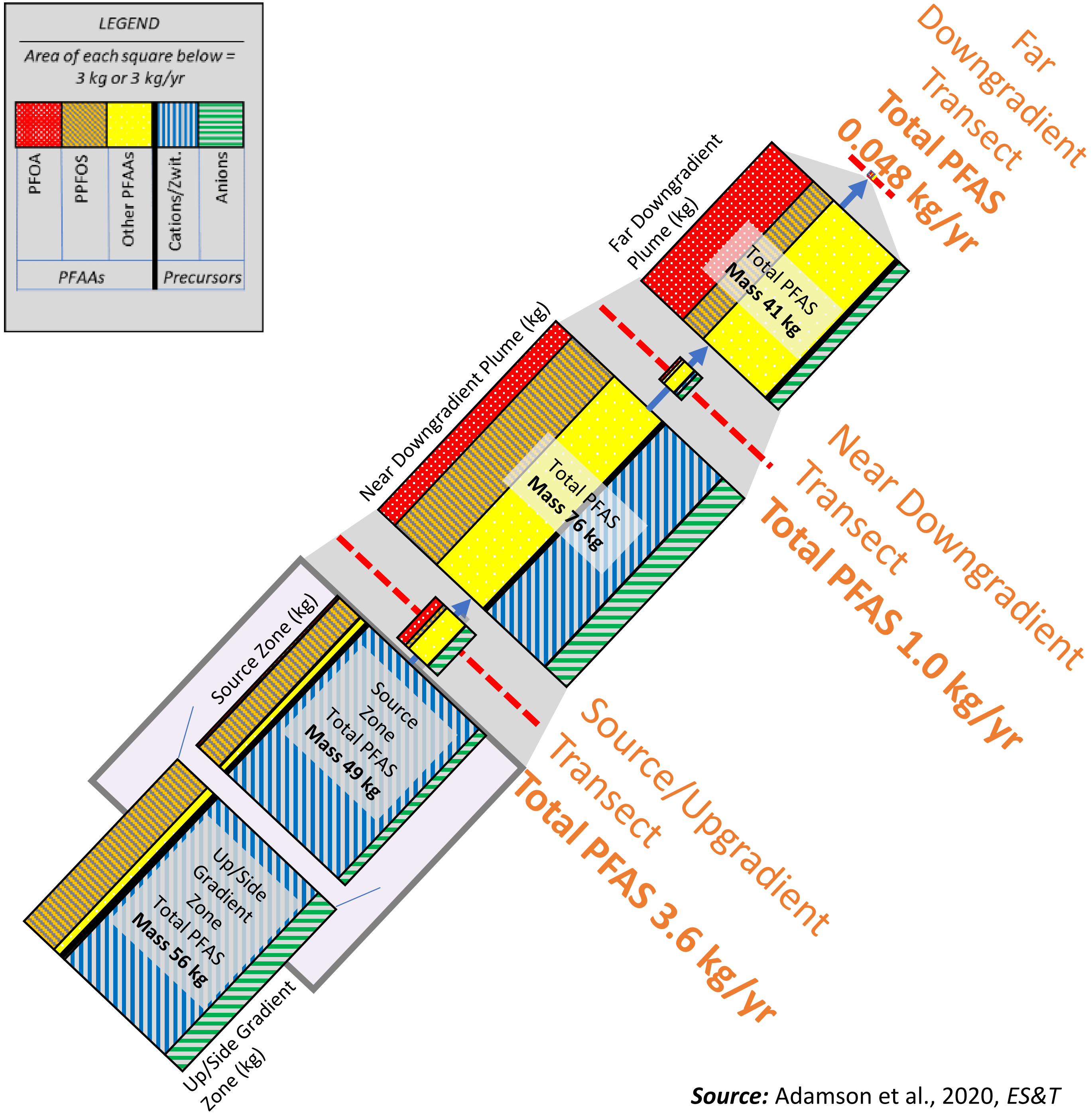


September 2022

Charles J Newell
Hassan Javad
Yue (Beatrice) Li
Nicholas Johnson
GSI Environmental

Steven Richardson
David T Adamson
John A. Connor
Poonam R. Kulkarni
GSI Environmental

Mass Balance Model:
Site 1 Example



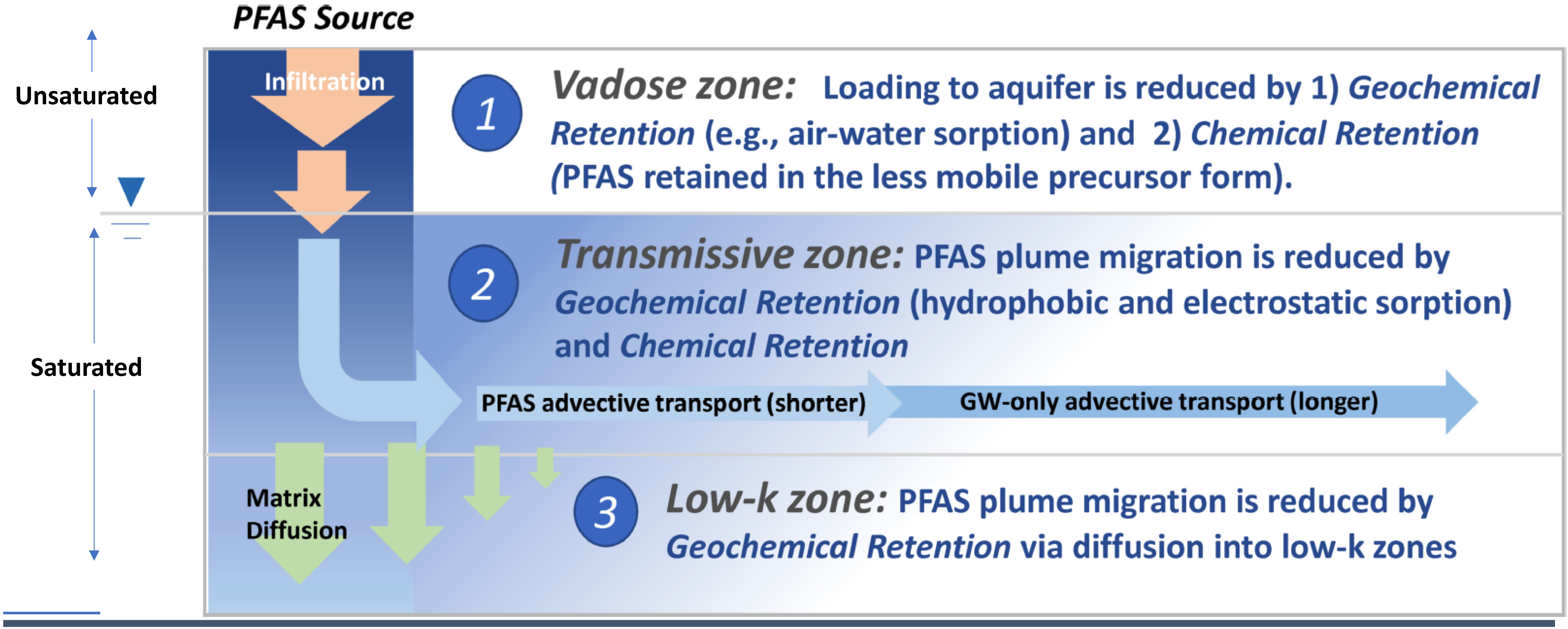
Source: Adamson et al., 2020, *ES&T*

- Mass discharge decreases by 99% between the source and the far downgradient transect
- 82% of remaining mass is associated with lower-k soils
    - Includes 94% of zwitterionic/cationic mass

KEY POINTS

- Confirms strong retention of zwitterionic/cationic PFAS due to preferential sorption characteristics
- Confirms influence of matrix diffusion processes

Key Processes: *Retention-Based PFAS Monitored Natural Attenuation (MNA)*



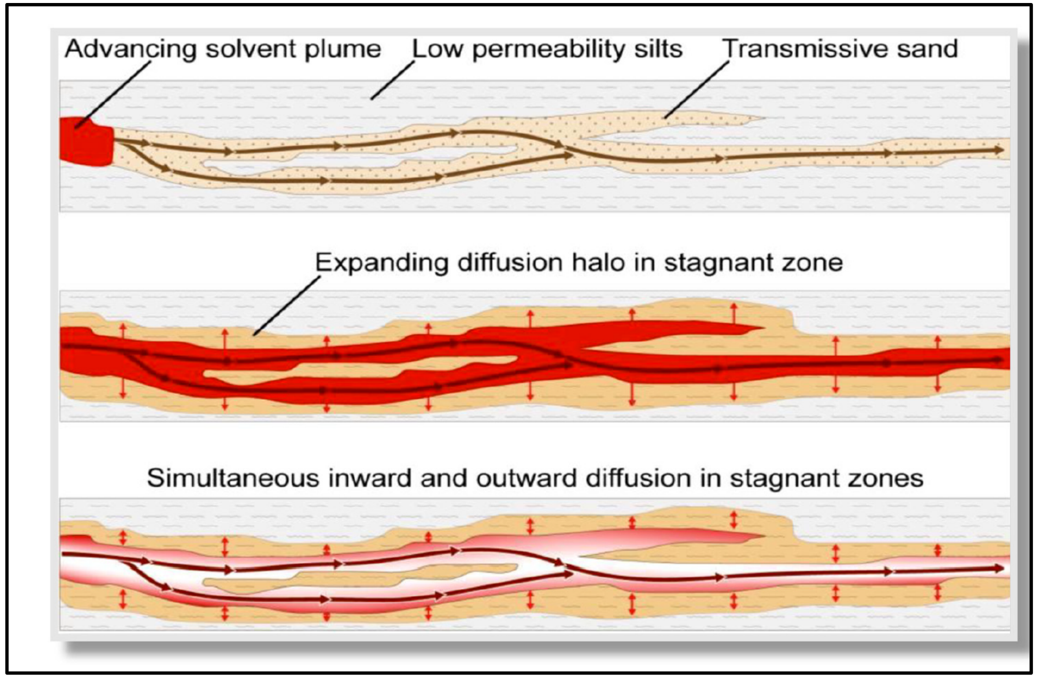
1 ***Vadose zone:*** Loading to aquifer is reduced by 1) *Geochemical Retention* (e.g., air-water sorption) and 2) *Chemical Retention (*PFAS retained in the less mobile precursor form).

2 ***Transmissive zone:*** PFAS plume migration is reduced by *Geochemical Retention* (hydrophobic and electrostatic sorption) and *Chemical Retention*

3 ***Low-k zone:*** PFAS plume migration is reduced by *Geochemical Retention* via diffusion into low-k zones

Key PFAS MNA Processes: Sorption and Matrix Diffusion

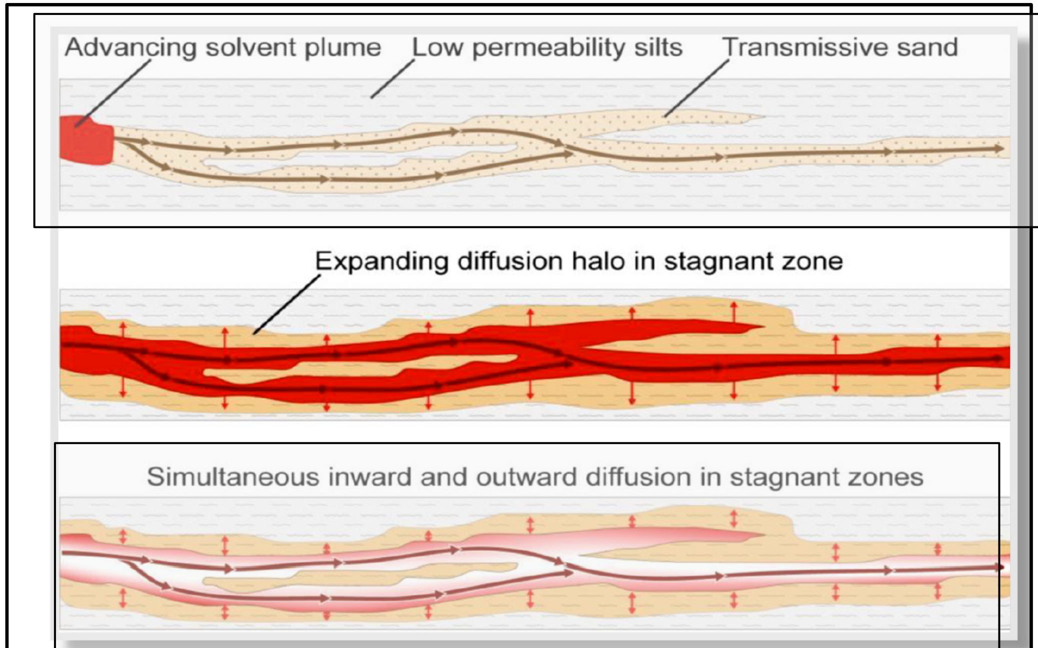
Plume Progression Over Time



- PFAS sorb to organic carbon on soils
  - more carbons = generally more sorption
- For PFAAs, similar sorption as chlorinated solvents
  - Retardation Factors in single digits
- Like CVOCs, PFAS diffuse in low-permeability geologic media
- But this matrix diffusion has different implications

Key PFAS MNA Processes:
Sorption and Matrix Diffusion

Plume
Progression
Over Time



PFAAs don’t degrade –
may be more expanding plumes.

But matrix diffusion
is retaining PFAS,
therefore slowing
plume expansion

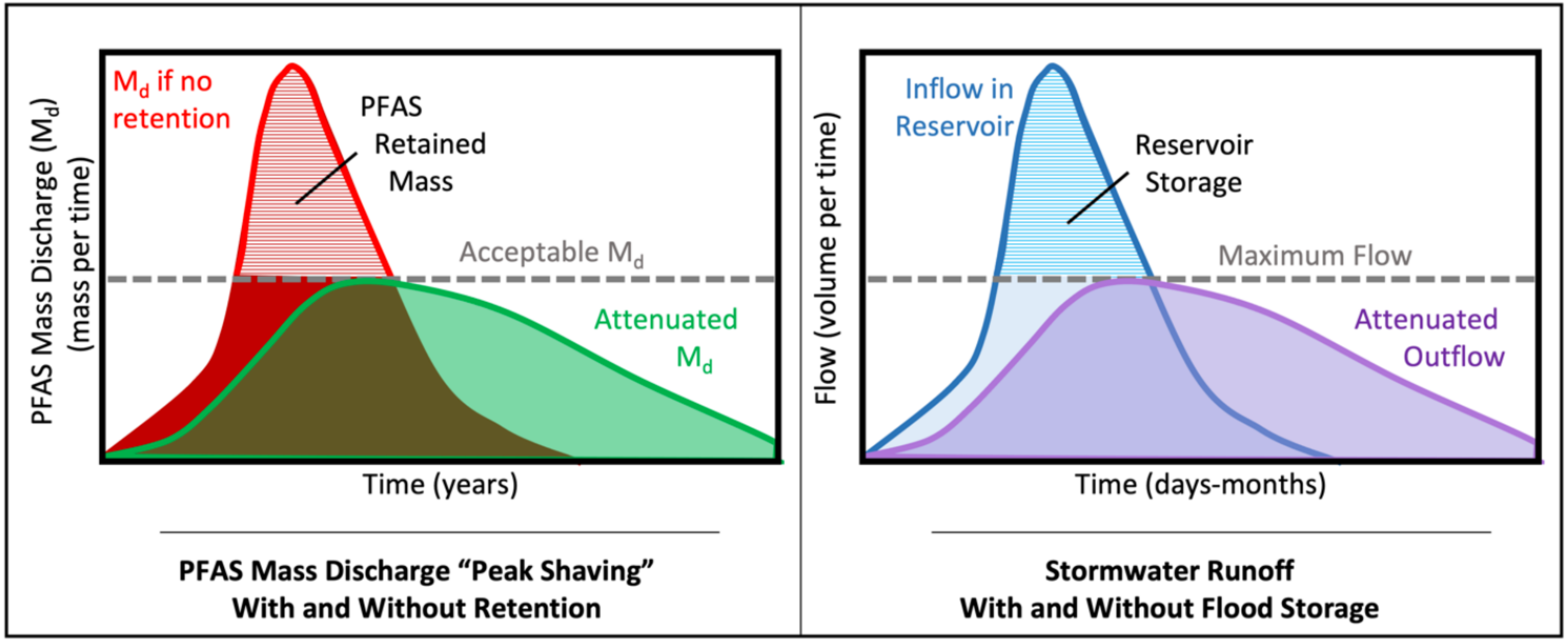
Most chlorinated sites down here –
matrix diffusion makes it harder to remediate

PFAS Retained Mass Can Result in Peak Shaving

Enhanced Attenuation (EA) Processes to Manage PFAS Plumes in Groundwater: Current, Emerging, and Speculative Approaches

Charles J. Newell, Hassan Javed, Yue Li, Nicolas W. Johnson, Stephen D. Richardson, John. A. Connor, and David T. Adamson

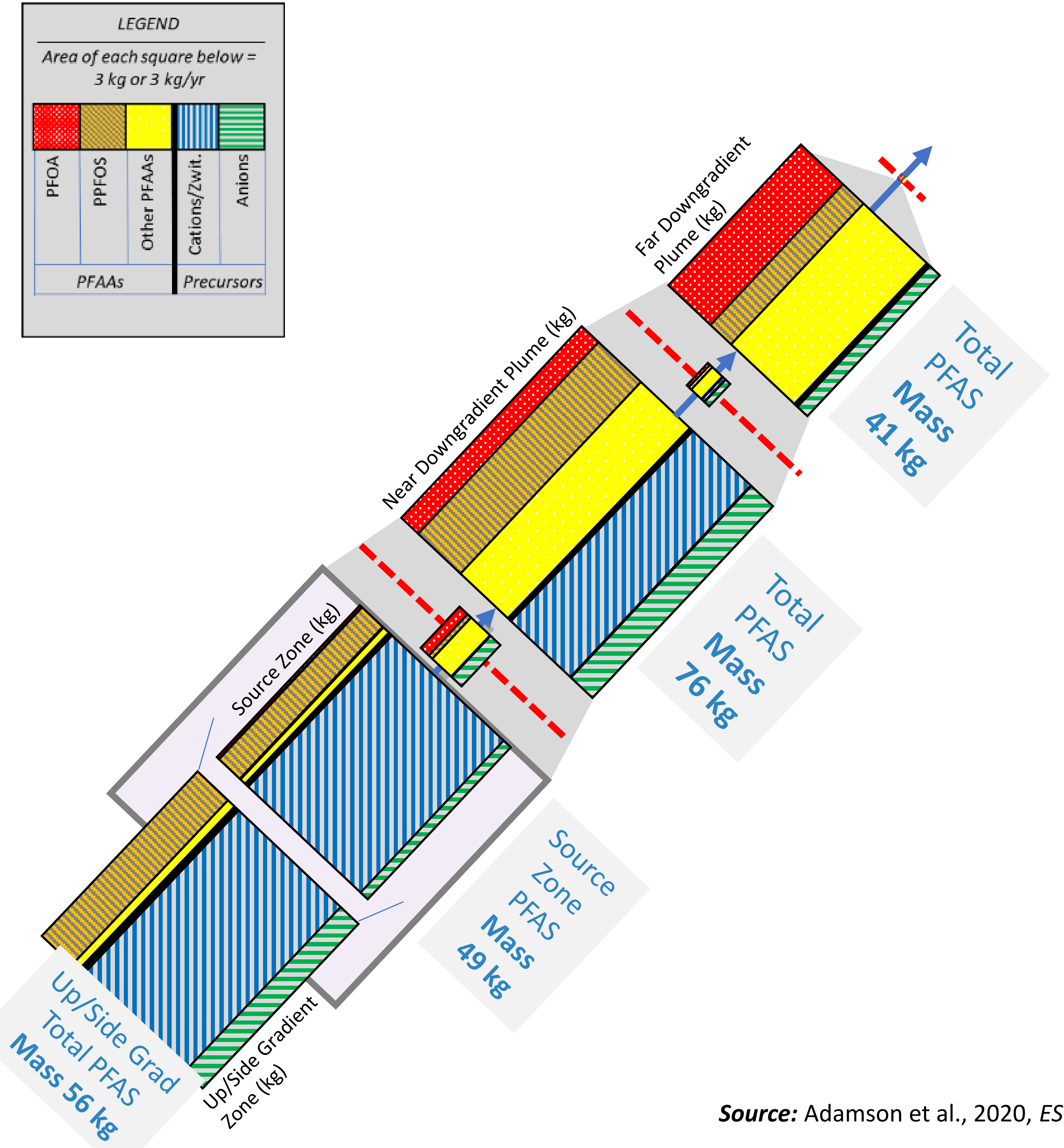
- Many PFAS retention processes produce mass flux "Peak Shaving"
- Similar to flood control reservoirs
- Can you "enhance" this process?



PFAS Mass Discharge "Peak Shaving" With and Without Retention

Stormwater Runoff With and Without Flood Storage

Mass Balance Model: *Site 1 Example*

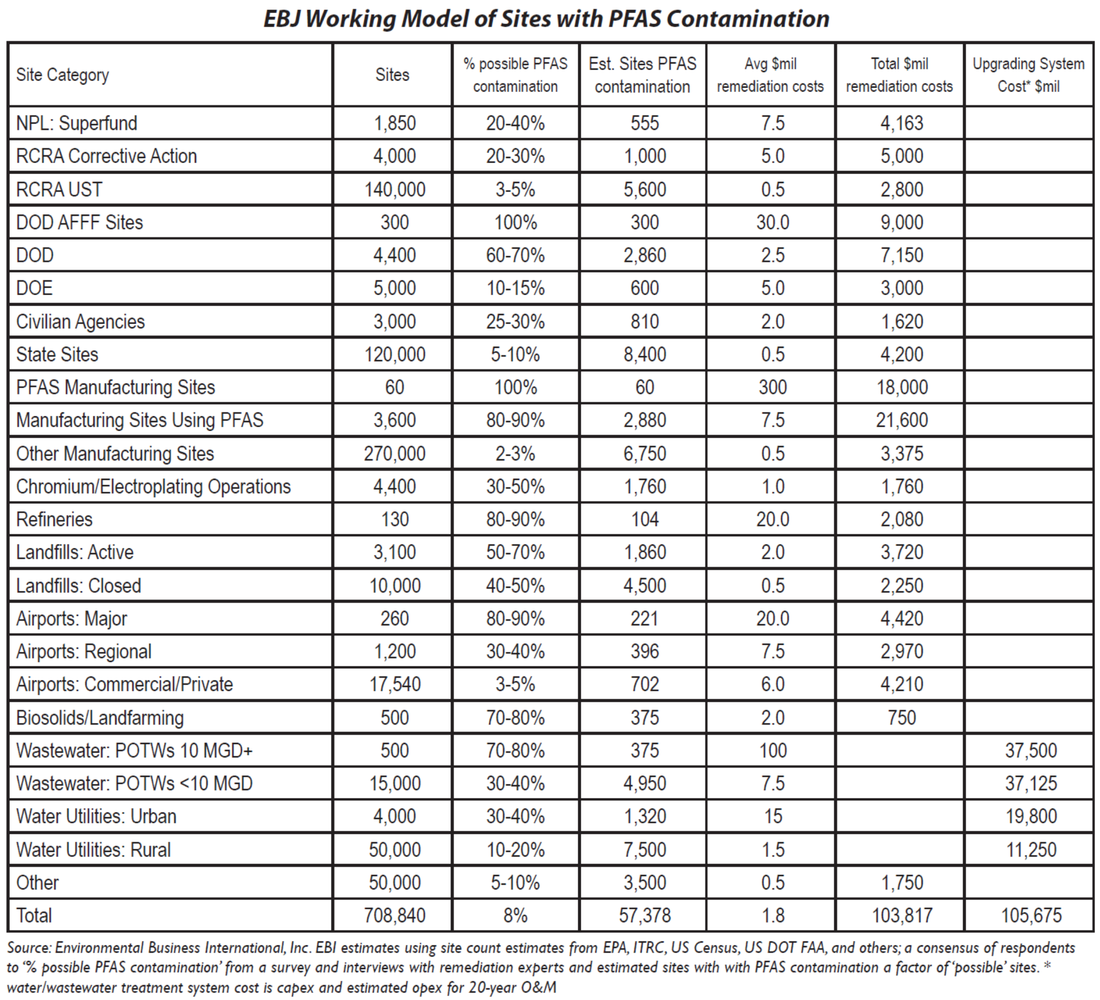


Source: Adamson et al., 2020, *ES&T*

- **Estimated total PFAS = 252 kg**
- 47% of remaining mass is in source/near-source areas
- 52% of remaining mass is in the form of polyfluorinated "precursors"
  - 83% of precursor mass is zwitterionic/cationic

Potential Number of PFAS Sites

- DoD Sites: $9 Billion
- Wastewater: $37 Billion
- Water Utilities: $31 Billion
- Refineries: $2 Billion



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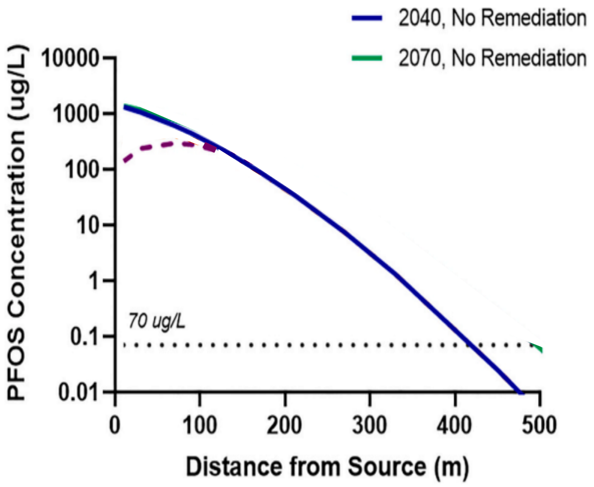
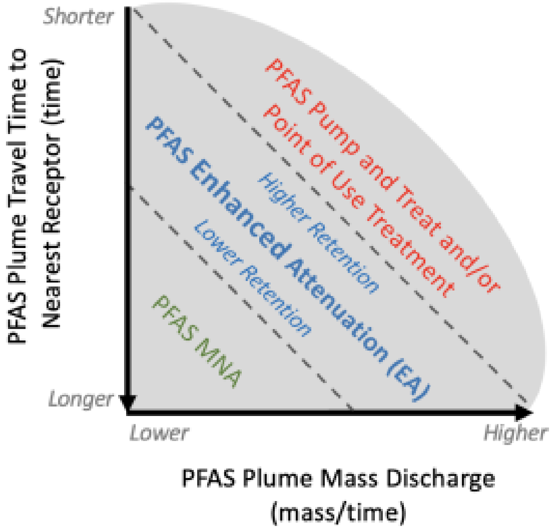
Managing PFAS Plumes in Groundwater Wrap-Up

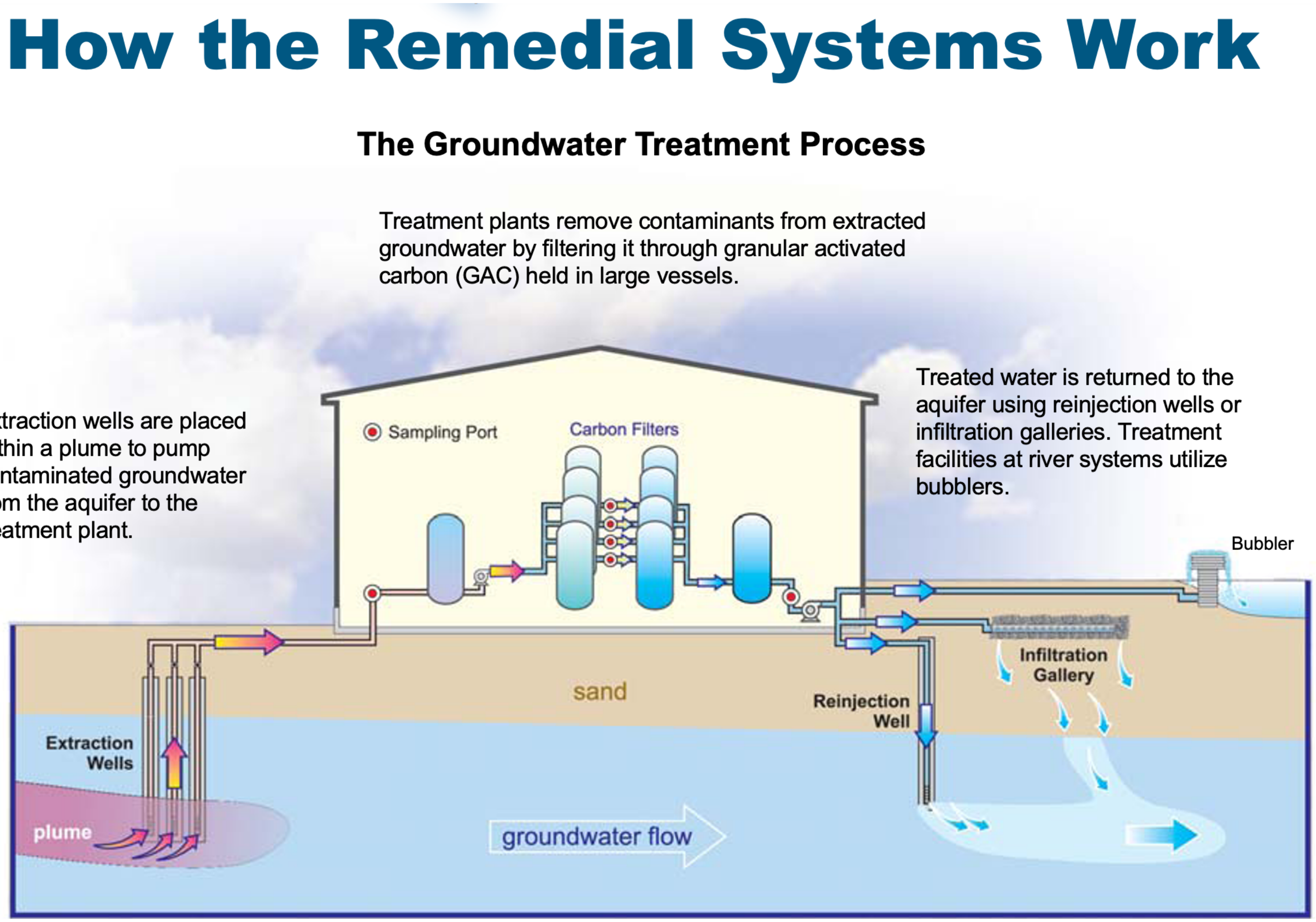
- More PFAS plumes may be expanding compared to "conventional" groundwater contaminants
- This means that plume control may be more important than source control, at least in the near term ("The horse has left the barn")
- Plume control options
  - Pump and Treat Systems
  - Point of Use Treatment
  - Enhanced remediation (e.g., PlumeStop)
  - Retention-Based MNA (?)





Potential Futures for PFAS Management?

- Scenario 1: **Groundwater Pump & Treat** is the predominant approach for PFAS plumes?



How the Remedial Systems Work

The Groundwater Treatment Process

Treatment plants remove contaminants from extracted groundwater by filtering it through granular activated carbon (GAC) held in large vessels.

Extraction wells are placed within a plume to pump contaminated groundwater from the aquifer to the treatment plant.

Treated water is returned to the aquifer using reinjection wells or infiltration galleries. Treatment facilities at river systems utilize bubblers.